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LEVEL II

12

Scanning Auger Analysis of Fracture Surfaces in Graphite-Aluminum Composites

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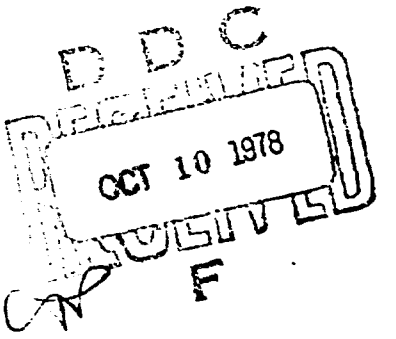
Interim Report



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Fracture interfaces of graphite-aluminum composites were examined by means of the high-resolution scanning Auger microprobe. Specimens were fractured in situ at 10^{-8} Pa vacuum, and the phases on the fiber and matrix sides of the fracture surfaces were identified by using a spacial resolution of 0.5 μm. Inert argon ion sputtering was used to provide estimates of the thickness of the various fracture phases. The most commonly found fracture phase was magnesium-aluminum oxide, which is present between the fiber and the titanium-boron rich layer that is applied to the fiber during processing.

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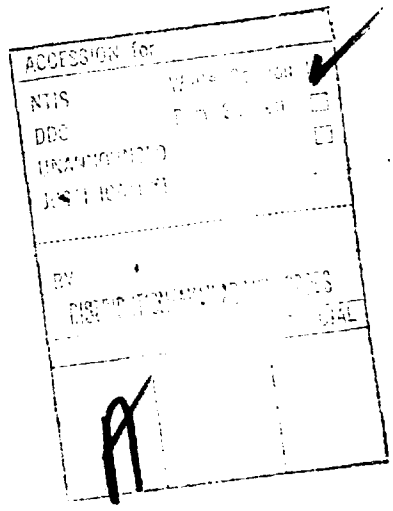


FIGURES

I. INTRODUCTION

Graphite-aluminum composites are being considered for numerous applications that require sufficient transverse strength to allow unidirectional fiber orientation for maximum stiffness and dimensional stability. The fiber-matrix bond strength must be maximized in order to achieve the required transverse properties. A recent study of the effect of processing and fiber type on the transverse strength of graphite-aluminum composites indicates that transverse fracture strength is dependent upon the nature of fiber-matrix interaction (Ref. 1). The transverse strengths for these composites are in the range 5 to 40 MPa, depending upon the processing method and fiber type. An understanding of the fracture behavior of the interfaces between fiber and matrix is essential before processing improvements can be made to increase transverse composite strength.

The objective of this work was to establish experimental techniques to permit the determination of the fracture paths resulting from transverse failure and the identification of the chemical species of the fracture phases. The fine fiber size (5 to 15 μm) and the extremely thin fiber-matrix interface region (0.05 to 0.2 μm) of these composites dictated the use of the high-resolution scanning Auger microprobe (SAM) for this study.

II. EXPERIMENTS

The graphite-aluminum composites examined in this study were produced by the titanium-boron chemical vapor deposition (Ti-B CVD) method. A description of this process can be found in a recent review article (Ref. 2). In this process, graphite fibers are coated with a thin layer (less than 0.1 μm) of titanium and boron prior to being infiltrated by molten aluminum. The coating promotes wetting with the molten aluminum yet provides a sufficient reaction barrier to prevent excessive aluminum carbide formation and hence fiber degradation. The basic infiltration process is designated S. Two other modifications were also examined. These include hydrogen precleaning of the graphite fiber prior to the Ti-B coating step, the H process, and pyrolytic carbon coating prior to the Ti-B coating step, the C process. The initial product of these processes is a composite wire approximately 1.5 mm in diameter. The wires are subsequently consolidated by the diffusion bonding into plates for mechanical testing and analysis. The composite materials consist of Thornel 50 fibers in an aluminum alloy 201 matrix. The 201 alloy (4.7 Cu, 0.8 Ag, 0.4 Mn, 0.35 Mg, 0.4 Zn, and 0.25 Ti) was selected because it represents the baseline alloy composition for which there is the greatest amount of the mechanical properties data. The Thornel 50 fiber is a highly graphitic rayon-precursor-based fiber with the following properties: approximately 6-μm diameter, a crenulated cross section, 2400 MPa tensile strength, 420 GPa Young's modulus, and 1.67 g/cm^3 density.

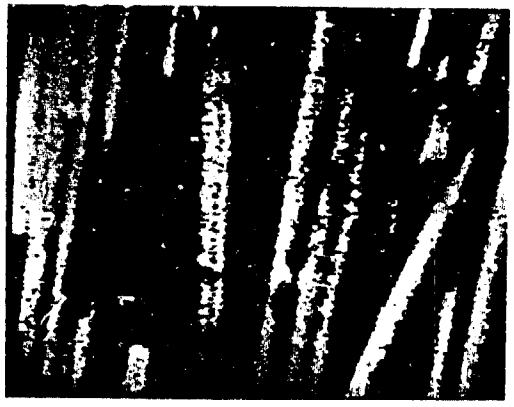
In order to unambiguously identify the fractured phases, the specimens were fractured <u>in situ</u> within the SAM under 10^{-8} Pa vacuum to prevent contamination of the fracture surface. Both the precursor wires and the consolidated composite materials were notched and fractured under impact loading conditions. The surfaces were then thorcughly examined to determine the reproducibility of the fracture path chemistry. A resolution of 0.5 μm is required for an effective focus on areas of interest on the fiber surface.

The SAM instrument used in these studies was the Physical Electronics Model 590 system. The spacial resolution of the system is approximately 0.2 μm. An electron beam spot size of about 0.5 μm was used to improve the signal to noise of the Auger spectrum. This resolution makes it possible to perform detailed studies on the fracture surface in the vicinity of the 5- to 10-μm graphite fibers. Descriptions of Auger electron spectroscopy (AES) are given in review articles (Ref. 3). The other prime advantage of using AES for this study is that the Auger electrons originate about 0.001 to 0.002 μm into the material. Therefore, the fracture-surface chemical analysis directly identifies the chemistry associated with the fracture path through the composite.

Micrographs of the fracture surfaces were made in the SAM while it was operating in the secondary and adsorbed current modes. Higher-resolution scanning electron micrographs were made with the scanning electron microscope. Elemental mappings of the fracture surface were made in both one and two dimensions. Examples of the two-dimensional mapping of carbon, oxygen, magnesium, and aluminum are shown in Fig. 1.

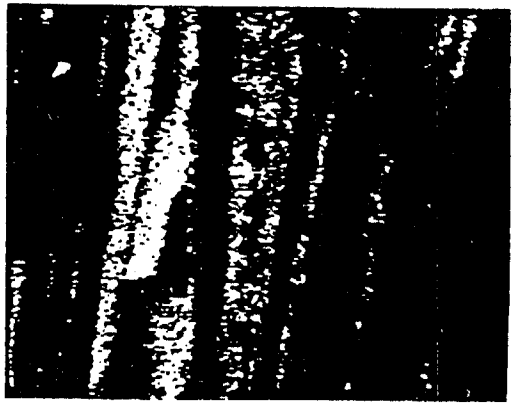
Combined AES and inert argon ion sputtering profiles, normal to the fracture surface, were measured to determine the chemistry near the fracture surface. Sputtering profiles were obtained by means of multiplexing techniques. The intensity of the dN(E)/dE peaks for six elements was monitored as the fracture surface was sputtered. A typical fracture of graphite-aluminum composite, where the chemistry of the fracture surface was obtained adjacent to the fiber and adjacent to the matrix, is indicated by the arrows in Fig. 2. Depth profiles were obtained on different samples that were sputtered back either to the fiber or to the graphite-aluminum matrix. The depths were calibrated on the basis of standard samples of tantalum pentoxide and are accurate only to about a factor of 2 because (1) different sputtering rates are associated with the chemistry of the composite fracture surface, and (2) the fracture surface is extremely rough.

SEM OF FRACTURED SURFACE

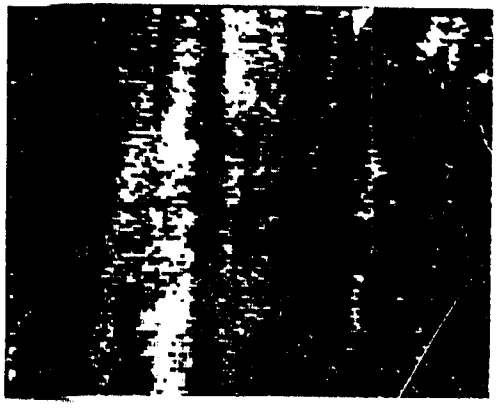


CARBON

ALUMINUM



OXYGEN



MAGNESIUM

Fig. 1. Element Mapping of Fractured Surface of T 50/2[illegible] Composite

Fig. 2. SEM of Composite with Locations for SAM Analysis on Fiber and on Matrix Above and Behind Fiber Shown

The data were evaluated in two ways. The first method was to use peak-to-peak intensities of the dN(E)/dE spectra combined with the sensitivity factors from the Handbook of Auger Electron Spectroscopy (Ref. 4) in order to obtain some degree of quantitative chemical analysis. The second part of the analysis involved the peak shapes of the various elements. The change in peak shape gives clues to the nature of the bonding of the elements. The dN(E)/dE spectrum for aluminum oxide and metal is given in Fig. 3. The aluminum oxide peak was detected at the fracture surface, and the aluminum metal peak was detected in the matrix after the oxide was removed by sputtering.

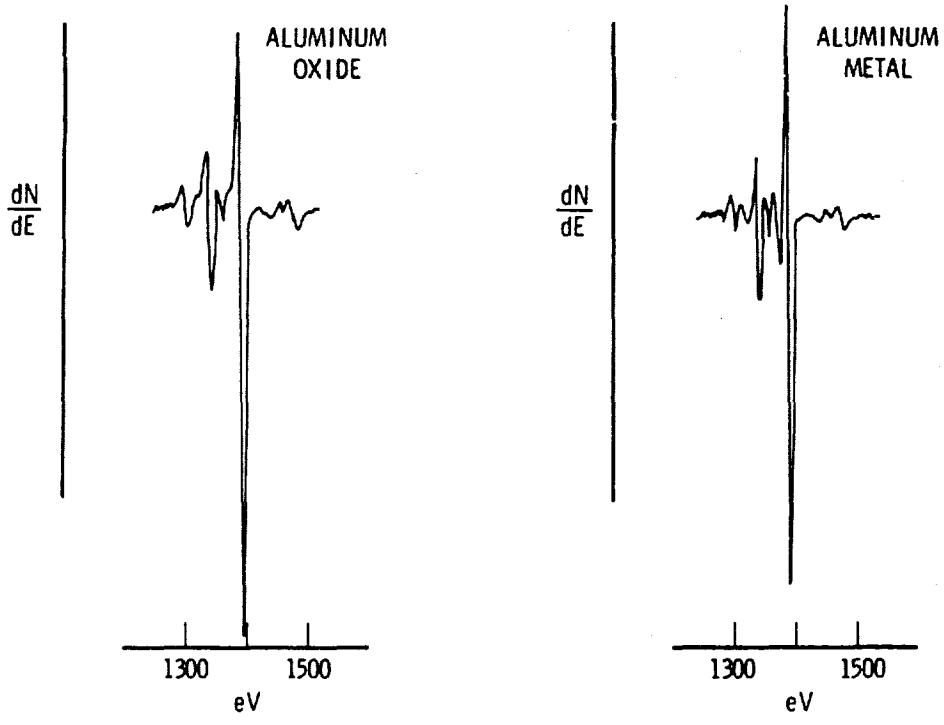


Fig. 3. Comparison of Al Auger Peaks in the Oxide and Metal Matrix Phases

III. RESULTS AND DISCUSSION

The most consistent result obtained in these experiments was the presence of the aluminum-magnesium oxide on the fracture surfaces of graphite-aluminum composites. In some cases, the fracture surface seemed to be predominantly in the oxide region. An AES spectrum taken from a fractured T 50/201 specimen is shown in Figs. 4 and 5. The AES spectrum shown in Fig. 4 is from the fiber side of the fractured interface, as shown in Fig. 2. Primarily, aluminum-magnesium oxide is present on the surface. Some graphite is seen in the spectrum, and it represents about 20 at%. The AES spectrum of Fig. 5 is from the matrix side of the fractured interface and is almost totally covered with the aluminum magnesium oxide. Investigation of the AES peak shapes (Fig. 3) for aluminum clearly revealed that virtually all of the aluminum and magnesium is present in the oxidized state. The other elements of interest at the interface are the small amount of titanium, copper, and boron. These will be discussed in more detail subsequently in reference to the inert argon in sputtering profiles.

The fracture that was dominant throughout the oxide layer (Figs. 4 and 5) was only one type of failure. Another type of failure occurred where the fracture apparently weaved from the oxide to the graphite interface or into the graphite and back again. In these cases, the fiber side of the fracture had a very high carbon content; the matrix side had significant carbon content but still had a large fraction of aluminum-magnesium oxide. There was some indication of fracture back into the aluminum matrix, as the spectrum indicated the presence of some aluminum metal. Figure 6 is a schematic of the envisioned fracture path. The SAM results strongly indicate that the weaving through the fiber-matrix interface had a periodicity smaller than the approximately 0.5-μm beam size used for these experiments, which was true for most of the materials studied. Only the relative amounts of graphite, oxide, and matrix varied. Where fiber-matrix bonding appeared to be lacking, the fiber side was totally graphite, and the matrix side totally oxide.

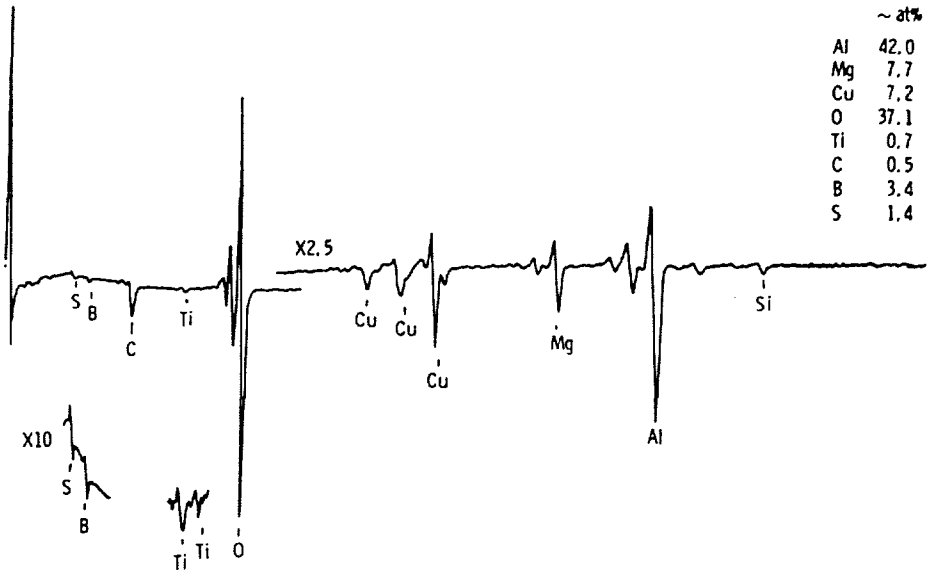


Fig. 4. SAM Spectrum of Fiber Side of Fracture in T 50/201 Composite

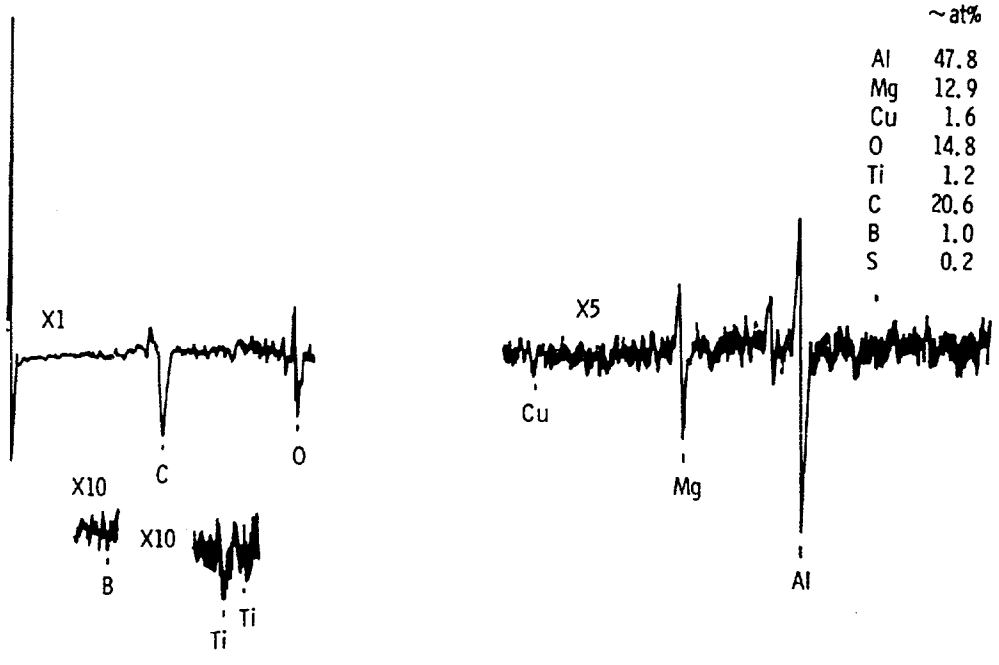


Fig. 5. SAM Spectrum of Matrix Side of Fracture in T 50/201 Composite

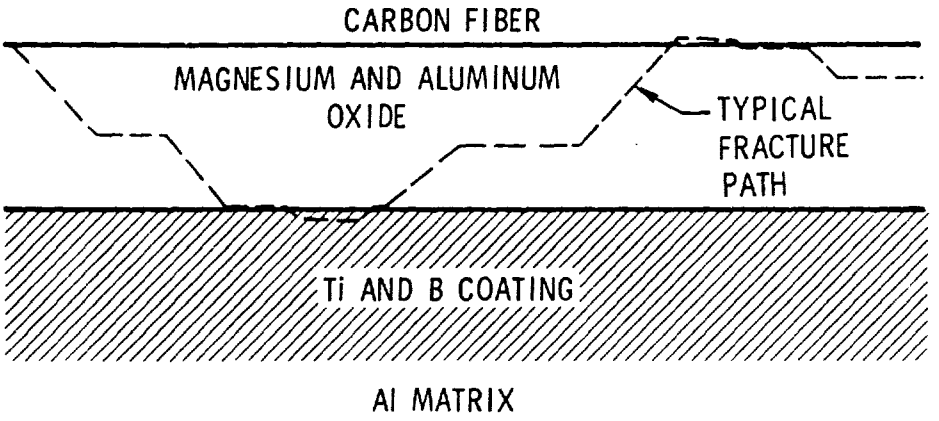


Fig. 6. Fracture Path in Graphite-Aluminum

The second significant result was obtained from the inert argon ion sputtering experiments. A typical profile for sputtering into the matrix side of the fractured fiber-matrix interface is shown in Fig. 7. Several significant features are evident. The first is that, in all cases, the surface magnesium and oxygen sputtered off at comparable rates, indicating that the magnesium was segregated to the interface as an oxide. The magnesium content in the alloys was significantly lower than in the oxide.

The second feature was that, in the cases of the Ti-B CVD-coated fibers, the titanium and boron were at low concentrations on the fracture surface and would reach a peak during sputtering into the matrix side of the fracture after the amount of aluminum-magnesium oxide was greatly reduced by the sputtering, indicating that when the oxide was formed it displaced the CVD titanium and boron from the fiber toward the matrix side of the oxide (Fig. 6).

The excess copper also indicates a maximum inside the oxide. In some samples, the copper maximum was deeper into the matrix than the titanium and boron and in others was coincident with the titanium and boron profile peak.

Another feature of the sputtering profile is the change in the shape of the AES peak for aluminum as it goes from the predominantly oxide shape on the fracture surface to the metallic aluminum in the matrix (Fig. 3). Sputtering into the graphite side of the fiber interface fracture indicates that when the oxide is removed, only the graphite fiber is present. No other significant layers were found.

The results obtained in this study indicate that the fracture path in the graphite-aluminum composites is not chemically simple. The presence of an oxide as a significant part of the fracture path is surprising. The origin of the oxide has not been clearly established but is most likely formed during the aluminum-infiltration process. It is not clear at present whether or not the oxide is deleterious in terms of the transverse strength. It does seem to promote adhesion to the graphite, particularly in those cases where the fracture is through the oxide. The displacement of the titanium and boron from the graphite interface is also significant.

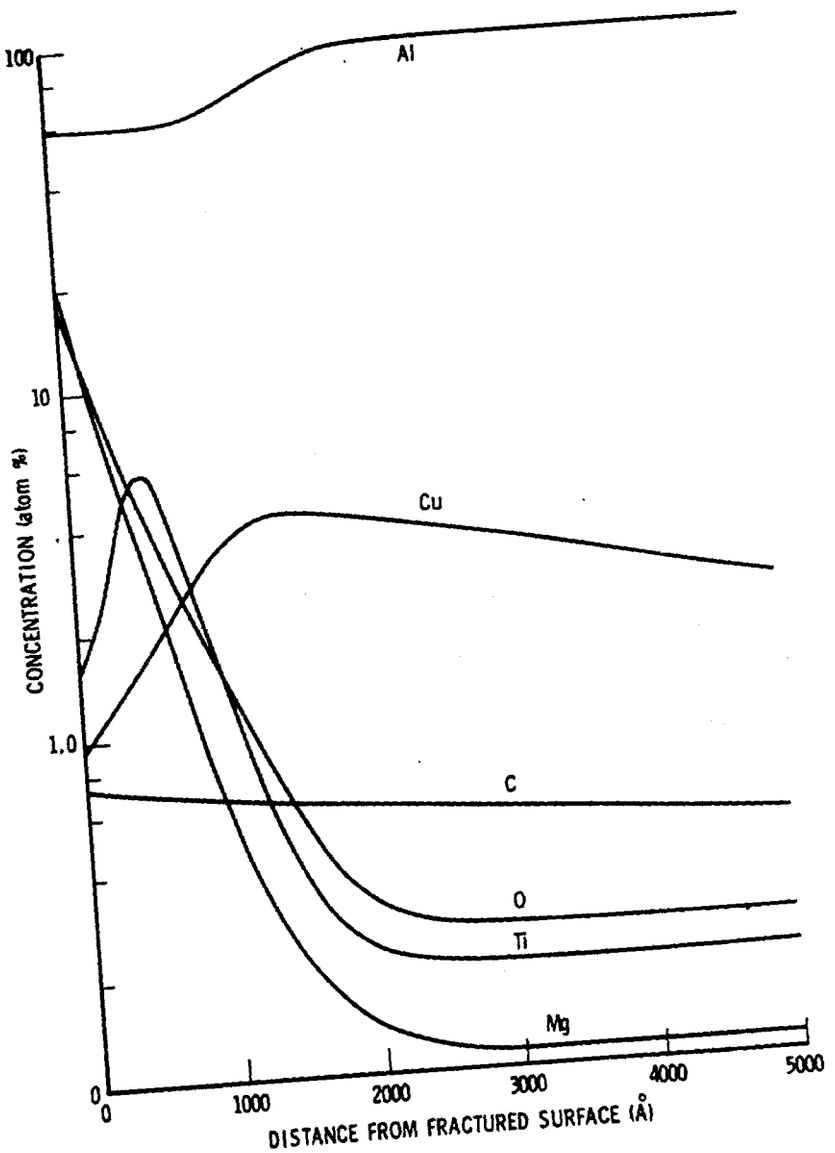


Fig. 7. SAM Element Profiles in Matrix Near Fractured Surface of T 50/201 Composite

At present, there is only meager data to relate fracture phase and fracture path to transverse strength. The difference in composition between the fiber side and the matrix side of the fracture of two composite wires was examined for T 300/201 (C), which had 10 MPa transverse strength, and T 50/201 (S) or T 50/20i (H), which had 20 MPa transverse strength. The greatest difference in composition occurred for the lower transverse strength composite (Fig. 8), indicating that the fracture path occurred between the distinct phases such as oxide and graphite fiber. The fracture path in the higher transverse-strength composite apparently was through a specific phase, in this case, the aluminum-magnesium oxide.

The combined oxide and titanium and boron displacement indicates that surface thermodynamics must play a dominant role in the kinetics of the interface formation. The results obtained here only concern the end of the process, a condition that is nonequilibirum, and does not define the process path that caused the complex interface that results in the equally complex fracture path. These results can be used as a basis for a much more detailed analysis of the fracture behavior as it relates to the chemical makeup of the interface.

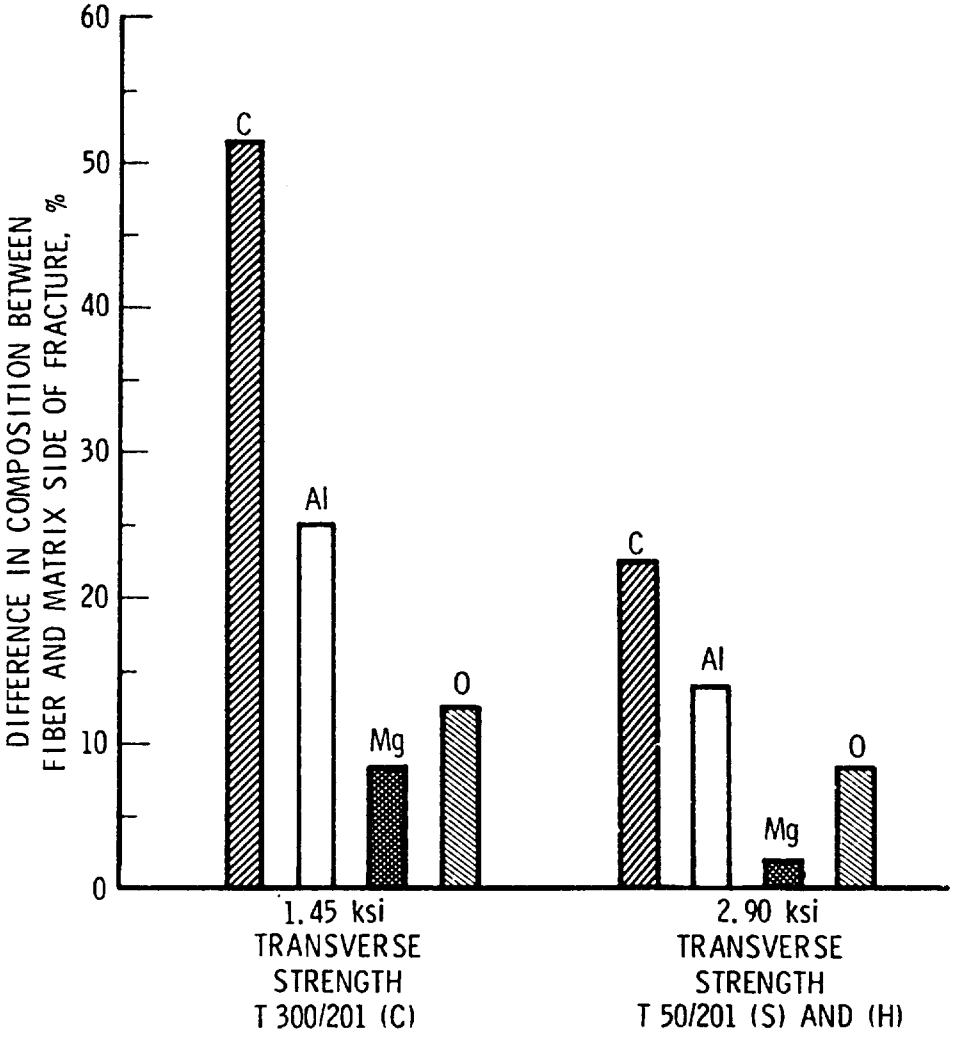


Fig. 8. Fracture Path Between Distinct Phases Favors Large Differences in Composition Between Fiber and Matrix Side of Fracture

IV. CONCLUSIONS

The results of this study are summarized as follows:

1. Scanning Auger microprobe techniques are capable of identifying chemical species at the fracture interface of graphite-aluminum composites.
2. The transverse fracture path in properly infiltrated composites is through the reaction layer between the fiber and the matrix. The actual path is complex and meanders between the fiber, the reaction zone, and the matrix.
3. In many cases, the fracture path was through an aluminum-magnesium oxide within the reaction layer. The results of Auger analysis indicates that the magnesium was totally in the oxidized form whereas the aluminum was present both as an oxide and as a metal.
4. Combined Auger analysis and inert ion sputtering indicate that the reaction zone of the graphite-aluminum composite consisted of an oxide-rich region adjacent to the fiber with the titanium and boron-rich region between the oxide and the matrix.
5. The highest transverse strength was associated with those composites for which the fracture path was predominantly through the oxide layer rather than between the fiber-oxide interface.

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