SCS-6 SiC FIBER - A CASE STUDY OF QUANTITATIVE AUGER
PROCEDURES FOR THE EVALUATION OF SMALL DIAMETER FIBERS

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ABSTRACT

Correctly used, Auger electron spectroscopy can quantitatively
determine the elemental composition profile of specimens with a
spatial resolution of approximately 0.1 micrometer. Factors
which affect the precision and accuracy of this technique are:
specimen surface texture, surface contamination, electron beam
parameters, data collection conditions and instrument
calibration, including the use of appropriate compound, as
opposed to elemental, standards. Suggested procedures for
correctly utilizing Auger analysis for small diameter fibers
will be presented during the discussion of the SCS-6 fiber, a
CVD SiC fiber made with a carbon monofilament substrate. Auger
analysis, and supporting neutron activation analysis data,
established that, other than surface-adsorbed oxygen, the SCS-6
fiber is oxygen-free. Auger analysis also indicated that the
SiC fiber is carbon rich near the carbon substrate, but is
stoichiometric one Si to one C out away from the substrate.

KEYWORDS: Auger spectroscopy; Fibers; SCS-6; SiC.

1. INTRODUCTION

SCS-6 fiber, a CVD SiC fiber deposited on a continuous carbon
monofilament (CMF) substrate, is an important reinforcement
fiber in the fabrication of titanium and titanium aluminide
metal matrix composites. Such metal matrix composites are
essential to the success of future technologies such as
hypersonic flight vehicles (1).

In turn microchemical analysis by Auger electron spectroscopy
(AES) provides valuable information on reinforcement media, on
matrix materials and on the interfacial zones between the
reinforcement media and matrices (2-7). It is the purpose of
this paper to detail procedures for correctly evaluating
materials by AES and, in particular, to define the
microchemical composition of SCS-6 fiber. The critical
importance of such procedures will be forcefully illustrated by
a comparison of our SCS-6 data with a recently published Auger
evaluation (8) of this fiber in which some of our suggested
procedures were not employed.

2. MATERIALS, EQUIPMENT AND EXPERIMENTAL PROCEDURES

2.1 SCS-6 SiC Fiber   SCS-6 is a continuous 142 micrometer
(5.6 mil) fiber consisting of CVD SiC deposited on a 33
micrometer (1.3 mil) carbon monofilament (CMF) substrate with a
3-4 micrometer carbonaceous surface coating. The etched
micrograph (Figure 1) shows two zones of SiC deposition, the
inner zone having a fine grained columnar structure (10-60 nm
grain diameter) which transitions to a rougher (70-140 nm)
grained columnar structure at the approximate mid-range point
in the SiC deposition. There is an approximately 1 micrometer
zone of pyrolytic carbon between the SiC and the CMF. A
minimal fiber tensile strength of 3450 MPa (500 ksi) is
specified, but the normal strength range is 3800-4500 MPa
(550-650 ksi). The Young's modulus of elasticity of this fiber
is 400 GPa (58 msi). The carbonaceous surface coating has been
specifically designed for fabrication and use in titanium alloy
composites.

2.2 Auger Electron Spectroscopy

2.2.1   Auger Process   AES is a microanalytical technique which determines the number, identity, distribution and, in some cases, the chemical state of atoms lying within 0.5-2 nm of the specimen surface. The horizontal spatial resolution of AES is primarily determined by the incident electron beam diameter which is a function of the electron optics, beam voltage and beam current. In our study the current of the 10 Kev electron beam was determined with a Farady cup positioned in the specimen plane.

For instrument calibration with reference standards, and for Auger depth profiling of fiber surfaces, a 0.76 microamp, 5 micrometer diameter, defocused beam was used. For high resolution Auger line scans across the fracture faces of fibers, a 30 nanoamp, 0.1-0.3 micrometer diameter beam was used.

2.2.2   Specimen Preparation and Cleanliness Following fracturing in air and inspection, the flattest SCS-6 fracture faces were mounted on the specimen holder, sonicated in freon to remove debris and inserted into a JEOL model JAMP-10S Auger spectrometer. Prior to specimen insertion, the analysis chamber was maintained at 9.3×10^{-8} Pa (7×10^{-10} torr) as measured by an ion vacuum gauge attached directly to that chamber.

Following specimen insertion, the vacuum was 2.7×10^{-7} Pa (2×10^{-9} torr). Chamber cleanliness was monitored with an in-line residual gas analyzer. Surface contamination was removed by etching the rotating specimen for 3-4 minutes under a 3 Kev, 0.5 microamp argon ion beam. The specimen rotation enhances the effectiveness of the ion beam in removing contamination and native surface oxides (9-11) from rough fracture surfaces.

2.2.3   Quantitative Analysis   Factors (sensitivity factors) for converting the Auger intensities for Si, C and O to atomic percents were determined from argon-etched SiC and SiO_2 standards. Green, transparent single crystal alpha SiC and hot isostatically pressed SiC (Cerac, Milwaukee WI) gave identical results for the Si and C sensitivity factors. The oxygen standard was 100 nm of thermal SiO_2 on single crystal Si. Sensitivity factors were determined for both the integral and derivative Auger spectra.

There was concern about the 3 Kev argon ion beam altering the surface composition of SiC standards and fiber specimens (12-14). In response, an alpha SiC crystal was placed in the spectrometer antechamber, pumped at 200°C, in the low 10^{-6} Pa (10^{-8} torr) range for 12 hours and fractured in situ. The fractured specimen then was transferred to the 2.7×10^{-7} Pa (2×10^{-9} torr) analysis chamber. The surface showed no detectable Auger oxygen signal. The Si and C Auger intensities were monitored while the surface was etched with 3 Kev argon ions. The carbon signal decreased and the silicon signal increased for 3-4 minutes (possibly from radiation enhanced diffusion), then stabilized at a similar ratio of carbon to silicon peak intensities as determined above for the alpha SiC and hot isostatically pressed SiC standards. These observations validate the use of "effective" sensitivity factors, i.e., factors calculated from a 3-4 minute argon

etched SiC standard and applied to SiC specimens which have been subjected to similar etching conditions.

2.2.4   Auger Line Scans and Depth Profiles   Auger line scans for Si, C and O (Figures 2 and 4) were made by traversing a 0.1-0.3 micrometer electron beam across an argon-etched fiber cross section. Integral mode intensity data was collected at 50-60 nm intervals, collecting for 125 ms at the Auger energy peak and for 125 ms at a selected back ground energy. This data collection sequence was repeated for each element, the data was then averaged, adjusted for back ground intensity, and mathematically smoothed. Utilizing the experimentally determined sensitivity factors, the Auger signal intensities were then converted to Si, C and O atomic percents and plotted as a function of position on the fiber cross section.

Auger depth profiles (Figures 3 and 5) of fiber surfaces were made by alternately eroding the surface for 30s with a 0.5 microampere, 3 Kev argon ion beam and collecting derivative mode data for Si, C and O utilizing a defocused 5 micrometer electron beam. The peak intensities were collected for 150 ms and back ground intensities for another 150 ms. An effective ion sputtering rate of 25 nm per minute has been assumed for the fiber surface based on the experimentally determined value of 25 nm per minute for a thin film SiO_2 standard in the same 0.5 microamperes, 3 Kev argon ion beam.

3 Neutron Activation Analysis   Neutron activation analysis (NAA) was chosen as the second method for determining the oxygen content of the SCS-6 fibers. It is a non-destructive, quantitative technique which utilizes 14 Mev

neutrons to convert oxygen 16 to nitrogen 16, which, in turn, emits detected 6.13 Mev gamma photons which are proportional to the bulk oxygen content of the specimen. The analyses were performed at IRT Corp, San Diego, CA.

3. RESULTS

3.1 Auger Evaluation of Standard SCS-6 Fiber, Specimen NA-1
Using the procedures detailed in Section 2, the Auger line scans for Si, C and O of a standard SCS-6 fiber, Specimen NA-1, were recorded (Figure 2). The 3-4 micrometer surface coating is approximately 90 at. % C and 10 at. % Si. The Si/C ratio is 1/1 from the inner edge of the surface coating into the mid-range point. This mid-range point marks the transition from rougher to finer grain SiC and is more clearly defined in the polished and etched micrograph of Figure 1 than the as-fractured cross section of Figure 2. From the mid-range point into the CMF, the SiC gradually becomes carbon rich, being 55-60 at. % C and 40-45 at. % Si adjacent to the substrate. Note that oxygen is not detectable in the line scan (the Auger detection limit for O is approximately 0.5 at. %).

The Auger depth profile (Figure 3) of Specimen NA-1 shows surface oxygen which falls below detectable limits within approximately 12 nm (0.012 micrometers) of the surface. Also note that the surface coating is somewhat more Si rich at the outer surface (80 at. % C, 20 at. % Si) than within the surface coating (90 at. % C, 10 at. % Si) (Figure 2).

3.2 Neutron Activation Analysis of Specimen NA-1   NAA indicated that the bulk oxygen content of specimen NA-1 was 0.13 wt. % which converts to approximately 0.12 at. %. This second analytical procedure confirms the Auger findings that the SCS-6 fiber contains no detectable oxygen other than surface adsorbed oxygen.

3.3 Auger Evaluation of SCS-6 Fiber, Specimen 2   As mentioned in the Introduction, Auger evaluations of SCS-6 fiber have been presented in the literature which differ from the

ata presented in Figures 2 and 3. Reference 8 reports
onsiderable oxygen throughout the SCS-6 fiber and Si/C ratios
hich deviate considerably from stoichiometric 1/1. The author
f reference 8 kindly supplied us with an SCS-6 fiber specimen
hich he had tested (Specimen 2); his Auger evaluations are
resented in Table 1. Using the procedures described in
ection 2 of this paper, we performed Auger line scans (Figure
) and a depth profile (Figure 5) on Specimen 2. Our results
are identical to those of Specimen NA-1 and differ markedly
rom the Table 1 data. We found that there is no oxygen other
han surface adsorbed oxygen, that the Si/C ratio is 1/1 from
he inner edge of the surface coating in to the mid-range point
.d that the SiC gradually becomes carbon rich in towards the
:F substrate.

4. DISCUSSION

1 Oxygen Content   NAA clearly supports the findings of
.r Auger evaluation, namely, that other than surface oxygen,
.e SCS-6 fiber is oxygen-free. The conflicting data presented
Table 1 and in reference 8 are clearly the result of
alyzing contaminated fiber cross sections. Moreover, a
rivative spectrum of "a freshly fractured SCS-6 fiber
oss-section" in reference 8 is quite similar to the spectrum
recorded for an atmosphere-exposed alpha SiC crystal. In
dition to the oxygen signal, such spectra have relatively low
to C intensity ratios compared to an argon etched surface or
an alpha SiC crystal fractured in a clean spectrometer
techamber (section 2.2.3). We hypothesize that the reference
study did not maintain a sufficiently clean vacuum system to
event contamination of the SCS-6 surfaces, even in the few
ses in which the fiber surfaces were sputtered with 4 Kev
gon ions prior to Auger analysis. The reference 8 results
re subsequently used by the author as a basis for suggesting
at the mechanical properties of SCS-6/Ti alloy composites
re influenced by this level of oxygen. In view of our
ndings the merits of this suggestion must be reevaluated.

4.2 Si/C Ratio   As mentioned in Section 4.1, the Auger
spectra of contaminated SiC surfaces have smaller Si to C
intensity ratios than contamination-free SiC. This observation
partially explains the Table 1 and reference 8 findings that
the SCS-6 fiber is carbon-rich, non-stoichiometric SiC.
Another factor which brings into question these findings is
that experimentally determined sensitivity factors were not
used to convert the Auger signal intensities to atomic %. In
section 2.2.3 we detail procedures for determining accurate
sensitivity factors which are a definite requirement for
quantitative Auger analysis.

5. SUMMARY

1. There is no oxygen in the body of the SCS-6 fiber.

2. Oxygen is only found on the outer 12 nm (0.012 micrometers)
   of the fiber surface.

3. Si/C ratio is 1/1 from surface coating into the mid-range
   point of the SCS-6 fiber.

4. SiC becomes increasingly carbon rich from the mid-range
   point into the CMF, being 55-60 at. % C and 40-45 at. % Si
   adjacent to the CMF substrate.

5. Useful Auger data requires attention to details, some of
   which are discussed in this presentation.

6. ACKNOWLEDGMENTS

7. BIOGRAPHY

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iseph D. Geller is the proprietor of and chief scientist at :ller Micro Analytical Laboratory which provides scanning iger microprobe, SEM and x-ray analytical services, as well as :andards for use with these techniques. Prior to founding iis company, he was the director of the electron microprobe id then the surface analysis laboratory of JEOL (USA), Inc. : is an active organizer in the American Vacuum Society, has iught courses in SEM, x-ray and surface analysis, and is a ibcommittee chairman of the ASTM E-42 surface analysis .mmittee. He has authored 30 technical papers. Mr. Geller -ceived his B.S. degree from the Rochester Institute of .chnology and a M.B.A. from Salem State College.

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TABLE 1
AUGER EVALUATION NOT USING SUGGESTED PROCEDURES*
SPECIMEN 2

| | ATOMIC % | | |
	C	Si	O
CMF	100	0	0
Graphite Layer	95	0	5
SiC inside MR point	62	24	14
SiC at MR point	60	25	15
SiC outside MR point	60	23	17
Middle of surface coat	91	9	0
Outer edge of surface coat	86	3	11

.ble 1 data was provided by reference 8 author.

SCS-6 FIBER
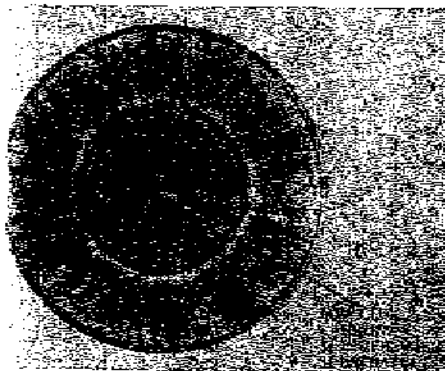
- Continuous 142 micrometers (5.6 mil) monofilament
- 33 micrometers (1.3 mil) CMF substrate
- CVD SiC
- 3450 MPa (500 ksi)
- 400 GPa (58 msi)
- Carbonaceous surface coating
- Ti Matrices

FIGURE 1. Micrograph of polished and etched SCS-6 fiber.

AUGER LINE SCAN OF SCS-6 FRACTURE FACE
SPECIMEN NA-1

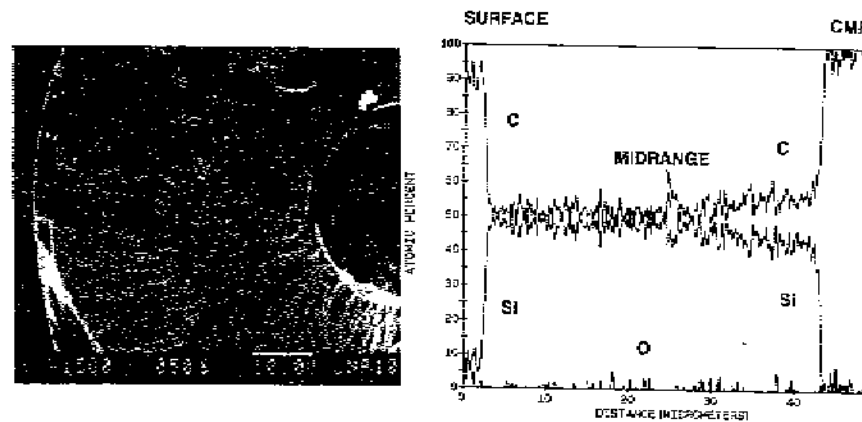

FIGURE 2. A 1500X micrograph of specimen NA-1 and the corresponding Auger line profile for Si, C and O.

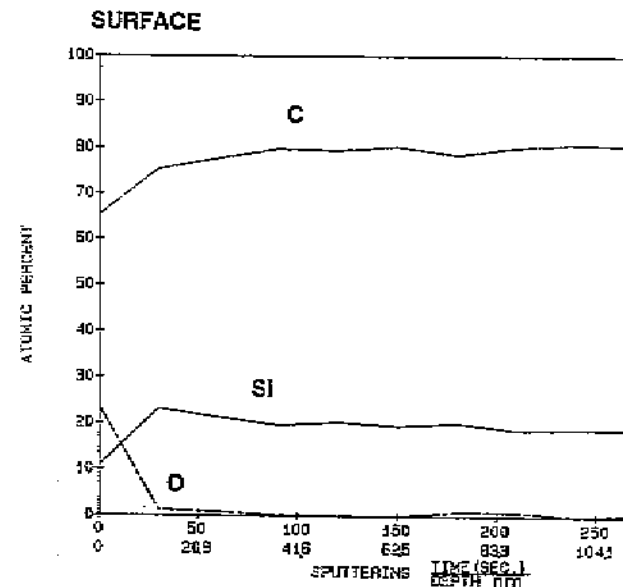## AUGER DEPTH PROFILE OF SCS-6 SURFACE
SPECIMEN NA-1

FIGURE 3. Auger depth profile of specimen NA-1.
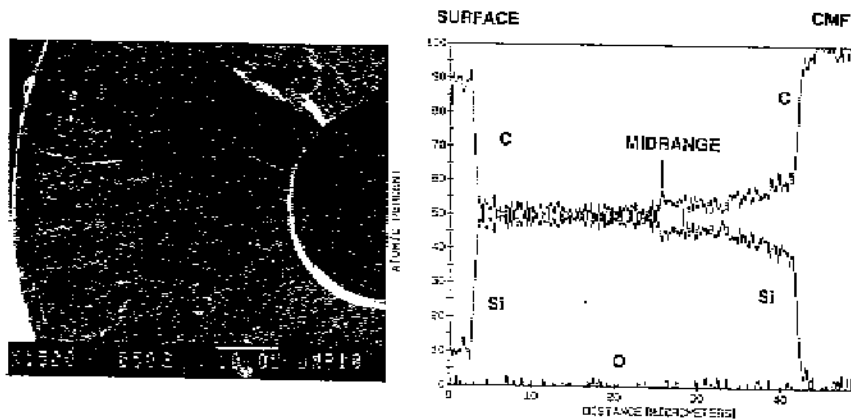
AUGER LINE SCAN OF SCS-6 FRACTURE FACE
SPECIMEN 2

FIGURE 4. A 1500X micrograph of specimen 2 and the corresponding Auger line profile for Si, C and O.

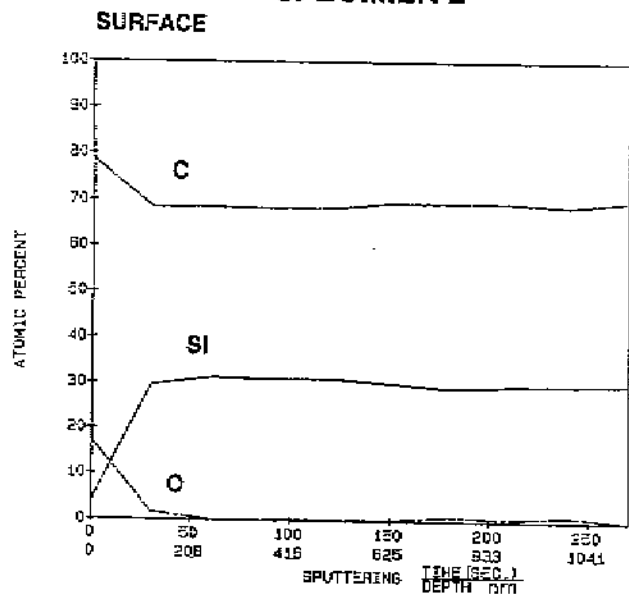## AUGER DEPTH PROFILE OF SCS-6 SURFACE
SPECIMEN 2

FIGURE 5. Auger depth profile for specimen 2.

DETERMINING AXIAL ERROR IN SAPPHIRE FIBERS BY OPTICAL METHODS.
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ABSTRACT

An optical procedure, derived from traditional methods of optical microscopy of geologic sample thin sections, is customized to measure orientation error in sapphire fiber optics production. Measurement of optic axis deviation in a single crystal sapphire rod or fiber is accomplished with a polariscope or microscope. Operator training time and equipment requirements are minimal. Measurement by microscope is very rapidly accomplished, with accuracy equal to X-Ray Laue measurements, when working with small (50-250 um) diameter fibers.

KEYWORDS: Sapphire; fiber; orientation; polariscope; microscope

INTRODUCTION:

Single crystal sapphire fiber may be grown directly from the melt in multiple arrays. Effective quality control during growth requires a simple, rapid, in situ determination of fiber orientation, without the difficulties of sample fixturing required by X-ray diffraction. The optical measurement technique adequately satisfies both of these needs. Production personnel, with a less than a day's training, are able to regularly produce reliable measurements within less than a minute.

The method incorporates traditional and techniques of optical microscopy. The following details insure success in determining the optic angle. With a microscope, the method can reliably provide accuracy in the order of 1/2 to 1 degree. A similar measurement may be accomplished, but with somewhat reduced accuracy, using a simple handheld or bench polariscope. Equipment modifications can significantly reduce the shortcomings of the polariscope.

Crystal basics:

The optical method used here makes use of the anisotropic character of sapphire. Since sapphire crystallizes in the hexagonal system, its optical properties are uniaxial. This means that there are two indices of refraction, with the index along the optic axis about 1.758, and perpendicular, 1.766. These index values are high, characteristic of covalent bonded, hard, moderately high density minerals. The difference between these two indices (termed birefringence) is 0.008, a value which is low as minerals go, and near quartz at 0.007. It is the birefringence which will determine many of the characteristics used in the following measurements.