CHARACTERIZATION OF SiC FIBERS BY SOFT X-RAY PHOTOELECTRON
AND PHOTOABSORPTION SPECTROSCOPIES AND
SCANNING AUGER MICROSCOPY

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ABSTRACT

Synchrotron radiation soft x-ray photoelectron and photoabsorption spectroscopy was used to characterize commercially obtained SiC fibers, which were produced by chemical vapor deposition (CVD) of SiC on a W core, followed by a carbon passivating layer. Depth profiling of the fiber through the carbon/SiC interface was done by making Si 2p and C 1s core level PES and PAS, as well as scanning Auger microscopy, measurements following Ar⁺ sputtering. No significant changes in either photoemission or absorption or Auger line shapes were observed as a function of the depth, which indicates that there is no significant interfacial reaction. The line shapes of the carbonaceous coatings are predominately graphite-like and those of the CVD SiC coatings are microcrystalline, with presence of disorder to some extent in both cases.

INTRODUCTION

Metal matrix composite (MMC) materials have long been regarded as having numerous technological applications in areas where their high strength-to-mass ratio is important, such as the aerospace industry [1]. SiC fibers and particulates are widely used as reinforcing materials in MMCs. The fibers are normally produced by chemical vapor deposition (CVD) of SiC on a W or C core, followed by a carbon passivating layer. This carbonaceous layer serves as a barrier to prevent interfacial reactions between the fiber and matrix that may be detrimental to the mechanical properties of the fibers. The SiC fibers are then imbedded in a metal (usually Ti or Al) matrix to form the composite material. These composites exhibit substantial strength relative to the unreinforced matrix alloys. However, the superior mechanical properties of the MMC depend to a great extent on the interface between the reinforcing material and the matrix. A great amount of effort has been spent studying interfacial reactions [2, 3] in the MMC of this type, but few studies have focused on structure of the fibers, which may be an important factor to understand the reaction kinetics.

We have initiated research aimed at gaining insight into the interfacial reactions occurring between the fiber and the matrix. As a first step we have tried to understand the structures of the SiC fibers by using synchrotron radiation soft x-ray photoelectron and photoabsorption spectroscopies (PES, PAS) as well as the scanning Auger microscopy (SAM). The results obtained on a commercially obtained SiC fiber are presented in this paper.

EXPERIMENT

The SiC fibers were purchased from Goodfellow Inc. and were produced by CVD of SiC on a tungsten core followed by a carbon passivating coating. The total diameter of the fiber is 100 μm . The W core is 10 μm in diameter, the SiC coating is 42 μm in thickness, and the outer carbonaceous coating is 3 μm . A bunch of the fibers with a length of about 1 cm were glued to a 1x1 cm² Ta plate using vacuum-compatible conductive silver epoxy. An optical micrograph image of the prepared sample is shown in Fig. 1.

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Fig. 1. An optical microgram of the prepared SiC fiber sample

The soft x-ray PES and PAS measurements were performed at the Synchrotron Radiation Center, University of Wisconsin-Madison. The light emitted by the "Aladdin" storage ring was dispersed by the Mark II grasshopper monochromator. For photoemission measurements, the incident light impinged on the sample at an angle of 45° with respect to the sample normal, and the photoelectrons were detected along the sample normal using a VG 100AX hemispherical energy analyzer. The overall energy resolutions for PES at 140 eV and 350 eV photon energies were 0.4 eV and 1.5 eV, respectively, which were estimated by measuring the Fermi level of a Ta metal at 140 eV and by measuring the full width at half maximum of the C 1s of the highly oriented pyrolytic graphite (HOPG). For PAS, the energy resolutions were experimentally determined to be 0.4 eV around the Si 2p edge and 1.0 eV around the C 1s edge. The PAS data was taken by measuring the sample restoring current and normalizing the incident light intensities to the photocurrent from an *in situ* copper-coated grid. A pressure of at least 5×10^{-10} Torr was maintained in the measuring chamber during data acquisition.

Auger electron spectroscopy experiments were conducted using a VG 100AX electron energy analyzer in conjunction with a LEG 200 small spot electron gun. A 6-keV electron beam at an incident angle of 45° was used, and the sample current induced was typically 150 nA. The beam spot size was about 20 μm . Auger electrons emitted along the specimen normal were detected by the electron energy analyzer, which was operated at a constant retard ratio of 10. The chamber base pressure was 5×10^{-10} Torr, and it rose to 5×10^{-9} Torr during operations.

To perform the depth profiling, an ion sputtering gun was used to mill away the sample. The Ar gas was leaked into the chamber to bring the chamber pressure up to 5×10^{-5} Torr, and the gun was operated at a setting of 2kV and 20mA. Data collection was performed right after sputtering.

RESULTS AND DISCUSSION

Soft X-ray Photoelectron and Absorption Spectroscopies

Figures 2 and 3 show the background-subtracted C 1s and Si 2p photoemission spectra as functions of ion sputtering time which is increasing from (a) to (d) or (e). The magnitudes of the emission peaks were normalized by the peak maxima to facilitate the lineshape comparison. The magnitudes of the C 1s peaks decrease with sputtering time while those of the Si 2p peaks increase. Prior to exposure of the SiC by sputtering, the C 1s lineshapes observed on the fiber remain identical to the one shown in Fig. 2(a) (full line), independent of the depth. The C 1s lineshape of the carbonaceous coating appears to be graphitic; the linewidth is significantly larger than HOPG, which indicates the presence of a significant amount of disorder [4]. It should be noted, however, that at least some of the disorder is due to the sputtering process itself. The peak asymmetry is associated with the delocalized π electrons in the sp^2 , trigonally bonded carbon [5]. Therefore, the electronic structure as well as the local atomic structure of the coating is similar to graphite, modified by the presence of disorder.

Fig. 2. C 1s PES data. The emission peak intensities are normalized by the peak maxima. The relative intensities are given by the multipliers: (a) $\times 1.0$, (b) $\times 0.46$, (c) $\times 0.44$, (d) $\times 0.35$, and (e) $\times 0.34$.

Fig. 3. Si 2p PES data. The emission peak intensities are normalized by the peak maxima. The relative intensities are given by the multipliers: (a) $\times 1.0$, (b) $\times 2.3$, (c) $\times 4.0$, and (d) $\times 5.8$.

Fig. 4. Simulation of the line (e) in Fig. 2

Fig. 5. Simulation of a Si 2p line in Fig. 3.

As sputtering proceeds, an extra component appears in the lower binding energy side of the C 1s line at the moment of exposure of the Si, as shown by lines (b) to (e). With increasing etching, the intensity of the component increases. A quantitative analysis of the C 1s line shape is not trivial since it requires a complete knowledge of the electron energy loss profile. However, it is possible to simulate the C 1s line shape of the carbonaceous coating, prior to the exposure of the Si, with several peaks [6]. From knowledge gained by this simulation, it is possible to analyze the C 1s lines measured after exposure of the Si. Figure 4 shows the results of simulations performed on the C 1s line (e) in Fig. 2. The top part shows the residuals of simulation. In reference to the Fermi level, the binding energy obtained for the C-C component is 284.3 ± 0.1 eV. The binding energy obtained for the second component is 282.9 ± 0.1 eV, which is within the range of values reported for α -SiC [7]. In order to gain a full knowledge of the C 1s line shape due exclusively to the SiC coating, PES should be performed on the selected area.

Fig. 6. PAS data of Si $L_{2,3}$ edge. Sputtering time increases from (a) to (d).

Fig. 7. PAS data of C K edge. Sputtering time increases from (a) to (e)

The Si 2p line shape appears to be symmetric as has been seen previously [8, 9, 10, 11] for amorphous SiC and microcrystalline SiC. The spin-orbit splitting of $2p_{3/2}$ and $2p_{1/2}$ is not distinguishable. This suggests that the SiC coating is in the microcrystalline form in which disorder may be present. A two-peaks simulation was attempted on the Si 2p lines. A typical result is shown in Fig. 5. The binding energy obtained is 100.4 eV, which is a characteristic value for Si in α -SiC [7]. The weak peak on the higher energy side of the Si 2p line is needed to significantly reduce the residuals of simulation. It is probably due to the existence of silicon oxide in the SiC coating, as supported by the SAM data presented below.

Figures 6 and 7 show the x-ray photoabsorption spectra measured near the Si $L_{2,3}$ and C K edges, respectively, as a function of sputtering depth. The π^* and σ^* resonances are clearly distinguishable in the C edge spectra. Recent measurements carried out on disordered graphite show similar spectra [12]. This correlates well with disorder observed by the C 1s PES. The presence of the π^* resonance is again a characteristic of the graphite-like structures. As sputtering

progresses, the Si signals increase while the C signals as well as the character of the graphite-like structure decrease. The broadness of the features in the Si L_{2,3} edge spectra may also indicate possible disorder in the SiC coating.

Auger Electron Spectroscopy

As observed by analyzing the XPS data, some oxide states may exist. The role that oxygen plays has drawn much attention regarding the long-term performance of Ti/SiC metal matrix composites. The presence of the O in the composites was reported to be the primary cause of the embrittlement of the interface between the fibers and the metal matrix [13, 14, 15]. Therefore, evaluation of the O present in the fiber appears to be necessary. Figure 8 shows survey scans performed right after ion sputtering in the carbon overlayer (a) and the SiC layer (b). It shows that the carbonaceous coating is rather inert to oxygen, while the oxide is always present in the SiC coating, as also observed by Upadhyaya *et al.* [16]. This may be due to the fact that Si has a higher chemical affinity for O than does C. This result suggests that some amount of the oxygen was embedded into the fiber during production.

Fig. 8 Survey scans of Auger electrons: (a) on carbonaceous coating, (b) on the SiC coating.

CONCLUSION

The carbonaceous and SiC coatings of the fiber have been characterized by using soft x-ray photoemission and photo absorption spectroscopies as well as Auger electron spectroscopy. The carbonaceous coating is made up of vitreous carbon and the SiC coating of microcrystallites. Both of these coatings are rather uniform in terms of chemical and structural makeup. The carbonaceous coating is rather inert to oxygen while the SiC coating is slightly oxidized. Selected area soft x-ray absorption spectroscopy studies on cleaved samples of both as-received and heat-treated fibers as well as Ti/SiC MMCs are in progress. In order to understand the fundamental reaction mechanisms between the fiber and the metal matrix, experiments examining the interaction between Ti and well-defined surfaces of HOPG and single crystal SiC are being undertaken. These studies, in conjunction with the present work, will greatly enhance our understanding of the interfacial reactions occurring in MMCs.

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Figure Captions

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