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SiC-Whisker-Reinforced Glass-Ceramic Composites: Interfaces and Properties

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Different types of SiC whiskers were incorporated into lithium aluminosilicate (LAS) and calcium aluminosilicate (CAS) glass-ceramic matrices. Interfaces in these composites were characterized using Auger spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM), and the observations were correlated with measurements of fracture toughness and strength. The chemistry and morphology of the resulting interfaces affected the composite strength and toughness and controlled the mode of crack propagation. Certain types of SiC whiskers were characterized by a carbon-rich near-surface chemistry that became more carbon rich after composite fabrication. In these materials, the flexural strength at 20°C increased by up to 400% and the fracture toughness increased by up to 500%. Crack propagation modes were characterized by crack deflection, whisker–matrix debonding, and crack bridging. In contrast, SiC whiskers with stoichiometric near-surface chemistry generally did not form carbon-rich interfaces during composite fabrication, resulting in composites with low strength and fracture toughness. [Key words: composites, glass ceramics, whiskers, interfaces, silicon carbide.]

I. Introduction

CERAMIC matrix composites are prospective materials for high-temperature structural applications, and a variety of materials systems are currently under consideration. Matrices can be broadly classified as polycrystalline, glass, or glass-ceramic, while reinforcements can be similarly classified as continuous fibers or discontinuous reinforcements, which include short fibers, whiskers, and particles. Composites reinforced with continuous fibers generally display higher levels of strength and toughness than similar composites reinforced with whiskers or short fibers. However, the processing temperatures necessary to fully densify or infiltrate the particular matrix are often above the range of thermodynamic stability for most continuous fibers presently available.[1–4] Furthermore, the fabrication of near-net-shape components is generally more difficult (if not impossible) for composites reinforced with continuous fibers as opposed to other reinforcement types.

Recent studies conducted at United Technologies Research Center and elsewhere on continuous fiber-reinforced glass and glass-ceramic composites led to the recognition that these types of composites are also limited by low through-thickness and interply shear strength, as well as a low proportional limit or matrix microcracking stress.[5–17] These properties are controlled by the fiber–matrix interfacial shear strength and the inherent fracture toughness of the matrix. Although the interfacial shear strength must remain low in order to facilitate toughening mechanisms in the composite, the inherent toughness of the matrix should be enhanced by the addition of whiskers, thereby improving composite properties, especially the proportional limit stress.

In this paper, we describe the results of a comprehensive study of whisker–matrix interfaces in glass-ceramic composites, and the effects of the interfacial characteristics on composite mechanical properties. Several different whiskers are used to reinforce lithium aluminosilicate (LAS) and calcium aluminosilicate (CAS) glass-ceramic matrices. Interface characterization is accomplished using several analytical methods, both before and after composite fabrication. Flexural strength and fracture toughness are measured at high temperature and ambient temperature, and modes of crack propagation are investigated. The objective of the present study is to arrive at a better fundamental understanding of interface characteristics controlling the mechanical behavior of SiC whisker-reinforced glass-ceramic composites. The understanding acquired will provide a basis for microstructural design of composites with enhanced mechanical properties.

II. Background

Because of recognized limitations of continuous fiber composites, much attention has been focused on whisker-reinforced composites with matrices such as alumina, mullite, and, to a lesser extent, zirconia and silicon nitride.[18–60] These studies revealed that the relative improvements in strength and fracture toughness compared to the unreinforced matrix differed substantially in ostensibly similar materials. Among the possible causes of this phenomenon were the different interactions between matrix and whisker properties, such as elastic modulus mismatch, thermal expansivity mismatch (causing thermally induced residual stresses), and chemical interactions, all of which varied with the particular matrix.

Whisker characteristics also appear to influence composite properties. Undoubtedly some of the apparent discrepancies can be attributed to batch-to-batch variations in the whiskers, although other factors also may be involved. The effect may stem simply from the amount of particulate matter included in the whisker batch, or from the whisker sizes, aspect ratios, internal defects, or surface roughness.[37] In addition, there are clear indications that the surface chemistry of the whiskers can significantly influence the composite toughness, although not the strength. Tiegs and co-workers[38] reported that SiC whiskers grown by Advanced Composite Materials Company (ACMC SC-9), Greer, SC (ACMC) and Los Alamos National

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Laboratory, Los Alamos, NM (LANL) were characterized by carbon-rich surfaces. When the whiskers were incorporated into alumina, the composite toughness was enhanced and fracture surfaces showed evidence of whisker pullout and debonding. However, whiskers grown by Tokai Carbon Company, Tokyo, Japan and Taheto Chemical Industries Company, Hyogo-Keu, Japan were characterized by oxygen-rich surfaces, and composites showed little toughness enhancement. Fracture surfaces showed no signs of whisker pullout and debonding. Similar results were reported by Vaughn *et al.*[37] In a recent study, Becher *et al.*[41] attempted to control interface chemistry by treating whiskers prior to composite fabrication. Whiskers with a carbon-rich surface resulted in high-toughness composites. However, when the same whiskers were oxidized prior to composite fabrication, an oxygen-rich surface was produced, resulting in low-toughness composites. Similarly, whiskers which initially exhibited oxygen-rich surfaces resulted in low-toughness composites, but when the same whiskers were heat-treated to produce a carbon-rich surface, the resulting composites showed enhanced fracture toughness.

Unfortunately, the relation between whisker surface chemistry and composite fracture toughness is not always unambiguous. For example, work of Krug and Danforth[39] and Phillips and Taylor[40] appears to partly contradict the references cited above. Evans[42] attributed the toughness enhancement in alumina–SiC whisker composites to the presence of thin interfacial films of silica glass. However, Claussen and Petzow[25] also observed thin glassy films in SiC–zirconia composites, but reported that whisker debonding and pullout were rarely observed because of *strong* interfacial bonding, concluding that the glassy films did not play a substantial role in toughening. Finally, the relatively few studies of whisker-reinforced glass and glass-ceramic matrices have shown consistent enhancements in room-temperature strength and fracture toughness.[18,19] From the brief review given here, it is clear that the toughening mechanisms in whisker-reinforced composites are not well established and may actually vary from system to system, depending on matrix properties and on whisker characteristics such as surface roughness, surface chemistry, size, and aspect ratio.

III. Experimental Procedure

(1) Materials

The glass-ceramic matrices selected for the present study were a lithium aluminosilicate (LAS-I) that crystallizes to a β-quartz-silica solid-solution phase ($(Li_2O, MgO)\cdot Al_2O_3\cdot nSiO_2$ ($n > 2$)) and a calcium aluminosilicate (CAS) that crystallizes to anorthite ($CaO\cdot Al_2O_3\cdot 2SiO_2$). The LAS-I matrix was similar in composition to Corning 9608 (Corning Inc., Corning, NY), except that a small amount of zirconia was substituted for titania as a nucleating aid. The same LAS-I matrix has been used in previous studies to make composites with a variety of continuous fibers.[8,13,14] Both of the glass-ceramic compositions were melted in an electric furnace in air, quenched in the glassy state, and ground into fine powder (~8 μm).

Five varieties of SiC whiskers were selected for incorporation into the glass-ceramic matrices, including the small-diameter (<0.7 μm) ACMC and Tokai whiskers, henceforth designated AC-1 and TK-1; the slightly larger (~1 μm) Tokai TWS-400 whiskers, designated TK-2; the large-diameter (~3 μm) American Matrix Co. (presently Advanced Refractory Technologies, Inc., Buffalo, NY) whiskers, designated AMI; and the largest VLS whiskers (5 to 8 μm), made at Los Alamos National Laboratory (LANL). All of the as-received whiskers were characterized using SEM and Auger spectroscopy to determine morphology and surface chemistry.

(2) Sample Fabrication

All of the composites fabricated for the study were formulated to contain 30 vol% whiskers (36 wt% for LAS matrices and 33.6 wt% for CAS matrices). Preweighed glass powder and SiC whiskers were mixed in an attritor (Szegvari, Union Process Company, Akron, OH) using mullite balls and propanol as a fluid medium. Attriting at a speed of 100 rpm for 3 h resulted in excellent dispersion of the whiskers and glass powder. After milling, the mix was dried in a flat bed, and aggregates were dispersed by hand as required. The dried blends were then hot-pressed in graphite dies for 30 min at 1300° to 1350°C (for LAS matrices) and for 10 min at 1450° to 1500°C (for CAS matrices) under a pressure of 13.8 MPa, resulting in full density. Composite panels were cut into bars for mechanical testing. To crystallize the matrices, LAS composites were heat-treated in argon for 8 to 24 h at 900° to 1000°C to achieve a β-spodumene/silica solid solution with the β-quartz structure, while CAS composites were heated for similar times at 1100° to 1200°C, resulting in a crystalline anorthite matrix. More than 12 different composites were fabricated using the different SiC whiskers and the LAS and CAS matrices.

(3) Whisker and Composite Characterization

All of the SiC whiskers used in the study were characterized prior to composite fabrication. Whisker size, shape, aspect ratio, and surface morphologies were characterized by SEM observations, while surface composition was measured by Auger spectroscopy in a scanning Auger microprobe (SAM) (PHI 600H, Perkin-Elmer Corp., Eden Prairie, MN). Argon sputtering was used to generate compositional depth profiles from each of the whisker types. The Auger spectrometer was calibrated for Si and C sensitivity factors using a high-purity SiC single crystal and a polycrystalline standard synthesized by high-temperature chemical vapor deposition, resulting in an accuracy level of ±2% to 3% in the measurement of Si and C concentrations. Because surface (and near-surface) chemistry generally determines the reactivity and interfacial bonding that occurs when the whiskers are incorporated into composites, this characterization step was regarded as critical to understanding the composite properties.

SAM depth profiling was also employed to characterize whisker–matrix interface chemistry, a procedure which has been routinely applied to continuous fiber-reinforced glass-ceramic composites.[8,13,14,16] The method relies on composite fracture along interfaces that exposes reinforcements and matrix troughs that are then accessible to the spectrometer probe. Compositional depth profiles were generated by alternately ion-beam sputtering to prescribed depths and acquiring spectra.

Composite microstructures were characterized (EM400T, Philips, Eindhoven, Netherlands) by standard TEM methods. Replica specimens of polished composite cross sections were prepared in order to assess the degree of matrix crystallization and to provide global views of the composite microstructures. Thin-foil specimens were prepared and used to identify phases, determine phase distributions, and identify possible interface reactions. In addition, high-resolution phase-contrast imaging was employed (JEM-2010, JEOL, Peabody, MA) to determine interface structure at atomic-level resolution. These observations were then correlated with results of Auger spectroscopy and with mechanical properties.

(4) Mechanical Properties

Composite flexural strength and fracture toughness was measured in air over a temperature range of 20° to 1000°C (flexural strength) and 20° to 800°C (fracture toughness). Flexural strength measurements were performed on bar specimens (5 mm × 2.5 mm × 76 mm) using a three-point bend fixture with a span of 63.5 mm. Fracture toughness measurements were performed using three methods. First, single-edge notched bar (SENB) specimens were prepared (5 mm × 2.5 mm × 76 mm) and a half-thickness notch was made using a diamond wafering blade. Samples were fractured in bending, and K_{IC} values were determined using the method described

in Ref. 62. Fracture toughness measurements were also performed by the controlled flaw method described by Chantikul *et al.*[68] Indent loads of 65 kg were used to introduce controlled flaws on the tensile side of the flexure bar, and samples were subsequently fractured in bending. Finally, additional fracture toughness measurements were performed using the indentation-crack-length technique.[63-67] An indentation load of 100 kg was used to ensure a crack-length-to-indentation-length ratio of two or more.[65]

IV. Results and Discussion

(1) Whisker Chemistry and Morphology

Compositional depth profiles from as-received SiC whiskers were obtained by Auger spectroscopy and are shown in Fig. 1. The measured composition of the AC-1 whiskers in the near-surface region was 60 at. % C and 40 at. % Si, representing a significant deviation from stoichiometry (Fig. 1(a)). As expected, a slight amount of oxygen was also detected at the surface. In contrast, Karasek *et al.*[69] performed surface analysis by X-ray photoelectron spectroscopy (XPS) on similar AC-1 whiskers and reported a much higher near-surface oxygen content.[69] In general, the AC-1 whiskers were among the straightest and smoothest of the various whiskers examined.

The TK-1 whiskers were similar to the AC-1 whiskers, although the surfaces were slightly rougher and the whiskers were less straight. The near-surface composition was approximately 58% C and 42% Si, and only a trace amount of oxygen was detected at the whisker surface (Fig. 1(b)). (Karasek *et al.*[69] reported moderately high amounts of surface oxygen in

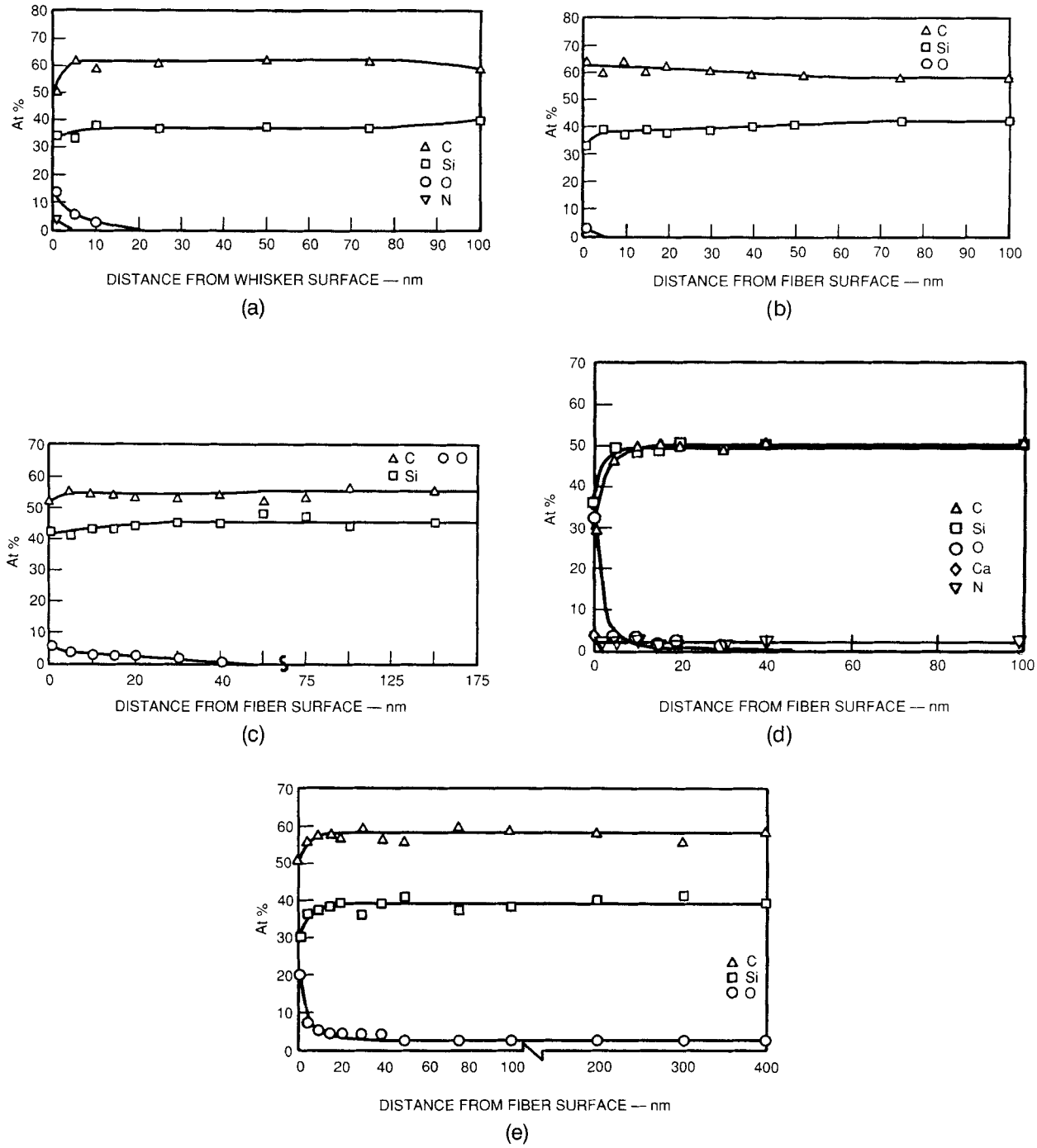


Fig. 1. SiC whisker compositional depth profiles. Quantitative Auger spectroscopy was performed on as-fabricated whiskers. (a) AC-1 type, (b) TK-1 type, (c) TK-2 type, (d) LANL type, and (e) AMI type.

these whiskers, based on XPS measurements.) Surface analysis of the TK-2 SiC whiskers revealed an average near-surface composition of 55% C and 45% Si and oxygen content to a depth of ~40 nm (Fig. 1(c)). Whisker diameters were larger than the TK-1 whiskers, although the diameters typically varied locally on individual whiskers, resulting in nodular and wavy surface morphologies.

While the AC-1 and TK whiskers were grown by vapor–solid (VS) processes which involved the reaction of silica vapors and carbon-bearing gases to produce solid SiC, the LANL whiskers were grown by a VLS (vapor–liquid–solid) process.[70,71] The former whiskers generally showed hexagonal cross-sectional morphologies, while the LANL whiskers showed rounded triangular cross sections with extremely smooth surfaces. The compositional depth profile for the type 5A LANL whiskers revealed nearly stoichiometric SiC (49% Si, 49% C), and a small but consistent amount of nitrogen (2%) in the near-surface regions (Fig. 1(d)). In addition, trace amounts of Ca and O were detected in the first 5 nm, and the oxygen content substantially exceeded the amounts in the AC-1 and TK whiskers.

The AMI SiC whiskers exhibited pronounced surface roughness that is reportedly associated with internal defects and their intersections with the whisker surface.[44] The whisker structure was characterized by a mixture of α-SiC polytypes, and the whiskers typically exhibited kinking, branching, and intergrowth. The near-surface composition was typically C-rich, and there was a relatively high oxygen content at the surface, similar to the LANL whiskers (Fig. 1(e)). The observation is consistent with a previous report[44] in which a 3-nm film of silica was detected at the surface of AMI whiskers. The oxygen content persisted through the near-surface region, resulting in an average composition of 58% C, 39% Si, and 3% O.

(2) Composite Properties

In the following section, results of flexural strength tests, fracture toughness tests, and modes of crack propagation for the different composites will be described. A brief description of the as-fabricated microstructures is presented to introduce the materials.

The microstructures of LAS-I matrix composites reinforced with LANL, AC-1, TK-1, and TK-2 SiC whiskers are shown in Fig. 2. Longitudinal sections were prepared by slicing composites perpendicular to the hot-pressing axis, thereby exposing the plane in which the whiskers tended to orient. The micrographs were recorded at similar magnifications, revealing significant differences in whisker size and amount of particulate matter. The LANL whiskers were substantially larger than the other types, and the ACMC whisker composites contained large SiC particulate matter, as did the Tokai whisker composites, albeit to lesser extents. All of the composites retained whiskers with aspect ratios >12.

(A) Flexural Strength and Fracture Toughness: Values of flexural strength and fracture toughness measured for the different composites and matrices are summarized in Table I. Flexural strengths were measured at 20°, 800°, and 1000°C, and fracture toughness measurements were performed on SENB

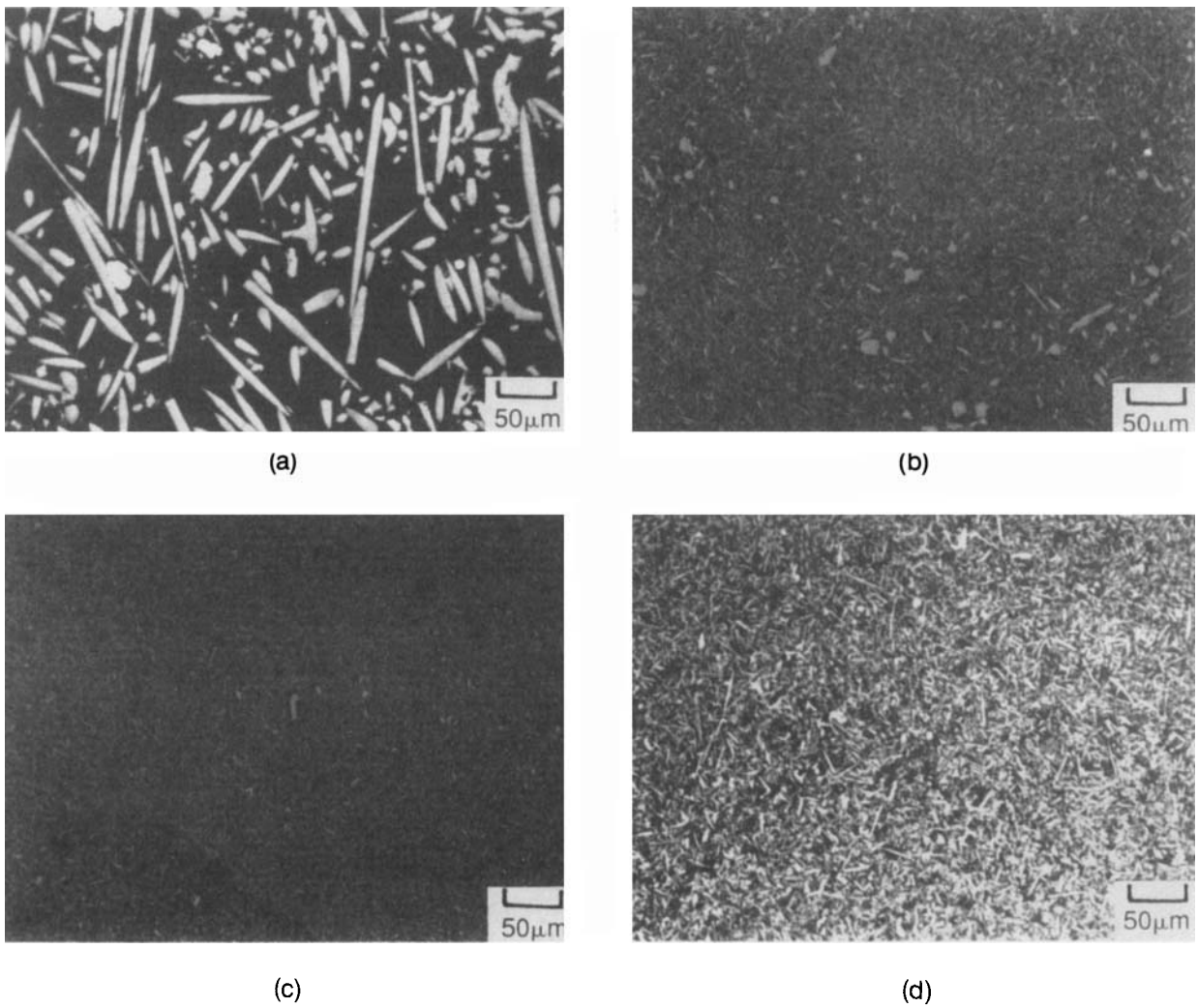


Fig. 2. Microstructures of LAS-I matrix/SiC whisker composites. Longitudinal polished sections of (a) 359-88 LANL SiC_w, (b) 289-88 AC-1 SiC_w, (c) 290-88 TK-1 SiC_w, and (d) 718-88 TK-2 SiC_w.

Table I. Properties of LAS and CAS Matrix/SiC Whisker Composites (30 vol% Whiskers)

Comp. No.	Matrix	Whisker	Flex Strength (MPa) RT	800°C	1000°C	RT K_{IC} (MPa · $m^{1/2}$)
	Corning 9608 LAS		103		<69	0.85
289-88	LAS	AC-1	393	400	290	4.44
290-88	LAS	TK-1	338	496	248	4.20
718-88	LAS	TK-2	372	358	310	4.06
645-89	CAS	TK-2	363	348	276	4.98
96-89	LAS	AMI	193	207	110	2.83
359-88	LAS	LANL	110	131	69	2.24

specimens at 20°C. Composites reinforced with AC-1, TK-1, and TK-2 whiskers showed 3- to 4- fold increases in strength (at all temperatures) compared to the unreinforced LAS-I matrix and an increase in fracture toughness of 3 to 4 MPa · $m^{1/2}$. The magnitude of toughness enhancement observed is larger than the toughness increases reported[41] for soda–lime and aluminosilicate glasses reinforced with 20 vol% SiC whiskers (ΔK^{wr} = 1.2 MPa · $m^{1/2}$). In contrast, the composite reinforced with AMI SiC whiskers showed approximately half the flexural strength and 60% to 70% of the fracture toughness of composites reinforced with the AC-1 and TK whiskers, while the composite reinforced with LANL whiskers showed no appreciable increases over the unreinforced matrix. The modest property levels obtained for the AMI whisker composite were attributed to surface roughness of the as-grown whiskers and the consequent inhibition of toughening mechanisms, as described below.

The fracture surfaces of several of the composites tested in flexure at 20°C are shown in Fig. 3. Whisker pullout of more than 2 to 3 whisker diameters was rarely observed, although evidence of strong interaction between cracks and whiskers was apparent from the roughness of the surfaces. The fracture surface of the composite reinforced with AMI SiC whiskers was smooth and differed substantially from the others, as shown in Fig. 3(d). Although there was some evidence of crack–matrix interaction and even whisker pullout, this occurred primarily in whiskers oriented in the fracture plane. Whiskers oriented at high angles relative to the crack plane generally fractured without pullout or debonding. The irregular surface morphology of the whiskers was especially apparent in the matrix troughs from which whiskers had pulled out (Fig. 2(d)). This factor, more than interface chemistry, appeared to be responsible for the low composite strength and toughness, as described in the next section.

Unlike composites reinforced with AC-1 or TK whiskers, composites reinforced with LANL whiskers showed low flexural strengths and only modest improvements in fracture toughness. As shown in Fig. 3(e), the fracture surface from the LAS-I/LANL SiC composite was macroscopically smoother than fracture surfaces of other composites. Despite some evidence of crack deflection, there were many sites where the matrix crack was not significantly diverted by the whiskers. Becher *et al.*[41] predicted that whiskers of larger diameter should result in corresponding larger increments of toughness compared to smaller diameter whiskers (all other factors being equal). However, the toughness increase is also related to the whisker/matrix interface through the strain energy release rate of the interface, which is inversely related to the debonded length of the whisker. Thus, changes in these parameters caused by changes in interface bonding are expected to affect the whisker contribution to the fracture toughness of the composite. In fact, as described in a subsequent section, the interfacial chemistry and whisker debond length are markedly different for the LANL SiC whiskers compared to the AC-1 or TK whiskers.

Figure 3(f) shows the fracture surface for a CAS matrix composite reinforced with TK-2 whiskers. The fracture surface is rougher than the LAS matrix composite reinforced with the same whiskers (Fig. 3(c)), indicative of the higher fracture toughness of this composite.

Flexural strength measurements were also performed at 20° and at 800°C on SENB (single-edge notched bar) specimens and on indentation-induced controlled flaw (CF) specimens, resulting in strength levels that were only 35% to 50% of the notch-free sample strengths (Table II). CF sample strengths were slightly lower than SENB strengths (as expected) because of the smaller crack tip radius of the former. The much lower strength observed for the SENB and CF samples indicate that the whisker-reinforced glass-ceramic composites were highly notch sensitive over a wide temperature range. In contrast, identical LAS glass matrices reinforced with continuous or discontinuous Nicalon fibers (NLM-202, Nippon Carbon Company, Tokyo, Japan) showed relatively low notch sensitivity, and SENB strengths were typically 80% to 90% of notch-free strengths.[72] The reasons for the difference are not presently clear, although reinforcement size and interface properties undoubtedly affect the associated crack propagation modes.

Fracture toughness measurements were also performed at 20° and 800°C using SENB and identation-induced CF specimens (Table II). No method of performing indentation testing at 800°C was available. The K_{IC} values measured at 800°C were compared to K_{IC} values measured at 20°C, suggesting that enhancement of fracture toughness caused by whisker reinforcement extended over the entire temperature range. The one notable exception was the SENB specimens of the CAS matrix composite, which yielded K_{IC} values at 800°C that were substantially lower than the CF specimens. No explanation for this observation is available. In general, the CF specimens resulted in the most consistent critical stress intensity values at both temperatures. These samples offered the additional advantages of simple sample preparation without machining, and the presence of a sharp crack. In addition, although only one measurement was possible per sample, as opposed to the indentation crack length measurements, the CF samples were well suited to high-temperature measurements of K_{IC} and avoided the uncertainties associated with microscopic measurements of crack lengths. The different techniques for measurements of fracture toughness of similar whisker-reinforced ceramic composites have been evaluated elsewhere.[73]

(B) Modes of Crack Propagation: A 15-kg load was applied to a modified Vickers hardness indenter fitted to a Rockwell hardness tester to introduce cracks into polished surfaces of whisker-reinforced glass-ceramic composites. Figure 4 shows typical crack paths caused by indentation loading in LAS- and CAS-matrix composites with TK-2 whiskers. The arrows indicate the directions of crack propagation, and the effect of the whiskers on the crack path is evident. Interface debonding, crack bridging, and fiber pullout were commonly observed along the crack paths. Cracks generally propagated around whiskers, either by debonding, deflection, or whisker pullout, except where whiskers were oriented normal to the crack plane. In these cases, the interface debonding energy was apparently sufficiently high that pullout could not occur, and the whiskers fractured. Crack paths were similar in LAS-matrix composites reinforced with AC-1, TK-1, and TK-2 composites. However, the LANL SiC whisker com-

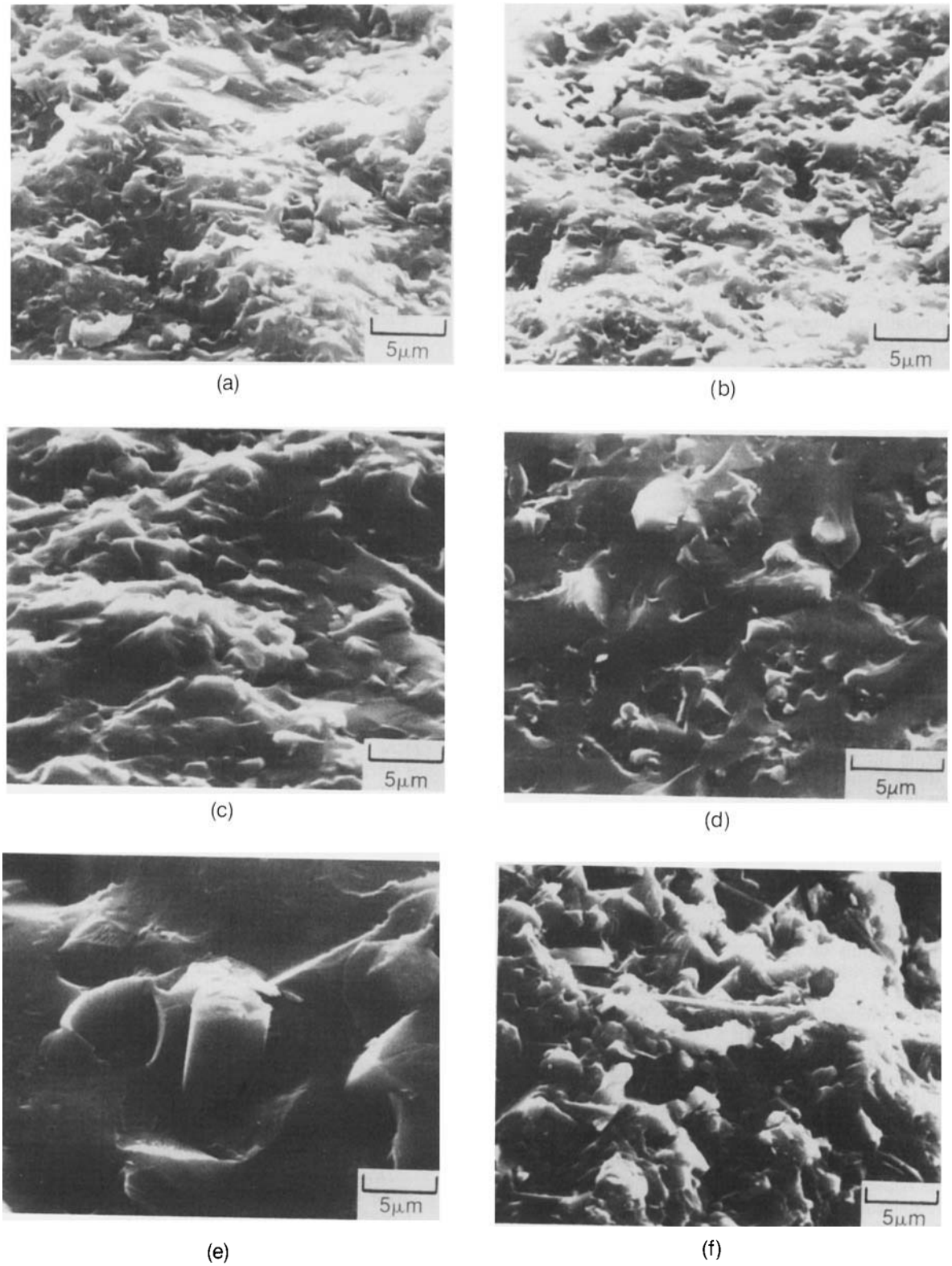


Fig. 3. Fracture surfaces of LAS-I (a–e) and CAS-I (f) matrix/SiC_w composites: (a) 289-88 AC-1 SiC_w, (b) 290-88 TK-1 SiC_w, (c) 718-88 TK-2 SiC_w, (d) 96-89 AMI SiC_w, (e) 359-88 LANL SiC_w, and (f) 499-89 CAS/TK-2SiC_w.

posites showed minimal evidence of interface debonding, crack bridging, fiber pullout, or crack deflection (Fig. 5). Cracks tended to propagate directly through the whiskers with minimal deflection or debonding. The absence of debonding is directly related to the interface chemistry, as described in subsequent sections. Furthermore, the relatively large diameter of the LANL whiskers (and the corresponding large interfiber spacing) may also affect the toughness, although the observed trends are contrary to published theories.[41]

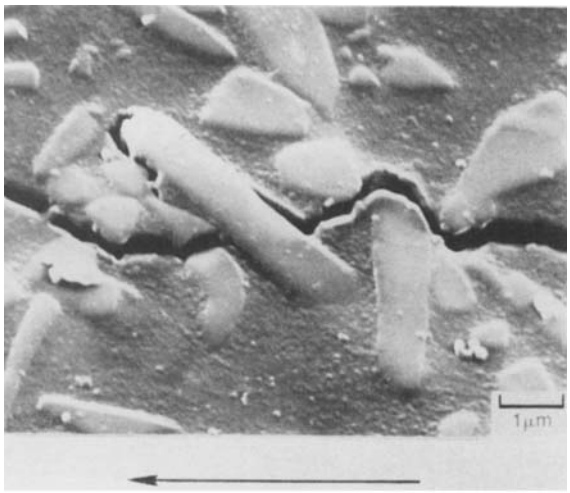
(3) Surface Analysis of Fractured Composites

SiC whiskers exposed on composite fracture surfaces were analyzed by Auger spectroscopy for LAS-I composites reinforced with AC-1, TK-1, TK-2, and LANL SiC whiskers and for CAS composites reinforced with TK-2 whiskers. The results, shown as composition depth profiles, are summarized in Figs. 6(a) to (c) and can be compared with similar composition profiles of the same whiskers prior to composite fabrication (Fig. 1). The surface and near-surface regions of the

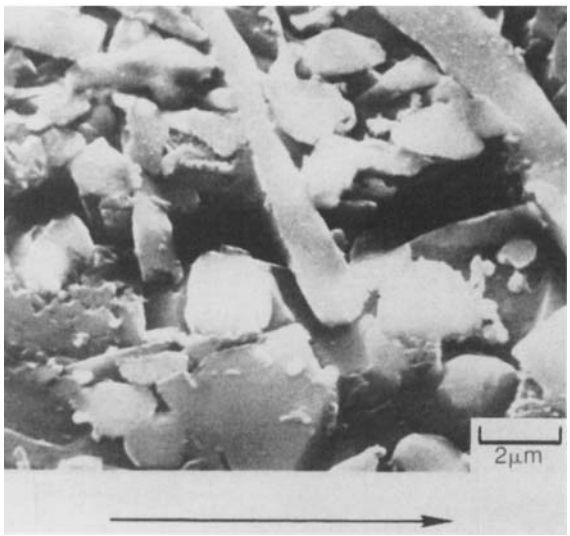
Table II. Fracture Toughness and Flexural Strength of LAS- and CAS-Matrix TK-2 SiC Whisker Composites (30 vol% Whiskers)

Comp. No.	Matrix	Whisker Type	Measurement Technique	K_{IC} (MPa·m$^{1/2}$) RT	K_{IC} (MPa·m$^{1/2}$) 800°C	σ (MPa) RT	σ (MPa) 800°C
646-89	LAS	TK-2	Flexure			327	
			SENB	3.98	3.68	150	138
			Controlled flaw	3.93	3.72	115	131
			Indent	4.47			
645-89	CAS	TK-2	Flexure			363	
			SENB	4.98	3.88	197	164
			Controlled flaw	4.72	4.73	146	150
			Indent	5.09			

TK-1 whiskers were enriched in carbon as a result of composite fabrication. At depths >50 nm, the carbon concentration was slightly diminished, and the oxygen concentration level had risen to ~3%. The AC-1 whiskers used in composite 289-88 yielded composition profiles similar to the TK-1 whiskers (Fig. 6(a)). Like the TK-1 and AC-1 whiskers, the TK-2 whiskers in composite 718-88 also showed carbon enrichment near the surface. However, unlike the TK-1 whiskers, the carbon enrichment was confirmed to a narrow zone within ~15 nm of the surface (Fig. 6(b)). This observation was unexpected, because the TK-2 whiskers were initially less carbon-rich than the TK-1 whiskers. In addition, substantial oxygen diffusion (~5%) and slight aluminum diffusion into the whisker occurred during composite fabrication. Similar composition profiles were obtained for TK-2 whiskers in CAS matrix composites.



(a)



(b)

Fig. 4. Crack propagation paths in (a) LAS-I and (b) CAS matrix composites with TK-2 SiC whiskers (718-88 and 499-89, respectively).

Surface analysis of the LANL whiskers in the LAS-I matrix (composite 359-88) revealed a slight carbon enrichment at the surface that was less than either the Tokai or ACMC whiskers (Fig. 6(c)). The composition of the bulk whisker was essentially stoichiometric SiC as in the as-received whiskers. A trace amount of oxygen was also detected, indicating diffusion into the whisker had occurred during composite processing. These whiskers were grown by a fundamentally different process (VLS), had much larger diameters, different crystal structure (β), far fewer defects, different cross-sectional morphologies, and lower impurity content. These were the only whiskers that did not form a substantial C-rich surface and did not suffer much change in "bulk" composition.

The origin of the C-rich surface layers that develop at whisker surfaces during composite fabrication is a peculiar phenomenon that merits comment. When Nicalon SiC fibers are used to reinforce LAS-I glass-ceramic matrices, a ~20- to 50-nm layer of carbon typically forms on the fiber surface during composite processing.[8,13,14] The carbon layer effectively imparts toughness to the composite by facilitating the deflection of matrix cracks. The source of the C-rich layer can be described by the following reaction:

$$SiC(s) + O_2(g) \rightarrow SiO_2(s) + C(s) \quad (1)$$

This reaction has the most negative free energy of all the chemical equilibria that describe the oxidation of SiC and is likely to exhibit reaction kinetics that are more rapid than other reactions requiring diffusion of a gaseous species away

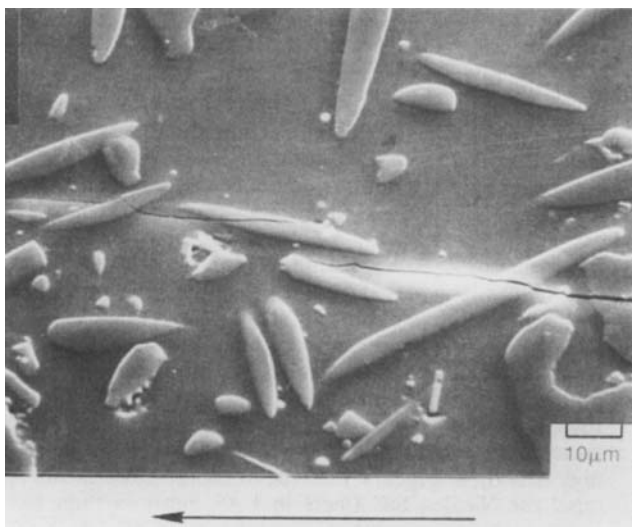


Fig. 5. Crack propagation path in LAS-I / LANL SiC_w composite (359-88).

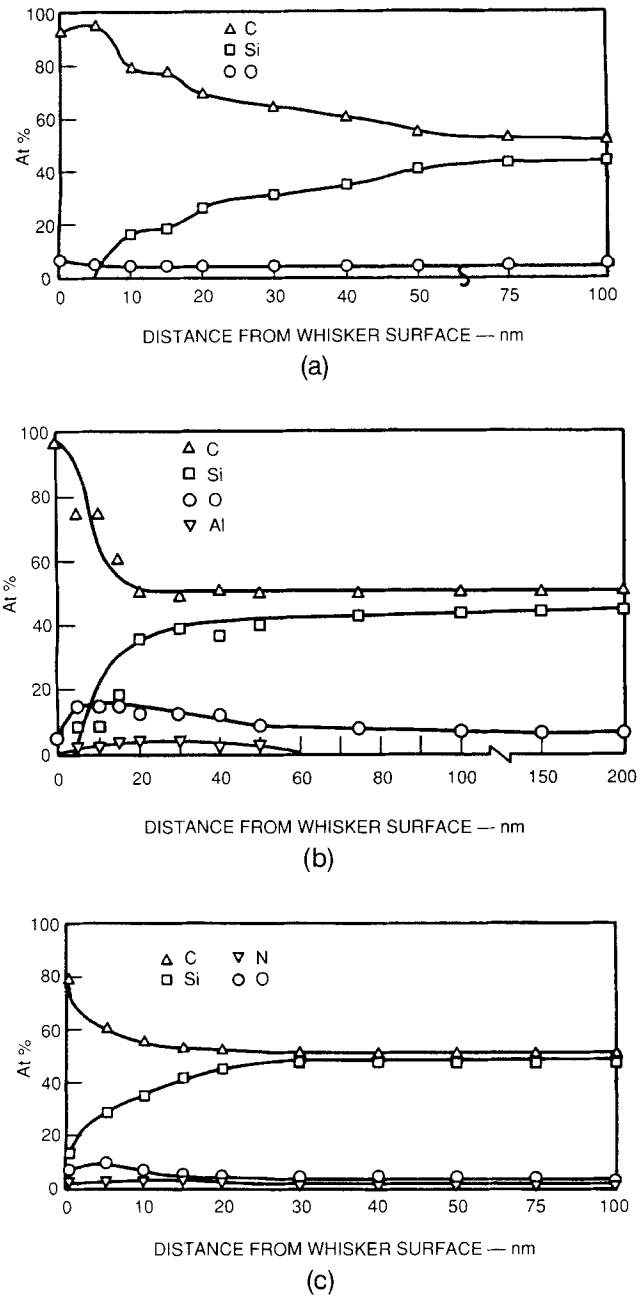


Fig. 6. SiC whisker composition depth profiles from LAS-I matrix composites: (a) TK-1 SiC_w from 290-88, (b) TK-2 SiC_w from 718-88, and (c) LANL SiC_w from 359-88.

from the reaction interface.[74,75] Thus, the excess carbon that comprises the C-rich layer at the fiber surface consists of carbon formed by reaction (1) and condensed carbon that is inherently part of the SiC fiber. Silica produced by reaction (1) can dissolve into the glass-ceramic matrix as long as the matrix is not locally silica saturated.

A similar "condensed carbon oxidation" reaction apparently occurs in the SiC whisker-reinforced glass-ceramic composites fabricated in the present investigation. Furthermore, whiskers with higher C/Si ratios near the surface generally result in higher carbon concentrations at composite interfaces. Although presently the mechanisms responsible for the observed enrichment of carbon at composite interfaces are not clearly understood, it appears that the reaction kinetics are more rapid for Nicalon SiC fibers in LAS matrices than for SiC whiskers. Cooper *et al.*[74] observed that residual carbon present in the microcrystalline Nicalon fibers enhanced the growth rate of the carbon layer compared with similar composites reinforced with pure SiC. Thus, SiC whiskers with C-rich stoichiometries or surface layers might form the desired interface layer more readily than stoichiometric SiC such as the LANL whiskers.

(4) Transmission Electron Microscopy

(A) TEM Replicas: Replicas were prepared from polished cross sections of all composites and examined by TEM. Examples of typical composite microstructures are shown in Figs. 7(a) and (b), micrographs of TK-2 whiskers in LAS and CAS matrices, respectively. The sections were taken parallel to the hot-pressing axis, revealing that whiskers generally were not in the plane of the section. The LAS matrix (Fig. 7(a)) consisted of fine grains (<1 μm) of a β-quartz-silica solid-solution LAS phase. The grains were separated by thin glassy films which were preferentially etched prior to replicating. In contrast, the CAS matrix consisted of anorthite grains (A) with relatively large grains (>5 μm) of α-alumina (Fig. 7(b)). The alumina grains appeared because the composition of the CAS matrix (40.2 wt% SiO_2, 38.7% Al_2O_3, 18.1% CaO, 2.0% ZrO_2, and 1.0% As_2O_3) was alumina-rich compared to stoi-

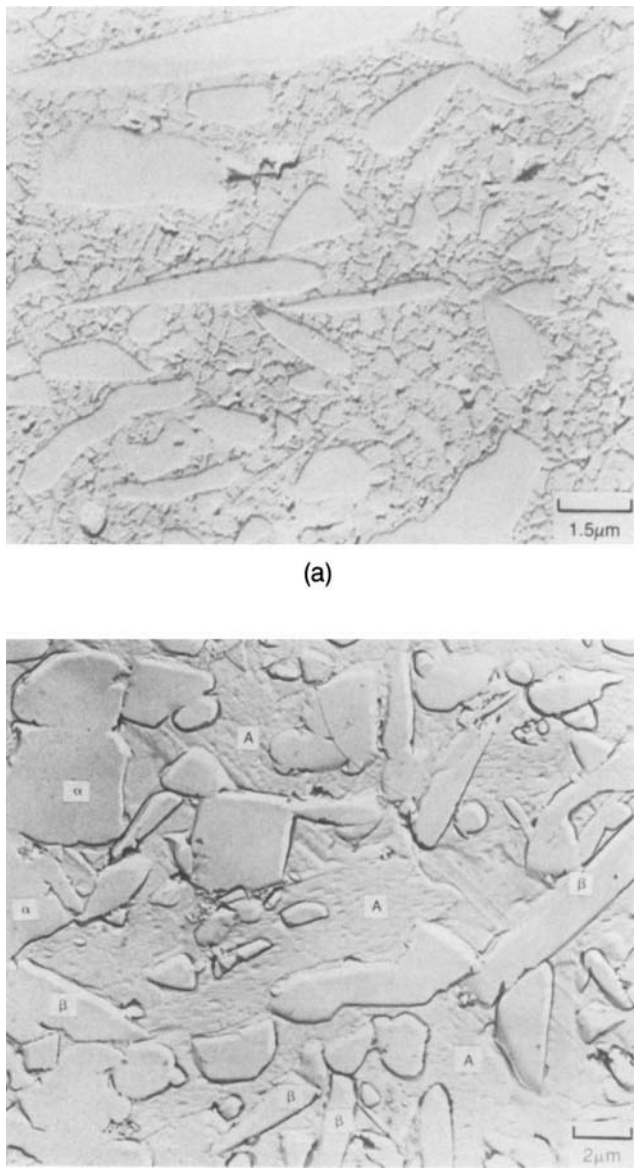
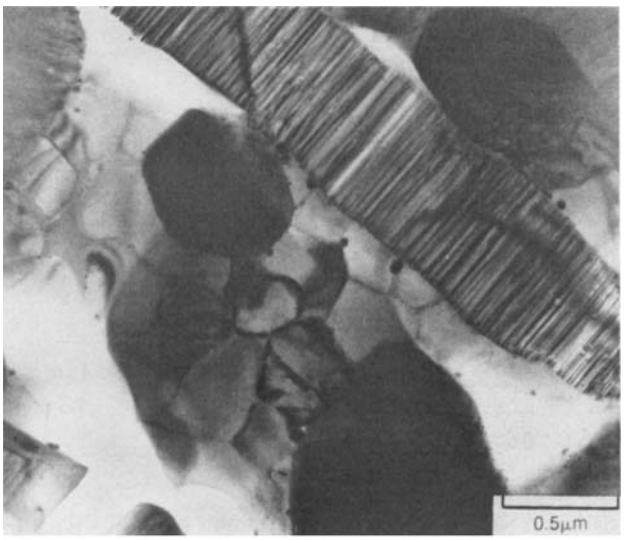


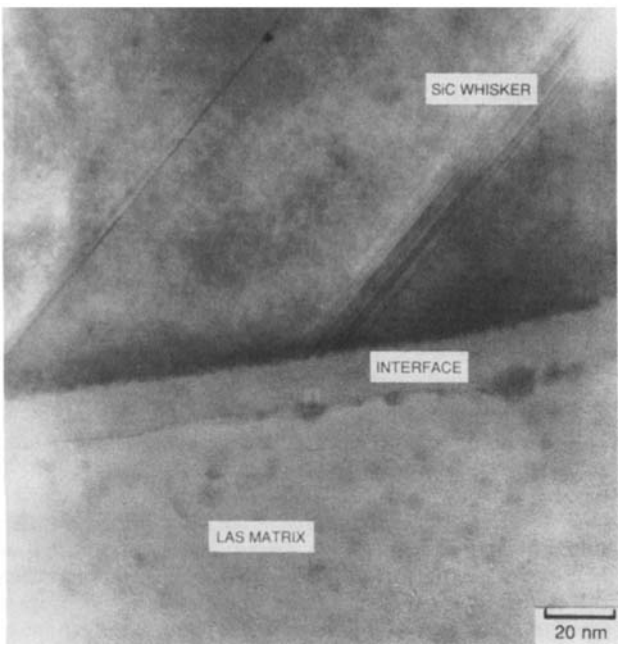
Fig. 7. TEM replica characterization of LAS and CAS matrices reinforced with TK-2 SiC whiskers: (a) 718-88 LAS/TK-2 SiC_w; (b) 499-89 CAS/TK-2 SiC_w. A is amorthite, β is β-SiC_w, α is α-Al_2O_3.

chiometric anorthite. Unlike the LAS matrix, there was a negligible amount of glassy phase in the CAS matrix.

(B) Thin-Foil TEM: TEM observations were made of LAS matrix composites reinforced with AC-1, TK-1, and LANL whiskers, and of CAS/TK-2 whisker composites. Figure 8(a) shows a typical region of the LAS/AC-1 composite after the material was ceramed to crystallize the matrix. The matrix consisted of fine crystals (0.2 to 0.5 μm) of β-quartz silica solid-solution LAS phase which were extremely beam sensitive and underwent a rapid disordering transition upon irradiation with 120-kV electrons.[13] Ultrafine inclusions of zirconia were also present in the matrix and appeared dark in the micrograph. The zirconia was added intentionally to enhance nucleation of the crystallization process. The AC-1 whiskers exhibited a high concentration of planar defects oriented transverse to the whisker axis, resulting in random mixtures of short-period polytypes.[45] Most AC-1 whiskers also exhibited a distinct core region that was characterized by impurity-bearing inclusions, a consequence of the whisker growth mechanism.[46] TK-1 whiskers exhibited the same stacking disorder as the AC-1 whiskers, although microphase inclusions in the core regions were not observed.



(a)



(b)

Fig. 8. TEM thin-foil characterization of SiC whisker/LAS-I matrix composites with (a) AC-1 whiskers and (b) TK-1 whiskers.

Interface characterization of the LAS/TK-1 composites was accomplished by high-resolution imaging. Figure 8(b) shows a phase-contrast image of the whisker–matrix interface region, in which there was a distinct noncrystalline layer approximately 15 nm thick. The observation is consistent with Auger spectroscopy measurements presented in Fig. 1(a), which revealed a carbon-rich interfacial layer of comparable thickness. Carbon enrichment of composite interfaces is a well-known phenomenon in LAS composites reinforced with Nicalon SiC fibers.[13,14] However, not all whiskers examined exhibited the distinct interface layer shown in Fig. 8(b), and it is proposed that layer formation in these composites is subject to chemical inhomogeneities in the LAS matrix and variations in whisker surface chemistry.

Analysis of TEM thin-foil specimens of the CAS/TK-2 whisker composite showed that three crystalline phases were present in the composite. Alumina (A), anorthite (B), and SiC (C) were identified from the X-ray spectra and selected area diffraction patterns, as shown in Fig. 9. (Zirconia was present as a nucleating agent, although it was not apparent in the microstructure as a discrete phase.) Unlike the LAS glass matrices, the matrix phases (anorthite and alumina) were stable under the electron beam, and no disordering reaction was observed. Virtually no residual glassy phase was present along grain boundaries or interfaces in the composite matrix. Although there was no evidence of interface reaction in diffraction-contrast images, phase-contrast images showed a layer of graphitic carbon at the whisker–matrix interface (Fig. 10). Lattice fringes in the graphitic phase were generally parallel to the whisker interface, implying that the basal planes tended to orient in this way. The thickness of the graphitic layer was variable, and a Si-bearing glassy layer was often associated with it. The glassy layer sometimes appeared between the whisker and the graphitic layer and sometimes between the graphitic layer and the matrix. Not all whiskers in the CAS matrix composite showed the distinct graphitic carbon layer, although a glassy layer was generally present. The exact composition of the glassy layer and its origin are presently unknown, although it is likely that some of the components are supplied by diffusion from near-surface regions of the whiskers. Similar interface microstructures have been observed in whisker composites after thermal oxidation, where oxidation of SiC whiskers results initially in thin layers of graphitic carbon and silica glass.[51]

Composites reinforced with the LANL SiC whiskers showed distinctly different interface morphologies than did the other composites. Whiskers typically exhibited facets and protrusions, as shown in Figs. 11(a) and (b). The appendages were frequently associated with planar defects intersecting the interface, although a causal relationship was unclear. Because the peculiar morphologies were not observed in as-grown whiskers, the features apparently developed during composite processing as a result of a dissolution–reprecipitation reaction. No interfacial layer was detected, in keeping with the Auger spectroscopy results shown in Fig. 6(c).

Faceting and appendage growth of LANL whiskers during composite processing have been observed previously in hot-pressed (HP) and reaction-bonded silicon nitride (RBSN) matrix composites.[47,48] Although the whiskers grow with rounded triangular cross sections, microscopic facets develop on low-energy {111} planes during hot-pressing, resulting in "fish-scale" configurations.[47] In RBSN matrix composites, pronounced faceting of the SiC whiskers was associated with low fracture toughness and strength,[48] suggesting that the interface morphology might lead to stress concentration and inhibit certain toughening mechanisms such as fiber pullout. In the present study, the LAS glass-ceramic matrix composite reinforced

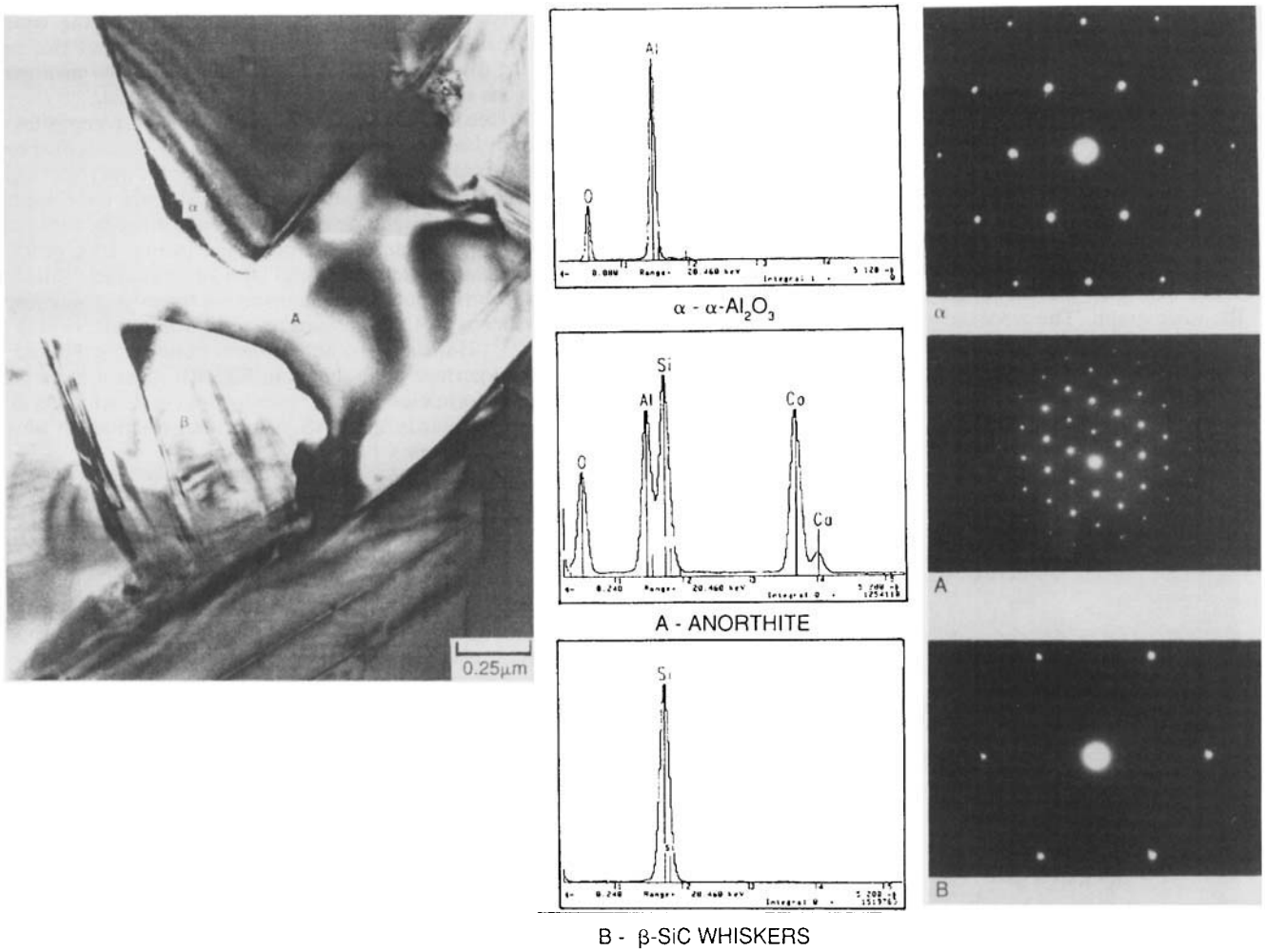


Fig. 9. Analytical TEM analysis of CAS matrix/TK-2 SiC_w composite (499-89).

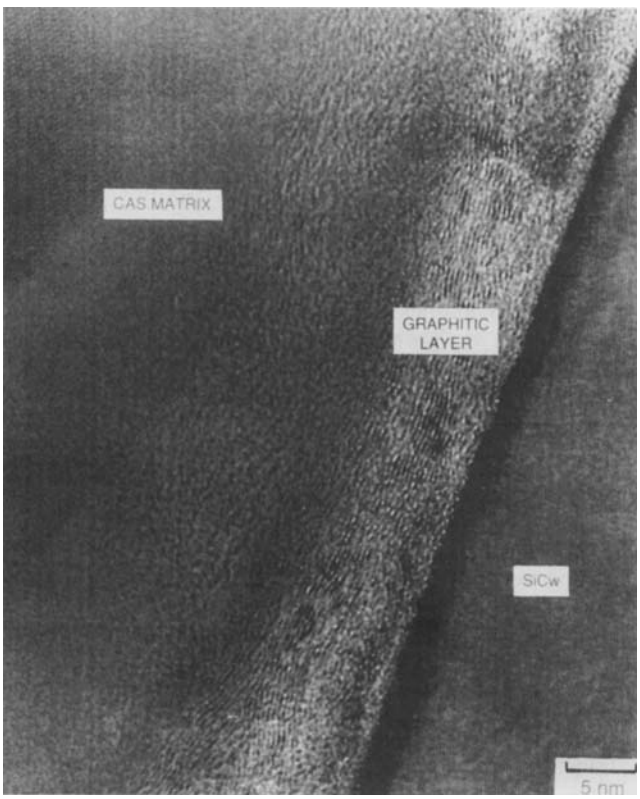
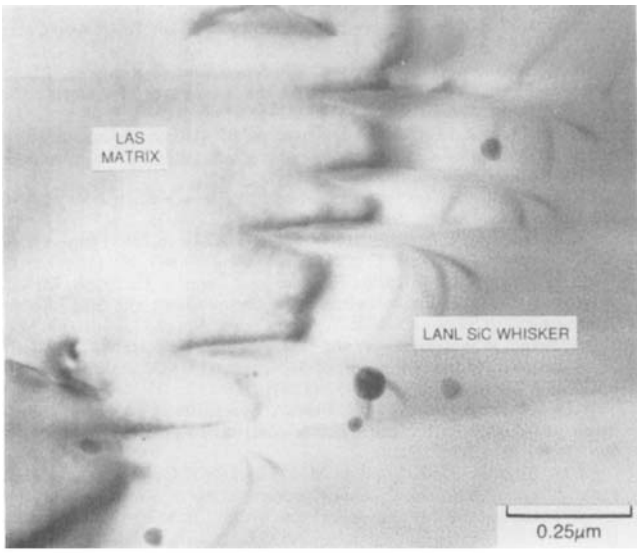


Fig. 10. High-resolution TEM image of CAS matrix/TK-2 SiC_w composite (499-89).

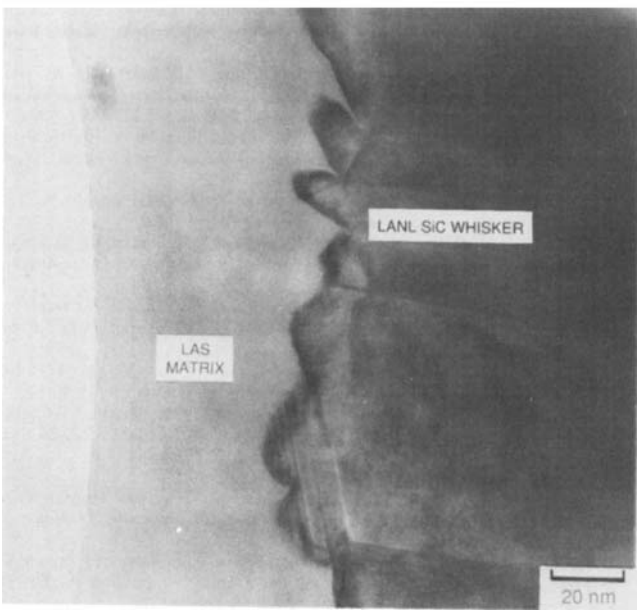
with LANL SiC whiskers showed lower flexural strength levels than similar composites with different whisker reinforcements. The poor composite strength can be correlated with the irregular interface morphologies shown in Fig. 11, which may have a greater effect on fracture toughness than the absence of a carbon-rich interfacial layer. Low composite strength and toughness levels were also observed in LAS/AMI SiC composites, in which the interfaces were characterized by a carbon-rich layer *and* rough profiles, suggesting that rough interface profiles can negate the advantages of a carbon-rich layer at the interface. Thus, one objective for microstructural design that emerges is that composite interfaces should be smooth to avoid stress concentration and facilitate toughening processes such as debonding and pullout. In addition, a weak interfacial layer facilitates energy-dissipating processes during fracture that improve fracture toughness.

V. Summary

It has been shown that surface chemistry and morphology of SiC whisker reinforcements have strong effects on the mechanical properties and fracture modes of glass-ceramic matrix composites. Those types of SiC whiskers that exhibited both a carbon-rich surface *and* a smooth surface profile resulted in composites with the highest levels of fracture toughness and strength. For example, AMI SiC whiskers possessed the desired carbon-rich surface chemistry, but because the whisker surfaces were so rough and irregular, the composites displayed poor mechanical properties. Whiskers with the desired characteristics resulted in composites with a four-fold increase in flexural strength and a five-fold increase in fracture toughness when compared with the unreinforced matrix.



(a)



(b)

Fig. 11. Whisker appendage growth resulting from composite fabrication in LAS-I/LANL SiC_w composite (359-88).

Composite processing generally caused significant modifications to the interface microstructures in the high-strength high-toughness composites. High-resolution TEM images revealed a graphitic carbon layer adjacent to many of the whiskers, and Auger spectroscopy of whiskers exposed on fracture surfaces revealed an increase in the near-surface carbon content. The carbon layer formed via a solid-state oxidation reaction between the SiC whiskers and the silicate matrix during composite processing.[70,71]

Investigation of crack propagation modes revealed that carbon-rich interfaces enabled strong interactions between cracks and whisker reinforcements. Interface debonding, crack bridging, and whisker pullout were all observed in these composites and contributed to enhancement of fracture toughness. In contrast, LANL SiC whiskers showed near-stoichiometric surface chemistry and an absence of the carbon-rich interface layer in the composites. More significantly, the whiskers developed rough surface profiles during composite synthesis, preventing sliding and concentrating stresses at the interfaces. Consequently, crack propagation in these composites occurred without the aforementioned energy-dissipating processes, and the fracture toughness and strength of the composite were low.

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