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ANALYTIC METHODS FOR STUDYING THE FIBER/MATRIX INTERFACE,(U)
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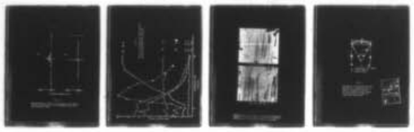

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⑥ Analytic Methods for Studying the Fiber/Matrix Interface

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In order to understand the mechanical behavior of metal matrix-graphite composites, it is necessary that the fiber-matrix interface be well characterized. This is of particular importance for transverse loading of the composite. The interface around the graphite composite is shown schematically in Fig. 1. The thickness of the property controlling interface could range from several monolayers in the case where impurities play a major role, to about 0.5 micrometers in the case of a thick carbide reaction zone. The information that an investigator would like to obtain about the interface includes the chemistry across the interface, the nature of the chemical bonding and its influence on fracture strength, the homogeneity of the interface, and the residual stress pattern. (Techniques appropriate for measuring residual stress accurately are not readily available and will not be described here.) In addition, the influence of process variables and subsequent thermal and mechanical treatments on the interface properties would be desired.

The most significant problem associated with characterizing

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the interface is directing the measuring probe to the interface. This will be discussed in some detail in a later section of the paper. In this paper ~~we will describe~~ some of the more successful techniques ~~[1]~~ 9 that have been used to make some measurements concerning the nature of the interface are described. The tools ~~to be~~ discussed are scanning electron microscopy (SEM), Auger electron spectroscopy (AES), inert ion sputtering (IIS), secondary ion mass spectroscopy (SIMS), and ion microprobe mass analysis (IMMA). Other techniques that are evolving, such as scanning transmission electron microscopy and its associated spectroscopic probes as well as lattice imaging in the transmission electron microscope, may very well play a future role in unraveling the nature of the interface. Forming any valid interpretations or descriptive models which define the cohesive strength of the interface will be difficult because of the large chemical and stress gradients in the vicinity of the interface.

The SEM has seen extensive use in composite studies already and will be discussed only briefly here. Fig. 2 shows a SEM micrograph of a fractured aluminum-graphite composite. A major point of interest is the apparent fracture in the vicinity of the graphite-aluminum matrix interface. This exposure of the interface helps alleviate the problem of getting to the interface. Coupled with the SEM in many systems is an energy dispersive x-ray spectrometer. This technique, which is very valuable in bulk analyses, has only limited value in studying interface chemistry since the chemical analysis is for depths into the samples of 0.5 to 1.0 micrometers, which is most cases is much greater than the interface thickness.

The approach that has shown the most promise in investigating the interface is AES in the scanning mode. The details of AES can be obtained in one of the many review articles [1-5]. The electron beam of a SEM is used as the probing beam to excite the Auger electrons. The electron beam diameter currently being effectively used for detailed AES surface chemical analysis is about 0.2 to 0.5 micrometers. The Auger electrons have the characteristic of originating in the first 0.5 to 2.0 nanometers, depending on their energy. This characteristic allows detailed chemical analysis on a local basis to be made of a surface. The other point of interest is the fact that the local chemical environment can lead to changes in the AES peak shapes. This is particularly true of the AES peak of carbon, where distinctive carbide peaks can be easily separated from the graphite peaks [6] as well as from each other. Similar behavior is shown for many metals in the oxide vs. metal state. An example of this is shown in Fig. 3 for the higher energy Auger peaks of aluminum. The differences between the metal and the oxide are immediately apparent. Much of the change in the AES spectra of the metal comes about from plasmon energy losses. This is shown more clearly in Fig. 4 for the energy loss spectra of energy analyzed back scattered primary electrons of similar energy interacting with the clean aluminum metal surface. In Fig. 4(a) the characteristic loss spectrum of Al metal displays the peaks associated with plasmon losses, which represent electrons that have given up discrete quanta of energy before leaving the solid. Fig. 4(b) shows the characteristic loss spectrum of aluminum oxide, which exhibits no plasmon losses because the electrons leaving the surface do not undergo a significant amount of discrete energy losses.

A complementary method to AES is the IIS. Inert ions in the 500 to 5000 electron volt range bombard the surface and remove the surface layer by layer as AES of these layers is simultaneously performed. In terms of the interface this allows the chemical profile through the interface to be determined. When fracture occurs in the vicinity of the interface the chemical profiles through the fractured interface can be obtained both into the matrix phase and into the graphite fibers. An example of this type of result for the aluminum-graphite composite sputtered back into the matrix is shown in Fig. 5. This profile shows that the fracture was predominantly in the oxide phase between the matrix and fiber and that the titanium and boron wetting agents used in the process were between the oxide and the matrix. These results will be discussed in more detail in the Amateau paper in these proceedings. One of the significant problems associated with inert ion sputtering of fractured graphite-metal matrix composites is shadowing effects. Fig. 6 shows a SEM micrograph of a fracture surface of an aluminum-graphite composite and a two-dimensional AES mapping of the argon Auger peak for the same area. The dark regions where no argon is found can be explained by the obstruction of the line of flight of the argon ions by the rough surface not allowing the argon ion beam to reach those parts of the surface. This problem is even more severe for longitudinal fractures where the surface is extremely rough. A second type of problem is that shadowing could also lead to redeposition of elements into other areas, leading to artifacts in the profiling analysis. For this reason, extreme care must be taken in obtaining and evaluating this data.

If the graphite-metal matrix composite does not fracture in the vicinity of the interface, other methods must be used to get at the interface. One method is to sputter through a metallographic cross-section through a fiber to get the interface. If this is done then the relative beam diameter of the probing beam and the fiber diameters play a major role. In the case of the IMMA the appropriate probing beam diameter is the diameter of the focused sputtering ion beam. This diameter is normally greater than two microns. In the case of AES the incident electron beam diameter is the appropriate diameter. This is usually greater than 0.4 microns. Fig. 7 shows a significant problem with this approach. If the appropriate beam is directed radially with the fiber, the geometry of Fig. 7 occurs. As soon as the outer edge of the beam contacts the interface, the quantity measured is a combination of both matrix and fiber. A geometric evaluation of the relative volume of the interface sputtered in the total volume, shown by the dotted rectangle in Fig. 7, is given by

$$V_R = \frac{\text{interface volume}}{\text{sputtered volume}}$$

$$= \frac{\frac{2\theta\pi}{360}[2R\tau + \tau^2]}{W\{R(1 - \cos\theta) + \tau\}}$$

Tables I and II show how both the probing beam size (2R sin θ) and the interface layer thickness, τ, for a fiber radius of three microns, influence V_R. They show that a small beam or large interface is required to get meaningful data. In addition, if the interface has more than one layer, as was shown in the sputtering profiles of Fig. 5 and schematically in Fig. 1, sputtering through the plane of polish would completely mask it since it would be going through all the layers simultaneously, unless they were very thick. A proper analysis of the relative volume would be a layer-by-layer chemical analysis where more detail would be observable in the probing data, but the general conclusion expressed here would not be changed. To accurately determine the interface thickness using sputtering experiments requires establishing standards for determing the sputter rate. Accurate methods for making standards representative of inhomogeneous material have not yet been developed.

Harrigan [7] has recently reported the results of profiles of the interface using IMMA. The averaging process generally reduced the sharpness of the interface but did provide some elemental information about the interface. In order to use IMMA to determine an oxide, oxygen-18 can be used as the sputtering ion. Oxygen ions are required to assist in making the IMMA profiles somewhat quantitative.

In conclusion, the following observations can be made about probing the graphite-metal matrix interface. If it fractures in the vicinity of the interface, then selective point AES analysis combined with inert ion sputtering allows the interface to be chemically analyzed. If not, then sputtering through the fiber must be done with either IMMA or AES. In all cases the experimenter must be alert to artifacts created by the measuring technique.

Acknowledgement

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TABLE I

3 μm fiber radius
17 nm interface thickness

Beam Width	2θ	V_R
2 μm	38.6°	.09
0.8 μm	15.0°	.36
0.4 μm	7.5°	.69

TABLE II

2 μm beam
3 μm fiber radius

τ nm	V_R
1.7	.01
17.0	.09
51.0	.23

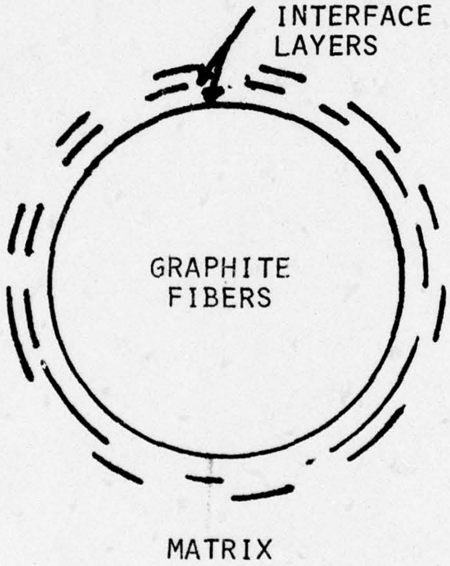
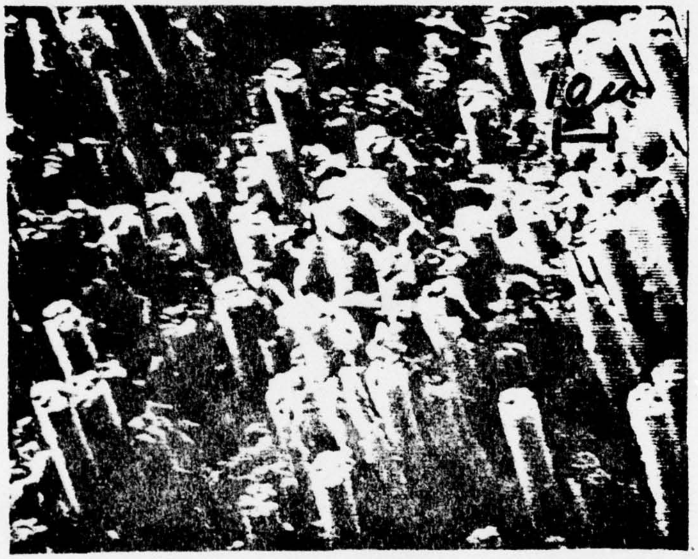


Fig. 1

Schematic of graphite fibers separated from matrix by multiple interface layers



ALUMINUM-GRAPHITE

Fig. 2

Scanning electron micrograph of Al-graphite composite fracture surface

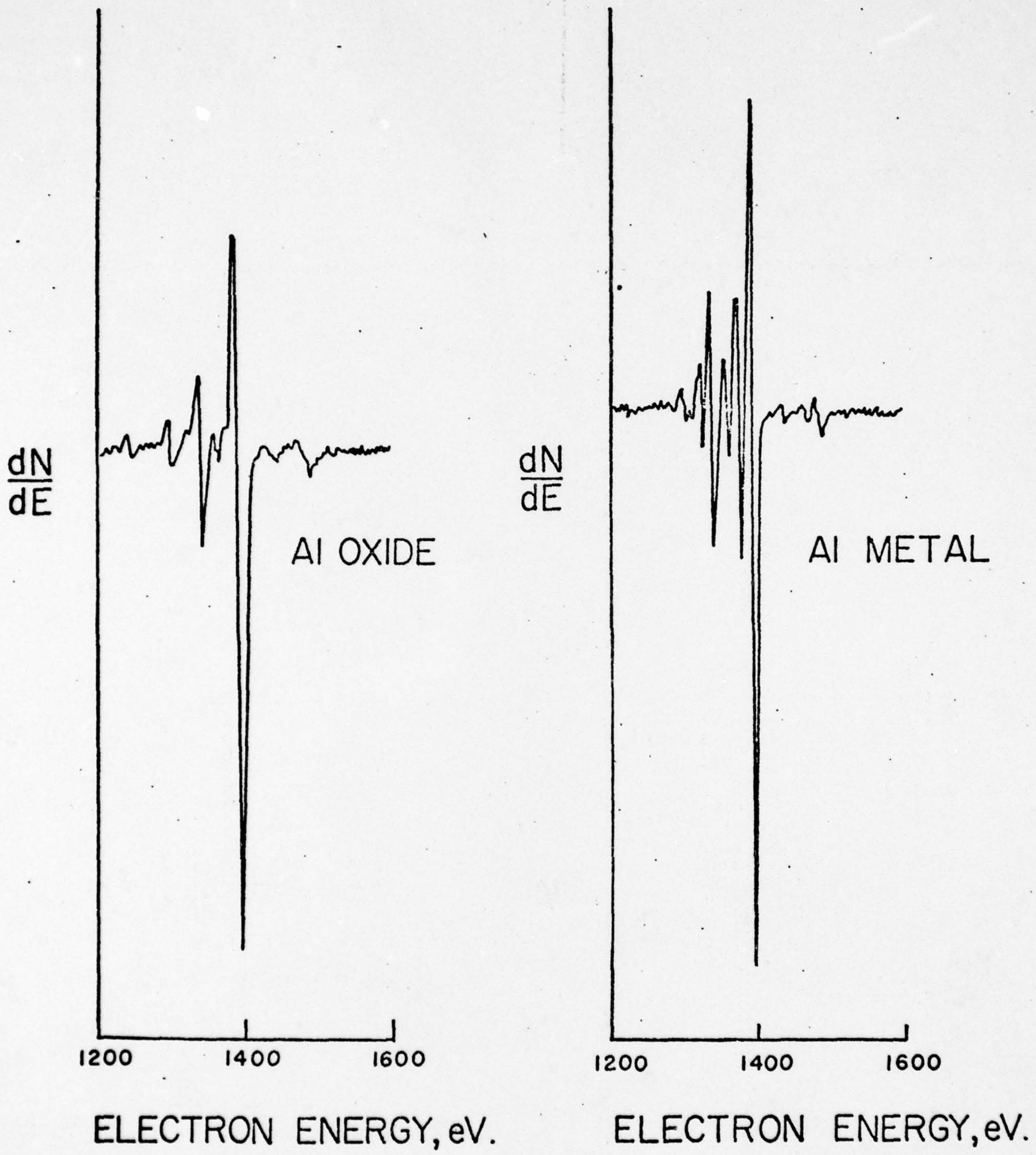


Fig. 3

Auger electron spectra of aluminum showing peak shape change going from oxide to metal

Fig. 4

Characteristic energy loss spectra for 1400 eV primary electrons on (a) aluminum metal and (b) aluminum oxide

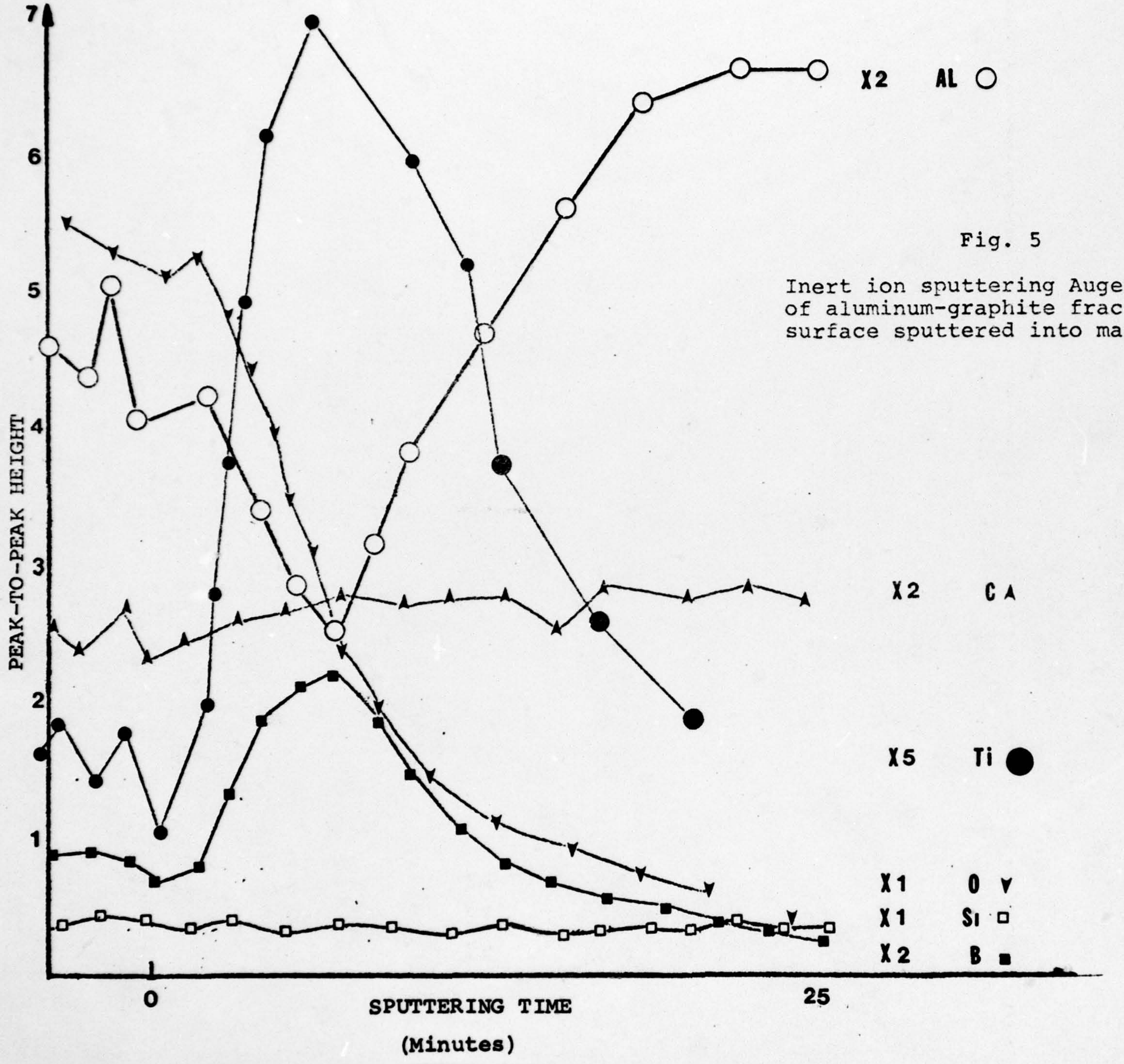
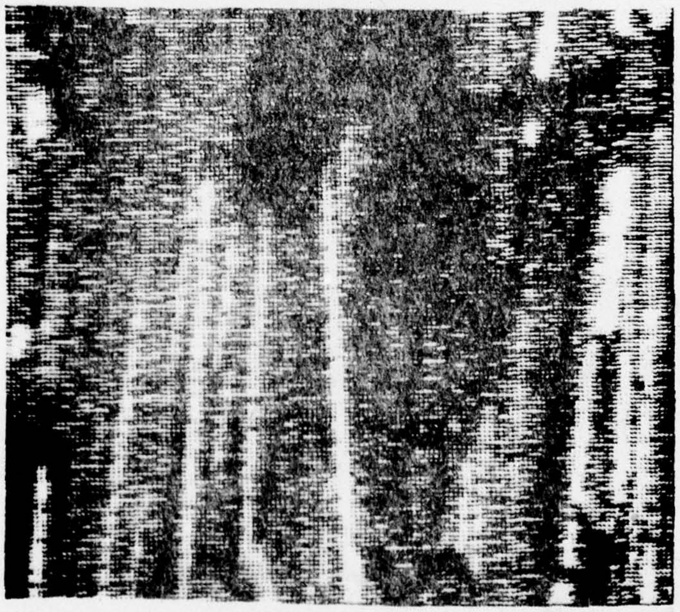


Fig. 5

Inert ion sputtering Auger profile of aluminum-graphite fracture surface sputtered into matrix

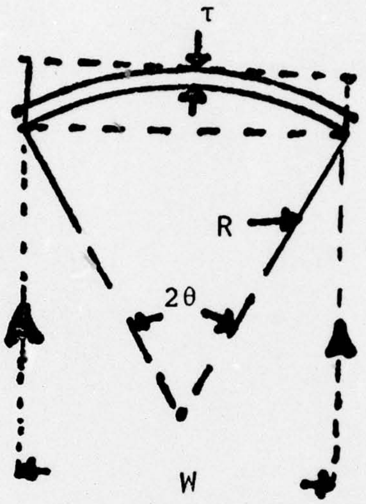
SEM MICROGRAPH



ARGON AES MAPPING

Fig. 6

Implanted Ar Auger map of sputtered aluminum-graphite fracture surface showing shadowing effects and corresponding SEM micrograph



τ - INTERFACE THICKNESS
R - FIBER RADIUS
W - BEAM WIDTH

Fig. 7

Schematic of geometry due to sputtering through plane of polish of graphite-metal matrix composite that leads to averaging of measured interface chemistry