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THE IN-SITU FRACTURE AND AUGER ANALYSIS OF NICALON* FIBERS

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ABSTRACT

A technique has been developed to fracture irradiated Nicalon fibers in a Scanning Auger Microprobe (SAM) and analyze the fracture surfaces without contaminating the specimen chamber. The technique, which was evaluated using as-received fibers, requires only minor modification of two standard specimen holders and should be applicable to other fibers or materials that can be broken under low loads in bending. The technique is simple, rapid, reduces beam charging, and eliminates the need for ion sputtering.

INTRODUCTION

Ceramic composites with continuous SiC fibers such as Nicalon are currently being developed for high-temperature

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structural applications. In producing these composites, the matrix material is often deposited on fiber preforms using chemical vapor infiltration (CVI).¹ The role of the strong SiC fibers is to toughen the inherently brittle matrix material. Because of this key role, there has been considerable effort in characterizing the fibers and understanding their properties. Yajima et al² first developed Nicalon and showed that the fibers were primarily composed of crystalline beta-SiC, C, and SiO₂. Later, Porte and Sartre³ presented evidence for an additional SiO_xC_y phase. The composition of Nicalon has been determined by chemical analysis,² Auger electron spectroscopy (AES),^{4,5,6} x-ray photoelectron spectroscopy (XPS),³ infrared spectroscopy,⁷ and probably others.

In the present study, a technique was developed to fracture fibers in-situ and analyze them in a Physical Electronics PHI 660 Scanning Auger Microprobe (SAM). Initially, this technique was devised to analyze Nicalon fibers that were irradiated and still slightly radioactive. Fracture of the fibers was to be used as a viable alternative to sputter-cleaning the fiber surfaces which would have contaminated the SAM specimen chamber. The in-situ fracture apparatus that was designed required only minor modifications to two standard holders; nothing on the basic instrument had to be changed. In order to evaluate the technique, two different batches of as-received Nicalon fibers were fractured, analyzed chemically by AES, and the results compared to those measured by other investigators. Finally, the advantages and limitations of the technique as well as possible applications are discussed.

EXPERIMENTAL

SiC Fibers

Two different batches of Nicalon fibers were analyzed in this

investigation. The first batch contained low-oxygen Nicalon fibers that were cured with an electron beam in a helium/hydrogen atmosphere. The company inspection sheet lists the oxygen content of the fibers as 0.6 wt %, as determined by using an oxygen/nitrogen analyzer. The second batch were Ceramic Grade Nicalon fibers that were cured in an oxygen environment and were expected to contain about 10 wt.% oxygen.⁷ For convenience, these batches will be called "Low-Oxygen" and "High-Oxygen" Nicalon fibers, respectively. The fibers ranged from 12 to 20 μm in diameter and typical fibers from the Low-Oxygen batch are illustrated in the scanning electron micrograph in Fig. 1. The fibers from the High-Oxygen batch were generally the same in appearance.

Fig. 1 Low-Oxygen Nicalon fibers.

In-Situ Fracture Apparatus

The apparatus that was used to fracture the fibers in the PHI 660 is shown schematically in Fig. 2. The simple setup makes use of two standard fracture mounts having 0.32 cm (1/8 in.) diam. specimen openings with set screws. One mount rests in the specimen stage and contains a small copper insert into which a small bundle of fibers are positioned and held in place with Epo-tek H20E-LC conductive epoxy⁸ as shown. The insert is held firmly in the mount with a set screw. A flexible copper retainer wire which is fastened to the mount with a small screw is attached to the top of the fibers with a small drop of epoxy. The retainer wire keeps the upper portion of fiber bundle from falling into the SAM chamber after fracture. This is an imperative requirement when fracturing irradiated fibers. A stainless steel blade is used to fracture the fibers by sharply bending them at the epoxy bond line. The blade (Fig 2) is attached to the second mount by first welding a 0.31 cm diam. pin to one end and subsequently securing the pin in the mount with the set screw.

Therefore, if one already has two standard fracture mounts, the only modifications needed to conduct in-situ fracture of fibers in a PHI 660 or similar instrument include: small copper inserts to hold the fibers, a small hole drilled and tapped to secure a retainer wire, conducting epoxy, and a small stainless steel blade with welded pin.

In-Situ Fracture Procedure

The actual fracture process was accomplished by remotely manipulating the second mount and attached blade with the specimen carrousel. This is shown more clearly by the photograph in Fig. 3. The carrousel was designed to hold six specimens and it can be rotated as well as moved in a direction to load specimens on the specimen stage. This latter

Fig. 3. Photograph of fracture apparatus.

motion allows the operator to fracture a fiber bundle by moving the blade across the bundle just above the epoxy line. Alignment of the blade to this point is conveniently achieved prior to fracture by using the X, Y, Z, and rotate controls of the specimen stage. After fracture, the flexible retaining wire may be gently bent using the blade to keep the upper portion of the fiber bundle from obscuring the analysis area.

Note also that the mount containing the fibers in Fig 3 is held in a cup on the specimen stage in the normal way and that it was unseated if the load exceeded 1-2 kg. This behavior limited the number of fibers that could be broken at any one time. In this investigation, 10 to 20 fibers were fractured without difficulty. Use of the standard specimen stage with its load limitation provides a built-in safety feature that prevents possible damage to the carousel mechanism from occurring. That is, the specimen mount will be unseated in the cup (but not lost) before the carousel mechanism can be overloaded.

Auger Electron Spectroscopy

Quantitative AES analyses of the fibers were conducted with the PHI 660 which utilizes a LaB₆ filament. The instrument had been upgraded with the necessary electronics to operate the PHI 5.3A software, and the Hewlett-Packard Apollo computer 10.3 software. Analyses were conducted with a relatively low electron beam accelerating voltage of 3kV and a beam current of 10 nA to minimize charging of the SiC fibers. The beam spot diameter was $\approx 0.3 \mu\text{m}$. The vacuum level during fracture and analysis was always less than 2.7×10^{-7} Pa (2×10^{-9} torr). Quantitative analysis was conducted with the PHI software and sensitivity factors supplied by Physical Electronics except for silicon. The sensitivity factors for silicon were $\text{Si1} = 0.212$ and $\text{Si2} = 0.094$, as determined by

analyzing a NIST SiC standard under the same conditions as used in this experiment.

RESULTS

In-Situ Fracture

Since the conductive epoxy is quite viscous and the Nicalon fibers have such small diameters, it was difficult to prepare a level epoxy surface and a number of different fiber orientations were observed after fracture. Fig. 4 shows some of the fiber orientations that were found after fracturing a bundle of Low-Oxygen Nicalon fibers. Fig. 4a is a micrograph of a single fiber after fracture that is ready for AES analysis. The rough outer coating visible just below the fracture surface is epoxy. Fig. 4b shows an adjacent area that contains a group of three fibers. An area closer to the epoxy base is seen in Fig. 4c with two fiber fractures that were analyzed. Sometimes all of the fibers in a bundle did not fracture completely or obscured the analysis areas as is evident in this area. This problem of debris was eliminated by simply moving the blade across the area again. However, most of the fibers were fractured by the first pass and the broken ends were held by the retainer wire. This variability in fiber orientation did not hinder AES analysis in any way.

For experiments where re-analysis may be required, it was discovered that a small amount of epoxy applied to the fiber bundle slightly above the top copper insert was advantageous. This was accomplished by dipping of the fiber bundle into the insert containing uncured epoxy and then lifting it slightly upward before permitting the epoxy to set. This allowed the height of the blade to be adjusted to a higher level than usual for fracture. Subsequent fractures could then be conducted at a later time on the same fibers by lowering the blade relative to the top of the insert and breaking off additional material.

Fig. 4. Typical fiber orientations found after fracture: (a) single fiber, (b) group of fibers, and (c) fibers at epoxy base.

AES Analysis

Typical survey spectra taken immediately after fracture of Low- and High-Oxygen fibers are presented in Fig. 5. Auger peaks for Si1, C1, and O1 were observed in both spectra which had somewhat noisy backgrounds, especially at higher energies. The noisy background is due to the lower counts collected using the relatively weak 3kV-10nA analyzing beam which was used to minimize specimen-charging. As expected, the oxygen peak in the spectra for the High-Oxygen fiber (Fig. 5b) was larger than that observed for the Low-Oxygen one (Fig. 5a). Further analyses of these peaks were conducted in the multiplex mode, i.e., 200 survey sweeps over each of the Auger peak windows. The results of these analyses on 5 fibers from each batch, with average compositions and standard deviations, are given in Table 1. The average composition obtained for the Low-Oxygen Nicalon fibers was 32 ± 8 Si, 64 ± 6 C and 4 ± 2 O at.%, and 32 ± 2 Si, 49 ± 1 C, and 19 ± 2 O at.% for the High-Oxygen Nicalon. The latter composition is compared to others found in the literature which are also listed in Table 1. The analysis method used is also noted. The amounts of Si and C measured in this study fall within the respective ranges established by the values from the literature, except O which is slightly higher. Fewer results were found for the Low-Oxygen Nicalon fibers in the literature. However, Takeda et al⁷ reported that the oxygen content of their low-oxygen Nicalon fibers ranged between 0.4 to "less than 3 wt.%." Since the wt.% of O is approximately the same as at.% in the Nicalon fibers, the present result of 4 ± 2 at.% is found to compare quite favorably with Takeda's especially if the standard deviation is kept in mind. Investigators such as Macey et al⁶ have pointed out that there is a great deal of variability in composition between one fiber and another.

Fig. 5. Typical auger spectra taken at 3kv and 10 nA for (a) low-oxygen Nicalon, and (b) high-oxygen Nicalon.

Table I. Composition of Nicalon Fibers

<u>Batch/Ref./Method</u>	<u>Si</u>	<u>At. %</u>	
		<u>C</u>	<u>O</u>
Low-oxygen-AES	25	70	5
	24	70	6
	40	58	2
	32	64	4
	<u>40</u>	<u>57</u>	<u>3</u>
	Ave.	32±8	64±6
High-oxygen-AES	29	50	21
	35	49	16
	32	48	20
	31	50	19
	<u>33</u>	<u>50</u>	<u>17</u>
	Ave.	32±2	49±1
<u>High Oxygen Nicalon</u>			
Simon & Bunsell ⁴ -AES	Batch-101	40.6	44.1
	-102	34.9	50.6
Yajima et al ² -Chem.		35.5	51.8
Porte & Sartre ³ -XPS		31	56
Macey et al ⁶ -AES		33	53
<u>Low Oxygen Nicalon</u>			
Takeda et al ⁷ -IR	-	-	≈0.4 - 3

DISCUSSION

The in-situ fracture and chemical analysis of Nicalon fibers was successfully conducted in a PHI 660 scanning Auger microprobe after simple modifications to two standard fracture mounts were made. The technique should be applicable to most other PHI SAM's and fibers made of other materials. However, the cross-sections must be small enough or the material weak enough to be broken at 1-2 kg. Advantages of the technique are: rapid analysis of bulk composition without the need to sputter and the ability to minimize specimen charging due to the electron beam. With this technique, a "bulk" composition near the center of the filament can be determined immediately after fracture. A conventional experiment in the SAM would require several minutes of sputtering to remove surface contamination and, perhaps, 30 minutes or more to reach the center region from the side of the fiber. So in-situ fracture would be convenient in cases where rapid analysis of the center region of a fiber is needed without sputtering. More importantly, when even very slightly radioactive specimens are analyzed in our instrument, ion sputtering is not an option because sputtered material would contaminate the specimen stage and chamber. Possible contamination is also a main reason for using the retainer wire which keeps the fractured fibers from falling in the specimen stage or chamber. There may be other situations that prohibit sputtering such as selective sputtering of a phase or element and/or a problem of re-deposition of an element during sputtering. With regard to charging, it was observed that less charging occurred when the Nicalon fibers were in intimate contact with the conductive epoxy, compared to fibers that were lying on or pressed into indium foil.

Other applications of the technique might include any situation where analysis is desired across a small cross-section. Modern SAM's with field emission guns and very small

diameter analyzing beams (<20 nm) would be able to use this feature in analyzing specimen cross-sections. Another possible application is the fracture of crystalline fibers so that the grain boundary composition might be analyzed. This traditional feature of AES might then be applied to much smaller specimens. The success of this latter application would depend solely on whether the material will fracture intergranularly. To help attain that goal, it would be possible with the present set-up to cool the specimen to $\approx -130^{\circ}\text{C}$ prior to fracture using the regular fracture cold stage. However, this would require that the retainer wire be secured inside the first collar, closer to the copper insert, so that the mount would fit inside the cold stage.

SUMMARY

The in-situ fracture and analyses of Low- and High- Oxygen Nicalon SiC fibers were conducted successfully in a PHI 660 Scanning Auger Microprobe. The measured compositions of the as-received fibers compared favorably with those found in the literature. The fracture apparatus required only minor modification of two standard fracture mounts. The technique is rapid, reduces beam charging, and offers a way to re-analyze the same specimens without remounting them. Most importantly, the technique eliminates the need for sputtering and can, therefore, be used to analyze irradiated fibers. However, fracture is limited to a small load of 1-2 kg. The technique should be readily applicable to most other PHI Auger microprobes and may find application in the future to cross-sectional and grain boundary chemical analysis.

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