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INTERFACIAL CHARACTERISTICS OF GLASS-CERAMIC MATRIX/SiC FIBER COMPOSITES

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RESUME

La région interfaciale fibre/matrice entre les matrice verres-céramique lithium aluminosilicate et une variété de fibre et trichites de SiC et/ou Si-C-N-O ont été examinées, principalement avec une électro-microscope à scan et une multi-sonde Auger à scan. On a trouvé que la chimie de l'interface varie grandement, dépendant sur le fibre particulier, ou lequel trichite qu'il est utilisé, et que la chimie de l'interface determine à un grand degré les propriétés mécaniques de le composite. En général les composés qui montrent un attachement de fibre/matrice de l'interface faible, sont fortes et durs, quand ceux qui montrent un attachement de l'interface forte, sont faibles et cassants.

ABSTRACT

The fiber/matrix interfacial region between lithium aluminosilicate (LAS) glass-ceramic matrices and a variety of SiC and/or Si-C-N-O fibers and whiskers was examined, primarily through the use of the scanning transmission electron microscope (STEM) and the scanning Auger multiprobe (SAM). It was found that the interfacial chemistry varied widely, depending upon the particular fiber or whisker utilized, and that the chemistry of the interface determined to a large degree the resultant mechanical properties of the composite. In general, those composites exhibiting a weakly bonded fiber/matrix interface tended to be strong and tough, while those exhibiting a strongly bonded interface were weak and brittle.

INTRODUCTION

For the past several years, ceramic matrix composite systems based on the reinforcement of glass and glass-ceramic matrices with Nicalon [1] polycarbosilane derived SiC based fibers have been under study at United Technologies Research Center (UTRC) [1]-[5]. The basic goal of this work was to develop a high strength, high toughness, low density ceramic matrix composite that exhibited a use temperature of at least 1000°C. This goal was essentially met with the development of the lithium aluminosilicate (LAS) glass-ceramic matrix/Nicalon fiber composite system [3]. However, during the course of this investigation it was found that certain fabrication conditions and/or matrix compositions resulted in quite weak and brittle composites with fracture characteristics quite different than that usually observed for this class of composite. For example, Fig. 1 shows the fracture surfaces of two different LAS matrix/Nicalon SiC fiber composites; one is a very strong (1050 MPa) composite with a very fibrous and tough mode of fracture (A), while the other is very weak (275 MPa) with a relatively brittle, non-fibrous fracture surface (B). In this particular case, the only difference between the two was that the weak and brittle composite contained a small amount of TiO₂ (~3wt%) as a nucleating aid in the matrix while the strong and tough composite did not. During hot-pressing, the TiO₂ reacted with the fibers forming a titanium silicide reaction product around the fibers that severely degraded their strength. This type of fiber/matrix interaction was easily identified from conventional SEM or electron microprobe analysis of the fracture surface.
In many other cases, however, composites that displayed the brittle type of fracture as shown in Fig. 1B did not evidence any detectable fiber/matrix interaction when analyzed by SEM, microprobe, or X-ray diffraction. In addition, other composite systems utilizing fibers or whiskers different than Nicalon also resulted in variable fracture behavior that could not be attributed to easily detectable fiber/matrix interactions. Thus, in order to gain an understanding of the factors controlling the type of fracture behavior observed in these composite systems, a comprehensive scanning transmission electron microscope (STEM) analysis of replicas of polished composite cross-sections as well as ion beam thinned composite sections and scanning Auger microprobe (SAM) analysis of composite fracture surfaces was undertaken. These analytical methods allowed the phase assemblages and microchemical composition of the fiber/matrix interfacial regions to be determined to a fine degree of spatial resolution. The results of this study are discussed in the following sections of this paper.

MATERIALS

The composite systems of interest in this study are listed in Table I. The lithium aluminosilicate (LAS) glass-ceramic matrices used in this study are designated LAS-I and LAS-III. LAS-I is very similar in composition to the commercially available Corning 9608 Corningware®, except that the ~3wt% TiO₂ nucleating agent used in 9608 has been replaced by ~3wt% ZrO₂. The LAS-III matrix composition is similar to that of LAS-I except 5 wt% Nb₂O₅ has been added and minor constituents such as ZnO, Na₂O and K₂O have been deleted. LAS-III is thus a more refractory glass-ceramic than LAS-I. Both of the matrix materials were purchased from Corning Glass Works, Corning, N.Y. as glassy powder of 8-12 µm average particle size.
Four different fibers and two types of SiC whiskers were utilized in this study. Two of the fibers were derived from polycarbosilane precursors. These fibers are Nicalon, developed by Prof. Yajima and coworkers at Tohoku University in Japan and now produced by Nippon Carbon Co., Tokyo, and distributed in the United States by Dow Corning Corp., Midland, Mich., and Tyranno, also developed by Prof. Yajima and now produced by UBE Industries, Tokyo, and distributed in the U.S. by Avco Corp., Lowell, Mass. Both fibers were obtained on spools of continuous length (~500m) tows. The Nicalon fiber had an average fiber diameter of ~13 μm and an average tensile strength of 2400 MPa. The Tyranno fiber exhibited an average diameter of 8.3 μm and a tensile strength of 2890 MPa. Both fibers consist of microcrystalline β-SiC with excess free carbon and SiO₂. In addition, the Tyranno fiber contains ~2wt% Ti which reportedly assists in retarding crystallization and grain growth at elevated temperature.

The MPDZ (methylpolydisilylazane) and HPZ (hydridopolysilylazane) fibers are organosilicon-polymer derived experimental fibers from Dow Corning Corp., Midland, Mich, in collaboration with Celanese Corp., Summit, N.J., being developed under DARPA funding. Both fibers are amorphous and consist of Si, C, N, and O, with the MPDZ fiber being higher in C than N while the HPZ fiber is higher in N than C. Both fibers evaluated exhibited average diameters of ~10 μm and tensile strengths of 1750-2400 MPa. These fibers were not available in continuous length but were obtained in oriented bundles of 10-20 cm in length.

Two types of SiC whiskers were utilized in this study, the Los Alamos National Lab. (LANL) α-SiC whiskers grown by a vapor-liquid-solid (VLS) process and α-SiC whiskers (Silag) from Arco Metals, Greer, S.C. The LANL whiskers tended to be both larger in diameter (3-8 μm) and longer (>100 μm) than the Silag whiskers (<1 μm diam and <60 μm in length).

The fiber coating to be discussed in this study was a chemically vapor deposited (CVD) carbon coating on the HPZ fibers. This coating was applied by Battelle Labs, Columbus, Ohio, under the aforementioned Dow Corning/DARPA program. Various carbon coating thicknesses were evaluated.

COMPOSITE FABRICATION

In the case of the continuous Nicalon and Tyranno fibers, the glass-ceramic matrix composites were fabricated by passing the yarn quickly through a bunsen burner in order to remove the sizing and then through an agitated slurry of glass powder, water, and an acrylic binder, onto a rotating drum. The resultant tape was then cut into the appropriate
dimensions and fiber orientations, heated in air to 600°C to remove the binder, and stacked in a graphite hot-pressing die to the desired thickness. The composites were hot-pressed at 6.9 MPa pressure at temperatures of 1200-1350°C and times of 15-30 min, depending on the matrix composition. Samples to be studied in the "ceramed" or matrix crystallized state were subjected to a post hot-pressing heat treatment at temperatures of 900-1150°C, again depending on the matrix matrix composition. For the LAS matrix composites, the ceraming step crystallized the major portion of the matrix into either the β-quartz-silica solid solution \([(Li_2O,MgO)\cdot Al_2O_3\cdot nSiO_2 (n>2)]\) or β-spodumene silica solid solution \([(Li_2O,MgO)\cdot Al_2O_3\cdot nSiO_2 (n>3.5)]\) phase. The remaining matrix consists of a continuous glassy grain boundary phase plus small crystals of mullite \(3Al_2O_3\cdot 2SiO_2\).

The shorter length MPDZ and HPZ fiber composites were fabricated similarly except that a hand dipping procedure was used to impregnate the fiber bundles with glass powder. The whisker composites were fabricated by blending whiskers and glass powder with water and a binder, pouring the resultant slurry into thin sheets, drying the sheets, and then cutting and stacking the sheets in the graphite die and hot-pressing as above.

**COMPOSITE INTERFACIAL ANALYSIS**

The main analytical tools utilized to study the glass-ceramic matrix/fiber composite interfacial areas were the scanning transmission electron microscope (STEM)[1] and the scanning Auger electron microprobe (SAM)[2]. The STEM was utilized to study replicas of polished composite cross-sections and ion beam thinned composite sections. The SAM was utilized to study fiber surfaces, both loose fibers and fibers lying in the plane of a composite fracture surface, and matrix troughs from which fibers had been pulled away. Both of these analytical methods were indispensable for the study of fiber/matrix interfaces due to their fine spatial resolution and, in the case of the SAM, the ability to detect low atomic number elements.

**Nicalon Fiber Composites**

Transmission Electron Microscope (TEM) Analysis

Typical TEM replicas of transverse cross-sections of LAS-I and LAS-III matrix/Nicalon SiC fiber composites in the as-pressed condition are shown in Fig. 2. The blocky or elongated crystals that can be seen in both samples are mullite \(3Al_2O_3\cdot 2SiO_2\) that tends to crystallize out of the glass upon cooling from the hot-pressing temperature. It is obvious from these two figures that a thin ring exists around the fibers at the fiber/matrix interface. The ring is larger for the LAS-III matrix composite and of somewhat different morphology. This ring was not present on the fibers to begin with and is never observed when these fibers are incorporated into resin matrix composites.

![Fig. 2. TEM Replica Characterization of (A) LAS-I and (B) LAS-III Matrix/Nicalon Fiber Composites (As-Pressed)](image)

[1] Phillips EM 400T
[2] Perkin Elmer Physical Electronics 600H
The identification of the observed fiber/matrix interfacial ring in LAS-I matrix composites was not successful by either X-ray diffraction of crushed samples or extraction by overetching with HF. For the LAS-III matrix composites, however, the outer portion of this reaction ring was identified as NbC from the above analyses. During hot-pressing, the 5% Nb2O5 in the LAS-III composition has reacted with the Nicalon fibers to form NbC. Other studies at UTRC have shown that Ta2O5 additives react in the same manner.

In order to characterize the LAS matrix/Nicalon SiC fiber composite interfacial area in greater detail, thin foils were prepared by ion beam thinning. During this process, it was found that the LAS matrix and Nicalon fibers generally did not thin at the same rates and that the weak fiber to matrix bonding made the preparation of good foils rather difficult. The greatest success was achieved with composites in which the fibers were lying essentially parallel with the foil surface. The TEM thin foil analyses were done on LAS-I and LAS-III matrix composites in the as-pressed condition.

Figure 3 shows TEM thin foil micrographs of both LAS-I and LAS-III matrix composites in the as-pressed condition. It can be seen that there exists a light colored interfacial zone between the SiC fibers and the LAS matrix: In the LAS-III matrix composite, the dark particles along the interfacial zone/matrix interface are NbC crystals. Energy dispersive X-ray spectroscopy (EDS) analysis of the interfacial region of both composites shown in Fig. 3 was performed in a stepwise fashion using a windowless detector for light element analysis and indicated that Al and a very small amount of Mg were diffusing into the Nicalon fibers to a distance of \( \sim 1500 \)Å for the LAS-III matrix composite and at least 5000Å for the LAS-I matrix composite as measured from the light colored interfacial zone. EDS analysis of the NbC particles in Fig. 3B verifies their high Nb content while EDS analysis of the light colored interfacial zone in both composites indicates a very high carbon content, as shown in Fig. 4.

Fig. 3. TEM Thin Foil Characterization of (A) LAS-I and (B) LAS-III Matrix/Nicalon Fiber Composites (As-Pressed)

Fig. 4. EDS Analysis of NbC Particles and Interfacial Zone from Composite of Fig. 3B
Selected area electron diffraction (SAED) analysis of the composite interfaces shown in Fig. 3 verified that the dark particles along the fiber/matrix interface of the LAS-III matrix composite were NbC. Diffraction patterns taken from the lighter colored crystals in the matrix confirmed them to be mullite, while the Nicalon fiber showed a characteristic ring pattern of microcrystalline β-SiC. The light colored interfacial zone in both composites gave a diffuse ring diffraction pattern that correlates quite well with that of carbon (ASTM Card 6-0675). This carbon layer is apparently quite weak when compared to either the matrix or fiber and therefore is the main contributing factor to the ability of these composites to deflect matrix cracks, giving rise to the observed high fracture toughness of these composites.

TEM analysis has also been utilized to investigate LAS matrix/Nicalon fiber composites that, for various reasons, were not very strong or very tough. Figure 5 shows the TEM replica analysis of polished cross-sections of two different composites that exhibited as-pressed RT flexural strengths of only 350-450 MPa compared to the usual LAS-III matrix/Nicalon fiber composite strength of 950-1050 MPa. Figure 5A shows an LAS-III matrix/Nicalon fiber composite that was processed at a maximum hot-pressing temperature of ~1475°C instead of the usual 1350°C, while Fig. 5B shows an LAS matrix/Nicalon fiber composite that was hot-pressed at the usual 1350°C temperature, but whose matrix contained 10 wt% Nb₂O₅ instead of the usual 5 wt% Nb₂O₅ for the LAS-III composition. Both composites exhibit rather severe fiber/matrix interaction. Both EDS and SAED analyses of extracted particles of the reaction phase found massive NbC formation at the fiber/matrix interface. Thus, control of hot-pressing temperature and matrix composition is vital for the fabrication of tough and strong composites in the LAS matrix/Nicalon fiber system.

**Fig. 5. TEM Replica Characterization of [A] LAS-III Matrix/Nicalon Fiber Composite Hot-Pressed at 1475°C and [B] LAS + 10% Nb₂O₅ Matrix/Nicalon Fiber Composite (As-Pressed)**

Scanning Auger Microprobe (SAM) Analysis

This analytical tool was utilized to investigate the surface and near-surface regions of Nicalon SiC fibers both before and after incorporation into composite form, and the matrix interfacial region of composite fracture surfaces. The SAM system used has a minimum electron beam spot size of less than 500Å with a typical Auger electron emission depth of 10-30Å. In this study the analyses were performed in the spot mode using a beam diameter of nominally 3000Å in order to provide a more integrated area of analysis. This instrument has excellent sensitivity for most low atomic number elements and has been used to detect elements down to atomic no. 3 (Li). Depth profile information was obtained by in situ sputtering with an Ar ion beam. Since the rate of material removal has been calibrated using a Ta₂O₅ standard, the depth profiles obtained for the Nicalon fibers and the LAS matrix must be taken as approximations.

A Nicalon SiC fiber that had been passed quickly through a bunsen burner flame to remove the vinyl acetate sizing was depth profiled from its surface inward in the SAM. Figure 6 shows the SAM depth profile for this fiber. From this data it appears that the surface of the as-flamed Nicalon fibers is high in oxygen and low in carbon. To verify
that this is the true chemistry of the fibers and not just created by the oxidizing bunen burner flame, a sample of Nicalon fiber with no sizing applied was also depth profiled in the SAM. The overall fiber chemistry and oxygen rich surface found for this fiber was very similar to that shown in Fig. 6.

When a strong and tough glass-ceramic matrix/Nicalon SiC fiber composite is fractured in the plane of the fiber orientation, many of the fibers lying along the fracture surface break free of the matrix. Careful selection of those fibers that are free of matrix debris can then be done for SAM analysis. Also, the matrix troughs from which fibers have pulled away from during composite fracture can also be SAM depth profiled.

Figures 7 and 8 show typical combined fiber surface and matrix trough SAM depth profiles for an as-pressed LAS-I and LAS-III matrix/Nicalon fiber composite, respectively. Some similarities and many differences in interfacial chemistry are apparent for these two composites. In general, the interfacial zone, as defined by that region of the composite interface that is markedly different in chemistry than either the matrix or fiber, is on the order of 6000-8000Å in thickness for LAS-III matrix composites and 1000-1500Å in thickness for LAS-I matrix composites. Both composites exhibit a carbon interfacial zone, which almost always stays primarily attached to the Nicalon fiber during composite fracture, that is quite thin (200-300Å) for the LAS-I matrix composite compared to the LAS-III matrix composite thickness of 500-1000Å. The NbC zone in the matrix trough of the LAS-III matrix composite can be seen clearly in Fig. 8 and appears to be on the order of 3000Å in thickness, similar to that found from TEM analysis.

Both composites also exhibit Al diffusion into the fibers from the matrix, also found from TEM analysis, but the depth of detectable Al in the LAS-III matrix composite fiber is much less than that of the LAS-I matrix composite fiber. Invariably, no Al is detected in the carbon layer between matrix and fiber, which is surprising. However, since the detectability limit for the SAM is on the order of 2%, some Al may be present. One of the interesting findings of the LAS-III matrix composite analysis (Fig. 8) is that Li, which exists in the LAS matrix in a concentration of ~2.5 wt% but which is never detected at this level from SAM analysis, appears to concentrate in the NbC particulate region. The glassy matrix in which the NbC particles appear to be imbedded, as seen from TEM thin foil analysis, may have a rather Li rich composition.

From tensile tests on Nicalon fibers that have been extracted from LAS matrix composites by HF dissolution of the matrix, it has been found that fibers from LAS-III matrix composites are always stronger than those from LAS-I matrix composites. This correlates well with the fact that LAS-III matrix composite flexural strengths are always higher than LAS-I matrix composite strengths. The reason for this may be that the increased amount of Al diffusion from the matrix into the fibers in LAS-I matrix composites compared to LAS-III matrix composites, as was seen from Figs. 7 and 8, is
contributing to degradation of fiber strength. It may also be possible that other matrix elements, such as Mg and, in particular, Li, may also be diffusing into the fibers in LAS-I matrix composites but cannot be detected from SAM analysis if they exist at levels below ~2wt%. Some evidence was seen from TEM thin foil analysis for Mg diffusion into the fibers. The NbC particulate layer in LAS-III matrix composites, while not continuous enough to be acting as a true diffusion barrier, may be acting as a sink for Li thus preventing or significantly decreasing its diffusion into the Nicalon fiber.

That the formation of the interfacial carbon layer in glass matrix/Nicalon fiber composites is necessary for a strong, tough composite was demonstrated by the SAM analysis of a fiber surface on the fracture surface of a high silicon glass (Corning 7930) matrix/Nicalon fiber composite. This composite was quite weak (200 MPa) and brittle,
with a rather well-bonded fiber/matrix interface. The SAM analysis of a fiber on this surface indicated that no carbon interfacial layer had formed in this composite and that the fiber surface had the same oxygen rich composition as it did before composite consolidation, as was seen in Fig. 6. Thus, matrix chemistry can indeed play a role in determining the final interfacial chemistry in these types of composites.

**Tyranno Fiber Composites**

These fibers, while similar in many ways to the Nicalon fibers, are also somewhat different in composition from Nicalon. Figure 9 shows the SAM analysis of a Tyranno fiber after removal of the sizing by passing the fiber quickly through a bunsen burner flame. Like Nicalon, the Tyranno fiber is not stoichiometric SiC but contains excess carbon and oxygen. Unlike Nicalon, Tyranno exhibits a somewhat less oxygen rich surface but a bulk oxygen content that is higher (~15 at%) than Nicalon (~9 at%), and contains ~3 at% Ti.

**Fig. 9. SAM Depth Profile for As-Received Tyranno Fiber (Flame De-sized)**

Figure 10 shows a typical TEM replica of a polished cross-section and a TEM thin foil of an LAS-I matrix/Tyranno fiber composite processed identically to that previously found to yield strong and tough LAS-I matrix/Nicalon fiber composites. This composite, however, was very weak (200 MPa) and exhibited a rather brittle fracture surface. From Fig. 10A, it can be seen that a rather irregular reaction ring exists around the fiber. From Fig. 10B, the reaction zone appears to consist of a rather thin carbon containing layer plus small crystals that contain rather high amounts of Ti. These crystals are dispersed in the matrix next to the carbon layer and have been identified from selected area electron diffraction analysis as TiC (ASTM Card 6-0614).

Figure 11 shows the results of SAM depth profiling across the fracture surface of this composite and verifies the presence of an interfacial high carbon containing layer. In addition to the carbon layer, a rather large amount of Al diffusion has occurred from the matrix into the fiber (more than for LAS-I matrix/Nicalon fiber composites, Fig. 7) plus some Ti now exists in the matrix as well as the fibers. The Ti is probably the result of depth profiling through some of the small TiC crystals.
The lower strength of the Tyranno fiber/LAS-I matrix composite compared to Nicalon fiber composites may be related to enhanced bonding at the interface due either to the higher oxygen content of these fibers or the formation of the TiC crystals at the fiber/matrix interface, or both. Previous experience at UTRC with Nicalon fibers of higher oxygen content also resulted in significantly lower strength composites.

**MPDZ Fiber Composites**

The MPDZ fibers made under the Dow Corning/DARPA program from methylpolydisilylazane polymer and evaluated at UTRC exhibited typical near surface chemistry as shown in the SAM depth profile in Fig. 12. While similar to Nicalon fibers in that they contain excess carbon over stoichiometric SiC plus ~10 at% oxygen in the bulk fiber, the MPDZ fibers also contain from 10-15 at% N, while Nicalon fibers exhibit only a trace (<2%) of nitrogen.
The fracture surface of an LAS-III matrix composite utilizing the MPDZ fibers was quite fibrous, as seen from Fig. 13, with a reasonable RT flexural strength of 525 MPa considering that the hand lay-up procedure used to fabricate the composite resulted in somewhat misaligned fibers. TEM replica and thin foil analysis of this composite (Fig. 14) indicates an interfacial structure quite similar to LAS-III matrix/Nicalon fiber composites (Figs. 2, 3) except that the carbon rich layer is somewhat thicker. The NbC crystals that form in the matrix near the carbon layer appear to be less numerous.

Figure 15 shows the interfacial composition for this composite, as determined by SAM analysis of a fractured composite surface, verifying the TEM observation of NbC particulate formation in the matrix and a relatively thick (500-750Å) carbon rich layer. A significant amount of Al diffusion has occurred from matrix to fiber as well as a small amount of nitrogen diffusion from the fiber into the matrix. Experiments with the MPDZ fibers in other glass and glass-ceramic matrix have shown that elemental diffusion of matrix constituents (Al,B,Mg,Ba) into the fibers during composite processing is much more pronounced for the MPDZ fibers than for Nicalon fibers, possibly due to the amorphous nature of the MPDZ fibers.
A major effort of the Dow Corning/DARPA program has been concentrated on the development of HPZ (hydridopolysilazane) fibers. Unlike Nicalon, Tyranno, or MPDZ fibers, HPZ fibers contain more nitrogen than carbon, as shown from a typical SAM depth profile in Fig. 16. The composition of these fibers may give them the potential to be more thermally stable than the previously mentioned fibers since the usual decomposition route of free carbon plus oxygen combination to form CO does not operate in the HPZ compositional system. Like MPDZ fibers, the microstructure of these fibers is totally amorphous from X-ray diffraction analysis.

Both LAS-I and LAS-III matrix composites were fabricated at UTRC utilizing HPZ fibers. Both types of composites were very weak in RT flexure (<50 MPa) and totally brittle, as shown in Fig. 17 for an LAS-III matrix composite. A SAM depth profile into the side of a fiber fractured from this composite and of a matrix trough indicated that no carbon rich interfacial layer had formed and that the fiber surface is somewhat oxygen rich, similar but to a lesser extent than that found for an as-received fiber. Both LAS-I and LAS-III matrix composites exhibited similar fiber depth profiles and both showed Al
diffusion into the fiber and a large amount of nitrogen diffusion into the matrix. Like MPDZ fiber composites, HPZ fibers in other glass or glass-ceramic matrices showed a large amount of matrix elemental diffusion into the fibers, especially for boron from borosilicate glass composites.

Figures 18 and 19 show the TLM replica analyses and TEM thin foil analyses of LAS-I and LAS-III matrix/HPZ fiber composites. From Fig. 18, it can be seen that fiber/matrix interaction is occurring for both composite systems. Interestingly, no NbC particulate formation was observed at the fiber/matrix interface for LAS-III matrix/HPZ fiber composites, as it is for this matrix with Nicalon and MPDZ fibers. Rather large NbC particles were found in the matrix near the fibers, but not necessarily immediately adjacent to them, as seen in Fig. 18B. From TEM thin foil analyses (Fig. 19), it was found that both composites exhibited identical interfacial compositions. The crystalline reaction product at the fiber/matrix interface was identified from SAED as a silicon oxynitride (ASTM Card 9-246). This card gives a formula for this phase as Si$_2$ON but it is more likely that the correct formula should be Si$_2$N$_2$O for charge balance to be maintained.
Since the fiber/matrix interfacial reactivity that occurs in this composite system results in very strong bonding between fiber and matrix, even if the fibers were not degraded in strength due to this interaction, the crack deflection mechanism that led to strong and tough composites in the Nicalon and MPDC fiber composites is not present in the HPZ fiber composites. Thus, strong and tough composites can never be achieved unless a weakly bonded interfacial layer can be designed into the composite system. To investigate the possibility of creating a strong and tough HPZ fiber composite by tailoring the fiber/matrix interface, CVD carbon coatings were applied to the fibers prior to composite fabrication. These coatings were applied by Battelle Labs, Columbus, Ohio and varied in thickness from ~400Å to over 5000Å.

A typical carbon coated HPZ fiber and its associated SAM depth profile is shown in Fig. 20. This particular lot of coated fibers exhibited a carbon coating of ~3500Å in thickness. When these fibers were incorporated into an LAS-I matrix composite, the result was a very tough and quite strong (~600 MPa) composite with a very fibrous fracture surface (Fig. 21), in stark contrast to the very brittle fracture surface of the uncoated HPZ fiber composite as was seen in Fig. 17. TEM replica characterization of the carbon coated HPZ fiber/LAS-I matrix composite showed that the carbon coating remained intact at the fiber/matrix interface after composite fabrication.
Figure 22 shows the SAM depth profile across the interface of this composite which was obtained by simultaneously profiling a fiber surface and a matrix trough on a longitudinal fracture surface of an as-pressed composite sample. It is apparent that the CVD carbon layer has remained on the fiber surface. The important points to note from Fig. 22 are that no Al diffusion from the matrix into the fiber has occurred nor has any N diffusion from the fiber into the matrix, both of which normally take place in uncoated HPZ fiber/LAS-I matrix composites. A small amount of O, Si, and N have diffused into the carbon coating while ~5 at% carbon has diffused into the matrix to a depth of ~3000Å. The carbon coating is thus acting as a very good diffusion barrier for this composite system, at least for the coating thickness evaluated.

**SiC Whisker Composites**

Two types of SiC whiskers have been evaluated at UTRC as potential reinforcements for LAS matrices in order to provide increased toughness and strength. Los Alamos National Labs (LANL) B-SiC whiskers and Arco Chemicals α-SiC whiskers were incorporated into LAS-I and LAS-III matrices. From the results of this study, both whiskers, which are essentially stoichiometric SiC with a small amount of oxygen present, gave composites that exhibited linear stress-strain behavior and fractured in a brittle
fashion. The whiskers were found to strengthen the matrices but did not alter the brittle nature of fracture appreciably. Unreinforced LAS-I and LAS-III exhibit a RT flexural strength of ~70-90 MPa. A LANL SiC whisker reinforced LAS-III matrix composite exhibited a flexural strength of 276 MPa while an Arco SiC whisker reinforced LAS-I matrix composite exhibited a RT flexural strength of 450 MPa.

Researchers at Corning Glass have also been successful in strengthening various glasses and glass-ceramics by the addition of SiC whiskers. Fracture toughness ($K_{IC}$) values reported for these composites were also significantly higher than that of the matrices alone; however, most of this increase can be accounted for by the increase in strength of the composite.

Figure 23 shows the fracture surface of an LAS-I matrix/SiC whisker composite indicating the rather brittle fracture nature. Some evidence of crack deflection and whisker/matrix debonding can be observed, but nothing like discontinuous Nicalon fibers in LAS matrices. From scanning Auger and TEM analyses, it was found that the carbon rich interfacial layer that forms at the fiber/matrix interface in Nicalon fiber reinforced glass and glass-ceramic matrix composites is not present in SiC whisker reinforced composites.
processed under fabrication conditions identical to those which produced tough Nicalon composites. Cracks advancing through the whisker reinforced composites for the most part encounter whiskers that are strongly bonded to the matrix, and so propagate through the whiskers with little if any deviation. The consequence is brittle fracture. Figure 24 compares the fiber/matrix interface as found from TEM thin foil analysis for LAS-III matrix composites with Nicalon SiC fiber and VLS SiC whisker reinforcements. While the NbC particulate layer formed at the interface for both types of composites, the weakly bonded carbon rich layer only formed in the Nicalon fiber composites.

Figure 24. TEM Thin Foil analyses of LAS-III Matrix/Nicalon Fiber (A) and SiC Whisker (B) Composites (As-Pressed)

Figure 25 shows the TEM replica and thin foil analyses for an LAS-I matrix composite with the Arco SiC whiskers. No interaction can be seen between the whiskers and matrix at the whisker/matrix interface. The interfacial bond strength in this system must be quite strong, however, since very little whisker pullout is observed on the fracture surface of this composite.

Figure 25. TEM Replica (A) and Thin Foil (B) Analysis of LAS-I Matrix/SiC Whisker Composite (As-Pressed)

For true toughness increases to occur for fiber or whisker reinforced ceramic matrix composites, the weakest link in the composite must be the fiber/matrix interface. This situation is present for Nicalon, MPDZ, and carbon coated HPZ fibers in LAS matrices, as has been demonstrated, but is not present for SiC whisker or uncoated HPZ fiber composites. It can occur for SiC whiskers incorporated in other ceramic matrices such as Al₂O₃. In this case the observed toughness increases¹¹ are due to an extremely thin glassy layer being formed at the whisker/Al₂O₃ interface. In this composite material, the weak link is this glassy layer between the SiC whiskers and alumina matrix.
CONCLUSIONS

From the results of this study, it has been found that polymer derived Si-C-O or Si-C-N-O fibers such as Nicalon, Tyranno, and Dow Corning MPDZ, that contain excess carbon and oxygen over stoichiometric SiC, form a carbon rich fiber/matrix interfacial layer when incorporated into LAS glass-ceramic matrices at elevated temperatures. The exact mechanisms for the formation of this layer are not totally defined but may be related to diffusion of oxygen and silicon ions down the silica activity gradient that exists from fiber to matrix, as suggested by Cooper. In any case, the formation of this weak interfacial zone in these composites is responsible for the high toughness observed in that it allows crack deflection to occur along the fiber/matrix interface and also allows load transfer from matrix to fiber to occur so that strengthening by traditional composite theory can take place.

In LAS-III matrix composites, that contain Nb2O5, a reaction also occurs at the fiber/matrix interface forming a layer of NbC particles. These particles, at least in Nicalon fiber composites, may act as sinks for certain elements that tend to diffuse from matrix to fibers with resultant fiber strength degradation, thus accounting for the higher strength of LAS-III matrix composites over LAS-I matrix composites. The Tyranno fibers, which contain a small amount of Ti, tend to form a relatively small number of TiC crystals at the fiber/matrix along with a quite thin carbon rich layer that contains some oxygen. The lower strength of the Tyranno fiber composites compared to Nicalon fiber composites may be related to enhanced bonding of the interface due either to the higher oxygen content of these fibers or the formation of the TiC crystals, or both, but cannot be defined for certain at this time.

The polymer derived high nitrogen content HPZ fibers from Dow Corning and the SiC whiskers from either Los Alamos or Arco do not form a weakly bonded carbon rich interfacial layer when incorporated into LAS matrices, and thus yield brittle composites with little or no fiber/matrix debonding. In the case of HPZ fibers, a reaction occurs forming crystalline silicon oxynitride at the fiber/matrix interface while the SiC whiskers form either NbC crystals with LAS-III matrices or no distinct reaction layer with LAS-I matrices, but in all cases a relatively strong fiber/matrix bond is formed. Only with a deliberately formed weak interface, such as CVD carbon applied to the HPZ fibers prior to composite fabrication, can a composite be achieved that exhibits a fibrous non-linear type of fracture behavior that results in a strong and tough ceramic material with these types of fibers. It is apparent from this investigation that the particular chemistry and/or microstructure of the fiber utilized in LAS matrix composites determines to a large degree the type of interface formed between fiber and matrix which, in turn, controls the type of composite behavior one can achieve in these systems.

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REFERENCES


D.S. Wilkinson: How stable are the carbon interfacial layers during exposure at elevated temperatures?

J.J. Brennan: During exposure at elevated temperatures (>500°C) in oxidizing environments, if a fiber intersects a cut or ground surface of the glass-ceramic matrix composite, the thicker carbon interfacial layers that exist in the LAS-III matrix/Nicalon fiber system or the CVD carbon coated HPZ fiber systems have been found to be relatively unstable with respect to oxidation. In addition, the NbC particulate interfacial layer that forms in LAS-III matrix composites is also subject to oxidation. The thinner carbon layers (100-200 m) that form in the LAS-I matrix/Nicalon fiber composites are quite stable in oxidizing environments due to a "plugging" mechanism that occurs at the composite surface that effectively seals the interface with a silicate glassy layer, greatly reducing further "pipeline" oxidation of the interfacial carbon layer.