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Focused ion beam milling of carbon fibres

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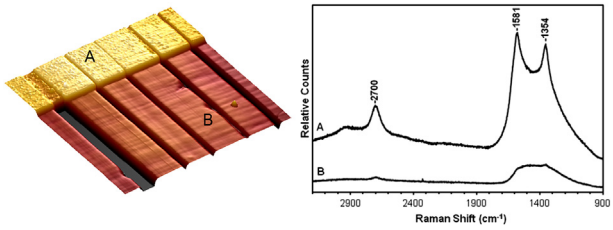
HIGHLIGHTS

- Focused ion beam (FIB) milling was used to mill flat surfaces on carbon fibres.
- Raman spectroscopy showed amorphous carbon was generated during FIB milling.
- The amorphous debris is detected as far as 100 μm from the milling site.
- This surface degradation was confirmed by nano-indentation experiments.

GRAPHICAL ABSTRACT



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ABSTRACT

A focused ion beam has been used to mill both individual carbon fibres as well as fibres in an epoxy composite, with a view to preparing flat surfaces for nano-indentation. The milled surfaces have been assessed for damage using scanning probe microscopy nano-indentation and Raman micro-probe analysis, revealing that FIB milling damages the carbon fibre surface and covers surrounding areas with debris of disordered carbon. The debris is detected as far as 100 μm from the milling site. The energy of milling as well as the orientation of the beam was varied and shown to have an effect when assessed by Raman spectroscopy.

1. Introduction

A focused ion beam (FIB) instrument uses a finely focused beam of ions (often Ga but more recently Ne and He) that can be operated at low beam currents for imaging or high beam currents for site specific deposition or ablation of material. Removal of material, or milling, is a technique used extensively in materials science for the etching or machining of samples, the nanofabrication of devices and the preparation of samples for further characterization.

A FIB instrument requires a source that emits charged ions in a high vacuum environment. Commonly ions are generated from a tungsten needle that is mounted below a reservoir of liquid Ga. These ions are focused onto the sample surface by electrostatic lenses and, for milling, the beam can be fixed on a specific position which leads to localized sputtering and the formation of holes or channels in the sample surface. For a comprehensive review see for example references [1,2].

The FIB technique is commonly used to prepare samples for

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transmission electron microscopy (TEM), which requires very thin samples, typically about 100 nm thick. This is particularly true for hard brittle materials such as carbon fibre and those used in the semi-conductor industry which can not readily be embedded and sectioned on an ultramicrotome. The disadvantages of FIB sample preparation are the potential for ion implantation and surface damage, such as dislocations and the formation of an amorphous layer adjacent to the milled surface [3–6]. Most studies use TEM to show the damage [5,7–14] although X-ray diffraction [15], X-ray Energy Dispersive Spectroscopy [14] and atom probe tomography [16] have also been used. Recently Sabouri et al. [17] used Raman spectroscopy to show that Ga ions implanted into a Si wafer can act as nucleating agents, promoting the recrystallization of Si at room temperature over a period of several hours. Shim et al. [6] investigated the effects of FIB damage on a Mo–alloy using nano-indentation, and reported enhanced dislocation plasticity and hardness for FIB milling both normal to and parallel to the surface.

This damaged layer can be minimised by FIB milling with lower beam voltages during final milling [4], or by further thinning with a low energy ion beam (IB). The latter approach, in which ions from a cathode impinge on the sample wafer at an angle, typically involves ex-situ transfer of the sample. The use of IB milling to prepare sections of carbon fibre for TEM was first reported in 1971 [7] for fibres embedded in an epoxy matrix, and has been used by several workers since [18–20]. It proved difficult, however, to prepare cross-sections due to the preferential erosion of the resin [18].

FIB milling allows much greater spatial control than IB thinning, allowing TEM specimens with greater uniformity of thickness to be prepared and samples to be selected with accurate site specificity. This was shown recently by Mucha et al. [21] who used FIB milling to prepare TEM samples of free carbon fibre as well as fibre/matrix interfaces. Preferential erosion of the matrix remains a problem but they describe in detail a process which overcomes this preferential thinning. Wu et al. [22] compared the suitability of FIB and IB, as well as ultramicrotomy, to prepare samples of carbon fibre/polymer suitable for the examination of the interface. They showed that all three methods have advantages, depending on what information is required from the sample.

In this work, FIB milling has been used on both carbon fibre composites and free carbon fibres. Various beam voltages and directions have been used and the resultant surfaces examined using nanoindentation and Raman spectroscopy to assess the extent of any structural modifications that might have occurred.

2. Materials and methods

2.1. Samples

The mechanically polished coupons were supplied by The Boeing Company and were used as received. They consisted of high modulus polyacrylonitrile (PAN) based M46J carbon fibres (Toray) embedded in epoxy resin 977-3 (Cytec). The free (un-embedded) carbon fibres used in this study were intermediate modulus IM7 (Hexcel) PAN based carbon fibre.

2.2. Focused ion beam (FIB) sample preparation

Both free carbon fibre and small samples of carbon fibre composite, mounted on a stainless steel substrate, were ion milled in a FEI Helios Nanolab 600 Dual-Beam Focused Ion Beam-Scanning Electron Microscope (FIB-SEM) to produce flat surfaces on the carbon fibre. A focused beam of Ga ions, at various beam voltages, was used to mill different areas on the carbon fibre surface. When imaging with electrons (SEM mode) the beam was at an angle of 52° to the surface resulting in foreshortening and making the radial cross-sections of fibres appear more elliptical than is actually the case.

2.3. Raman spectroscopy

Raman spectra were obtained using an inVia confocal microscope system (Renishaw, Gloucestershire, UK) with 514 nm excitation from a Modu-Laser Stellar-Pro ML/150 Ar ion laser through a 50 × (0.75 na) objective. Incident laser power was 4.5 mW and coaxial backscatter geometry was employed. This configuration results in a submicron spot size with a maximum power density of 820 kW/cm^2 at the sample. It was found that this power density provided the best signal to noise without damaging the sample. Spectra were collected over the range 100–3200 cm^{-1} and averaged over at least 4 scans, each with an accumulation time of 30 s. The Raman shifts were calibrated using the 520 cm^{-1} line of a silicon wafer. The spectral resolution was approximately 1 cm^{-1}. Laser power was measured at the sample using an Ophir Nova power fitted with a PD300-3W photodiode head.

All spectral manipulation was carried out using Grams AI v 9.1 software (Thermo Fisher Scientific Inc). Deconvolution of the spectral region between 1800 and 900 cm^{-1} was accomplished using a band model reported by Sadezky et al. [23]. Fits were based on the usage of a minimal number of band components, each represented by pseudo Voigt functions. All peak heights were limited to the range greater than or equal to zero. In the initial fitting steps the band centres were only allowed to vary by ±5 cm^{-1} from the approximate frequencies given by Sadezky et al. [23]. In the final refinements all parameters were allowed to vary unconstrained. All reported component percentages are based on intensity but area calculation provided similar trends.

2.4. Scanning probe microscopy (SPM) nano-indentation

Images and force curves were collected with a Digital Instruments Dimension 3000 Scanning Probe Microscope fitted with a diamond probe on a cantilever with a spring constant of 178 N/m. Images were collected in tapping mode at a scan speed of 1 Hz. Force curves were collected in force-volume mode where a 16 × 16 matrix of indents was made on a 3 × 3 μm area. The trigger was set at 100 nm and hence the maximum load during the force curves was 17.8 μN.

3. Results and discussion

The mechanically polished surface of a typical test coupon contains both transverse and radial sections of M46J carbon fibres embedded in the 977-3 epoxy matrix. FIB milling, with a 30 kV ion beam normal to the surface, has resulted in an eroded and smoother area which is readily visible in the SEM image (Fig. 1 left). Clearly the epoxy matrix has eroded at a greater rate than the carbon fibres, leaving the fibres slightly proud of the matrix. A SPM height image (Fig. 1 right) of several transverse fibres at the boundary of the milled area confirmed the erosion, showing that about 240 nm of the transverse fibre had been milled away. Roughness measurements verified the increased smoothness, with a roughness (root mean square average) of 2 nm for the FIB milled fibre compared to 6 nm for the original mechanically polished surface. Both of these surfaces were nano-indented using the SPM in force volume mode. In general, penetration (10–30 nm) of the tip into the surface was insufficient to obtain reliable data on the modulus of this material. However, the SPM indentations did highlight an issue with the FIB milling. The surface of the FIB milled fibre showed residual indents, of approximately 4–6 nm depth, which were not apparent on the mechanically polished surface