Coatings of Aluminum Oxide and Magnesium Oxide on Carbon Fiber Surfaces

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A specially designed high-vacuum chamber system was used to prepare films on carbon fiber surfaces and to test the effectiveness of these films in preventing fiber oxidation. Changes in surface chemistry were monitored by transfer of the fibers, without air exposure, into an X-ray photoelectron spectrometer (XPS) attached to the chamber. Fibers were coated with magnesium oxide and aluminum oxide by evaporation of the metals in a low oxygen partial pressure. The chamber allowed the fibers to be heated to high temperature under vacuum or in a potentially oxidizing environment. The effect of oxidation was also monitored by exposing the fibers to oxygen ion etching. Oxygen ion etching at ambient temperature was found to generate different functional groups on the fiber surface, which could be clearly distinguished in valence band but not in the core level photoelectron spectra. These functional groups can be removed by heating the fiber to high temperature. When the fibers were coated with either aluminum oxide or magnesium oxide heating was found to cause no significant loss of metal oxide, and the films appear to be potentially protective of the underlying fiber toward heat and oxidation. Wavelength-dispersive X-ray spectroscopy showed that the oxide films appeared uniform and were not cracked on heating. No elemental magnesium or aluminum was found in the films.

Introduction

Carbon–carbon (C–C) composites use carbon fibers to reinforce carbon matrices to produce light and strong materials. The high specific strength and stiffness, low thermal expansion, and the potential ability to withstand high temperatures mean that carbon–carbon composites have important applications in the aerospace industry. For example, they can be used in aircraft brakes, missile heat shields, and nozzles. Unfortunately, carbon materials are readily oxidized at high temperatures, and this represents the most serious problem inhibiting their practical uses. Therefore, good oxidation protective systems are needed in C–C composites in order that full advantage of their structural properties can be taken.

Studies[1–4] have been carried out on some metal and metal oxides coatings on carbon fiber surfaces as a means to improve the protection of the fiber surfaces and to enhance the adhesion between the fiber surfaces and various matrices. Aluminum oxide and magnesium oxide coatings have been studied in carbon–metal composite systems,[1] but we are not aware of any report on the effective use of these coatings for protection of the carbon fiber surface in carbon–carbon composite systems.

In this work, aluminum oxide and magnesium oxide were coated onto carbon fibers in a specially designed high-vacuum chamber system and the surface chemistry studied using X-ray photoelectron spectroscopy (XPS). We find that stable coatings can be achieved, and these coatings are retained on the fiber, even after heating to high temperature.

Experimental Section

The carbon fiber used in this work was Du Pont E-120 untreated and unsized high modulus (120 Msi) pitch-based carbon fiber (Lot 558-1). It was sent to our laboratory directly by the manufacturer, and no pretreatment was performed on the sample before the experiments. The magnesium oxide (MgO) powder sample (Lot WEJG) was purchased from Mallinckrodt, Inc. The magnesium metal ribbon sample (Lot 855834) was purchased from Fisher Scientific Co. The magnesium metal rod sample was obtained from Aldrich. The rod diameter was 6 mm, and its purity was 99.9+%.

Special Vacuum Chamber. A high-vacuum chamber system was specially designed and constructed for investigating the surface chemistry of carbon fibers associated with their use in C–C composites. This high-vacuum chamber system was attached to our ES200B (AEI) XPS spectrometer main chamber through an ultrahigh-vacuum gate valve, which allows us to transfer the sample treated in the high-vacuum chamber directly into the XPS instrument without exposure to the air. Figure 1 shows a schematic diagram of this high-vacuum chamber system. A sample can be treated in various gas atmospheres or at different vacuum levels (up to 10^{-7} Torr) in the chamber. Carbon fiber samples can be heated to over 2000 °C by passing up to 20 A of dc current through the fiber, and the temperature of the fiber can be monitored by an optical pyrometer mounted just outside the viewport of the chamber. The gas phase in the chamber can be analyzed by a quadruple mass spectrometer, and the sample can also be bombarded with an ion gun. The pressure inside the chamber was monitored by a Convectron gauge (low-vacuum range) and a quadruple (1–100 amu) mass spectrometer (VSW Vacuum Analyst) to monitor the high-vacuum range and the partial pressure of evolved gases.

In this work, a bundle of carbon fibers was cut into a length of 3.5 cm, with both ends tied with a piece of aluminum foil. If the sample was going to be heated above 700 °C, but below 1400 °C, the ends were tied with nickel foil. If the temperature was higher than 1400 °C, then tantalum foil would be used. One end of the fiber sample was mounted onto a metal sample holder. The sample was inserted into a insertion block with a long sample probe, and pumped to a vacuum by a rotary pump. Then the sample was transferred into the high-vacuum chamber. The

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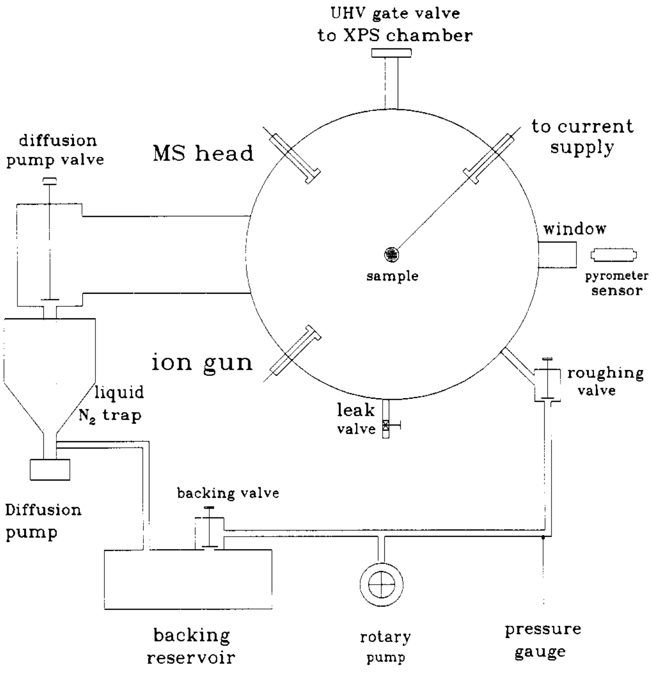

Figure 1. Diagram of the special vacuum chamber.

sample probe and the sample were electrically connected, but they were insulated from the chamber body by Teflon sleeves and Viton O-rings. Samples to be heated had the end of the fiber bundle that was not attached to the sample probe positioned so that it could be connected to a movable metal clamp. This metal clamp was mounted in one of the 2.75-in. ports of the sample chamber on a movable bellows system and could be tightened and moved up and down from outside the chamber. A dc current was supplied to the sample through this metal clamp and the sample probe, and the sample heated to 1300 °C. Samples to be coated with aluminum or magnesium oxide had a piece of aluminum foil cut into small ribbons or magnesium ribbon respectively wrapped around the fiber bundle before the sample probe was inserted into the chamber. Pure oxygen gas was then leaked into the chamber to give an oxygen partial pressure of 1.5×10^{-3} Torr or less before the heating was started. Typical coating times were 1 min for magnesium and 2 min for aluminum. After the sample was heated or treated in any other ways, the chamber was pumped to high vacuum (10^{-7} Torr) and the metal clamp was moved away from the fiber bundle. Then, the UHV gate valve separating the chamber from the XPS instrument was opened, and the sample was transferred into the spectrometer main chamber. The sample was grounded by connecting the sample probe to the system ground. The sample probe passed through a Teflon seal which separated the chamber vacuum system from the instrument vacuum system after the UHV gate valve separating the systems had been opened.

The MgO powder sample was mounted on a metal sample holder using double sided tape. The sample was placed into the insertion block and evacuated for 2 h before transfer into the ES200B instrument for XPS analysis. The magnesium metal ribbon and rod sample were cut to a length of about 4 cm and mounted on the metal sample holder. The ribbon and rod samples were analyzed on the HA100 XPS instrument which had a separate UHV chamber attached to it. After the initial XPS analysis of the ribbon or rod surface, the sample was withdrawn to the separate UHV chamber to carry out argon ion etching (5 kV and 2 mA) using an ultrahigh-purity argon gas source. After the ion etching, the chamber was pumped to UHV, and the sample returned to the spectrometer chamber for surface analysis. The ribbon sample was etched once and analyzed twice, while the rod sample was etched twice and analyzed three times.

Instrumentation. The XPS spectra of the carbon fiber (all spectra in Figures 2–4) and magnesium oxide powder samples (spectra in Figures 6a and 7a) were collected on an AEI (Kratos) ES200B X-ray photoelectron spectrometer, while the XPS spectra of the magnesium metal ribbon and rod (spectra in Figures 6b–f and 7b–f) were collected on a VSW HA100 XPS instrument. The ES200B was operated in the FRR mode (ratio 1:23) with a base pressure of 10^{-9} Torr, and the HA100 also operated in the FRR mode (ratio 1:50) with a base pressure of 10^{-10} Torr. Mg $K\alpha_{1,2}$ X-ray radiation (240 W) was used in both instruments. The energy analyzer resolutions on both spectrometers were of the same order as the X-ray line width (about 0.7 eV). The spectrometer energy scales were calibrated by using a copper sample.[5] The curve fitting of the XPS C 1s and O 1s core regions spectra was carried out using a nonlinear least-squares curve-fitting program with a Gaussian/Lorentzian function.[6,7] The C 1s binding energy of graphitic peak was taken as 284.6 eV for calibration purposes.

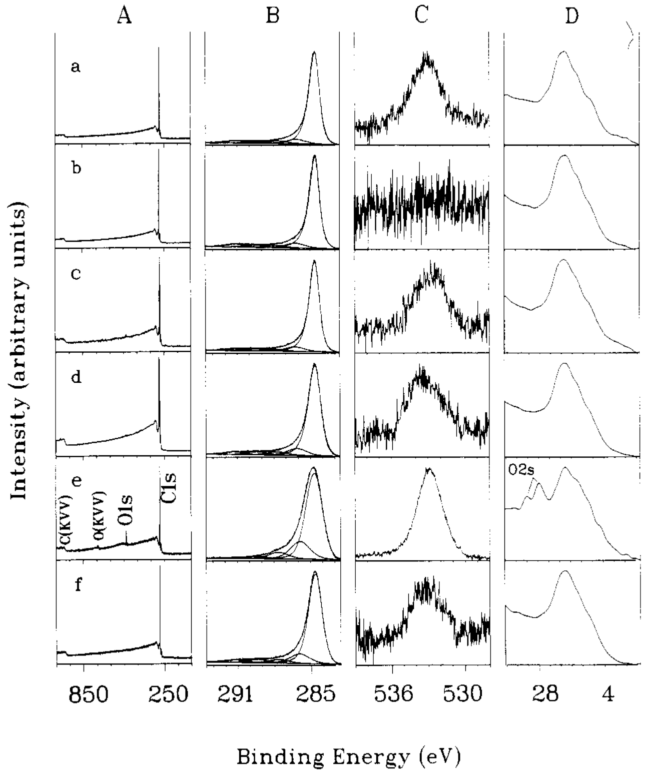

Figure 2. XPS spectra of E120 carbon fibers treated in the special vacuum chamber. (A) Overall scan. (B) C 1s core region. (C) O 1s core region. (D) Valence band. (a) Untreated; (b) 5 min at 1300 °C at 10^{-7} Torr; (c) 10 min in 10^{-3} Torr of pure O_2; (d) O_2 ion-etched for 5 min at 1300 °C; (e) O_2 ion-etched for 5 min at room temperature; (f) as (e), but heated to 1300 °C for 5 min.

The electron microprobe used in this study was an ARL SEM-Q microprobe with scanning electron microscopy (SEM), energy-dispersive (EDX) and wavelength-dispersive (WDX) X-ray analysis capabilities. The typical pressure in the analysis chamber was 1×10^{-5} Torr. A synthetic OV95 crystal was used for wavelength-dispersive X-ray analysis of carbon, oxygen, and nitrogen present on the fibers.

X-ray diffraction (XRD) studies were carried out with a Scintag XDS 2000 instrument. The X-ray radiation wavelength used was Cu $K\alpha_1$ (0.154059 nm) with an X-ray power of 1800 W. The data were collected using the normal step-scanning mode with a step size of 0.02°. The samples were normally mounted in a Mylar tray.

Results and Discussion

Samples were examined after treatment by XPS *without removal* from the vacuum system. Figures 2 and 3,

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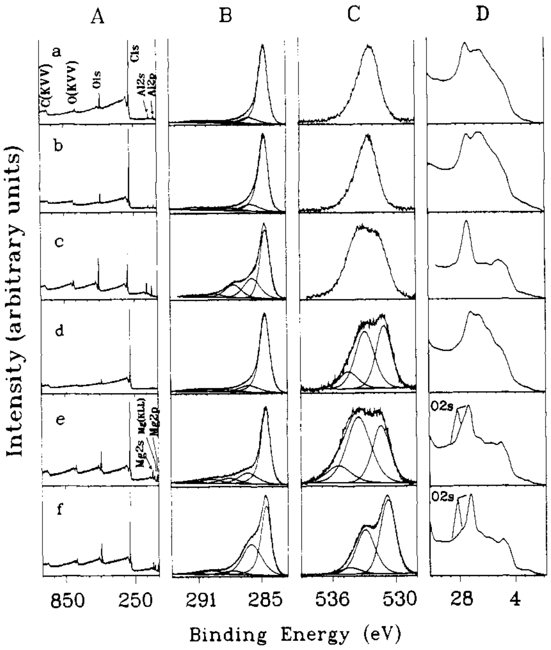

Figure 3. XPS spectra of E120 carbon fibers coated with oxidized aluminum and oxidized magnesium thin films. (A) Overall scan. (B) C 1s core region. (C) O 1s core region. (D) Valence band. (a) Coated with oxidized aluminum in ~10^{-4} Torr of pure O_2 at 1300 °C for 2 min; (b) as (a), but heated to 1300 °C for 20 min at 10^{-7} Torr of pressure; (c) as (a) but using 1.5×10^{-3} Torr of pure O_2; (d) coated with oxidized magnesium in 10^{-3} Torr of pure O_2 at 1300 °C for 2 min; (e) as (d), but using more magnesium metal; (f) as (e) but heated to 1300 °C for 10 min at 10^{-7} Torr of pressure.

columns A–D, show XPS spectra for the overall scan, C 1s core region, O 1s core region, and valence band, respectively. All the valence band spectra in Figures 2 and 3 were smoothed by using a quadratic/cubic central smooth with 9-point (1.5 eV) width and 100 repeats.[6]

The changes in the partial pressure of various evolved gases in the special vacuum chamber was monitored with time as the fibers were heated in the vacuum system at 1300 °C. Gases with fragments at m/e 16 (O^+), 18 (H_2O^+), 28 (CO^+ and/or N_2^+), 32 (O_2^+), 41 and 43 (hydrocarbon), and 44 (CO_2) were detected in all cases. These gases were residual gases in the vacuum system of the special chamber, together with gases evolved from decomposition on the heated fiber surface. Changes in the partial pressure of these gases with heating time did provide useful comparative information.

All the samples discussed below were removed from the vacuum system and studied by X-ray diffraction which gave very similar spectra typical of those previously reported[8] for E120 fibers. These studies showed that the bulk of the fibers were unaltered by heat treatment, oxygen ion etching, or coating with oxidized aluminum or magnesium films.

Heat-Treated Carbon Fibers. The C 1s spectra in Figure 2 were all curve-fitted using five-component peaks. It is known that certain types of functional groups exist on carbon fiber surfaces, even on the fibers that are unsized or untreated. Each functional group gives rise to a signal in the XPS spectrum with a particular range of binding energies[8–14] (and references therein). There are four types of oxygen-containing functional groups on the fiber surfaces which we have named oxide 1 to oxide 4, with their C 1s component peaks having chemical shifts from the main graphitic peak of about 1.5, 3.0, 4.5, and 6.1 eV, respectively. Oxide 1 contains hydroxide-type (C–OH) and ether-type (C–O–C) groups, and oxide 2 carbonyl-type (C=O) groups. Oxide 3 corresponds to the C 1s peak of carboxyl (COOH) or ester (COOR) types of groups. Oxide 4 probably corresponds to $-CO_3^-$ type of groups, and the π–π^* shakeup satellite also lies in this range. Oxide 1 and oxide 2 were the principal functional groups on the fiber surfaces.

Figure 2a shows the spectra of the untreated E120 carbon fiber sample. The overall scan (Figure 2a,A) showed an intense C 1s peak at 284.6 eV and some weak C(KVV) Auger features at about 993 eV. The C 1s region (Figure 2a,B) showed a typical narrow graphitic C 1s peak at 284.6 eV with an exponential tail on the higher binding energy side and a very small amount of oxide 1 component. The O 1s region (Figure 2a,C) showed a very weak peak at about 533.3 eV, even though the overall scan hardly showed any oxygen signal. The valence bond (Figure 2a,D) showed an intense C 2s peak at about 18 eV and a very weak O 2s shoulder feature at about 24 eV. Other features below 16 eV were the combined contributions from C 2p and O 2p. The oxygen content might be due to some very small amount adsorbed oxygen gas and moisture on the fiber surface.

Figure 2b shows the spectra of the fiber sample heated to 1300 °C for 5 min at 10^{-7} Torr in the high-vacuum chamber. The XPS spectra showed that this sample has a surface chemistry that is very similar to that of the untreated fiber sample, except that the very small amount of adsorbed oxygen on the untreated fiber was removed by heating, as shown in the O 1s region (Figure 2b,C) and the valence band (Figure 2b,D).

Figure 2c shows the spectra of a carbon fiber sample after exposure to a partial pressure of 10^{-3} Torr of pure oxygen gas inside the chamber for 10 min. The XPS spectra indicated that there is little change in the surface chemistry of this sample compared with the untreated sample, other than a small increase in the oxygen content as shown in the overall scan (Figure 2c,A), O 1s region (Figure 2c,C) and valence band (Figure 2c,D) spectra.

Figure 2d shows the spectra of the sample bombarded with an O_2 ion beam (6 kV and 2 mA) for 5 min while the sample was heated to 1300 °C under a partial pressure of oxygen of 10^{-3} Torr. The XPS spectra are similar to those of the untreated fiber.

Oxygen etching at ambient temperatures causes substantial oxidation, as seen in Figure 2e, which shows the results for a sample bombarded with an O_2 ion beam (6 kV, 2 mA) under 10^{-3} Torr oxygen atmosphere. Besides showing a very intense C 1s peak at 284.6 eV and weak C(KVV) Auger features at about 993 eV, the overall scan spectra (Figure 2e,A) also showed a fairly intense O 1s peak at 533 eV and some weak O(KVV) Auger features at about 745 eV. The C 1s spectrum (Figure 2(e)–B) shows

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Table 1. Intensity Ratios and Approximate Atomic Ratios and Thickness Values[a]

	% C 1s as graphitic carbon (from C 1s curve fitting)	C 1s (graphitic)/ Mg or Al 2p intensity ratio	O 1s/Mg or Al 2p intensity ratio	oxygen/Mg or Al atomic ratio (approx)	oxide thickness based upon uniform surface layer (Å)
E120 fiber coated with oxidized Al					
(i) in ~10^{-4} Torr pure O_2 at 1300 °C for 2 min	79.5	32.0	3.54	1.16	0.9
(ii) as (i) but then heated to 1300 °C for 20 min	75.0	19.3	3.91	1.28	1.4
(iii) as (i) but using 1.5 × 10^{-3} Torr pure O_2	52.0	2.17	2.71	0.90	8.8
E120 fiber coated with oxidized Mg					
(i) in 10^{-3} Torr pure O_2 at 1300 °C for 2 min	65.1	23.8	6.19	1.30	1.4
(ii) as (i) but using more Mg metal	55.2	3.74	3.99	0.84	7.7
(iii) as (ii) but then heated to 1300 °C for 10 min	40.0	3.41	4.06	0.85	8.4

[a] The inelastic mean free paths of used in the calculations above were calculated using the Seah and Dench equations (Seah, M. P.; Dench, W. A. *Sur. Interface Anal.* **1979**, *1*, 2).

some broadening of the main graphitic peak together with an increase in the amount of oxide 1 and oxide 2. The O 1s spectrum (Figure 2e–C) also showed a dramatic increase in the intensity of the peak at 533 eV compared to the other spectra in Figure 2C. However, the most interesting spectrum is the valence band (Figure 2e,D), which has an intense C 2s feature at about 18 eV and two well-separated intense O 2s peaks at 28 and 32 eV corresponding to hydroxide and epoxide functionality respectively. The O 1s spectrum did not show two separated features since these two functionalities occur at the same binding energy. Our previous work[8,11-13] reported that the XPS valence band spectra are often more sensitive than the core regions to the chemical changes that occur on carbon fiber surfaces. Clearly, O_2 ion beam bombardment of the carbon fiber surface at ambient temperature generated a significant amount of hydroxide-type and epoxide-type functionality.

These functional groups were removed from the surface of the O_2 ion-etched fiber sample by heating the sample to high temperature again. Figure 2f shows the spectra of the same sample as in Figure 2e after heating to 1300 °C for 5 min under a vacuum of 10^{-7} Torr. Figure 2f gave spectra very similar to those in Figure 2d. It is thus not surprising that the O_2 ion etching of the fiber at 1300 °C did not form any surface functionality, since any such functionality would be lost on heating.

The variation of evolved gases monitored by mass spectrometry indicated an initial rise in the partial pressure of the peak at $m/e = 18$ (H_2O^+) during the first minute of heating when this peak had generally twice the partial pressure of other components in the spectrum (except for residual nitrogen in the vacuum). This peak had the highest partial pressure in samples that had been previously O_2 ion etched. This result is compatible with the XPS data, since the etched samples had significant surface functionality which was lost on heating. XPS data suggested that the surface functionality caused by etching contained substantial amounts of hydroxide-type functionality, which might we expected to yield water on decomposition.

Metal Oxide Coated Carbon Fibers. Comparison of the overall spectrum of the untreated carbon fiber (Figure 2a,A) with that of the fiber coated with magnesium or aluminum oxide (Figure 3A) clearly indicates the presence of these oxide coatings on the fiber. Detailed regions are shown in Figures 3 and 4. The thickness of the coatings on the fibers depends upon the conditions used. In this study thin and very thin films were prepared, and their surface topology and thickness were estimated by XPS and X-ray emission spectroscopy.

The XPS relative areas were used to estimate thickness. The films can be seen to be thin because the underlying C 1s peak with its characteristic graphitic peak shape could be identified in all the XPS studies of the fibers. The percentage of the C 1s region corresponding to graphitic carbon (obtained from the C 1s curve fit) decreased as the metal oxide coating thickness increased (as expected). The area ratio of this graphitic carbon and the Mg or Al 2p peak from the oxide coating could be used to estimate an *approximate* thickness for the oxide film by assuming a uniform layer of oxide. Table 1 gives values for the estimated film thickness. It is important to remember that these values represent an *average* for the whole sample of 3000 fibers. Another estimate of the film thickness is the relative intensity of the O 2s feature from the metal oxide layer in the valence band spectrum (Figure 3D), which increases with film thickness. Two types of film can be identified. Thin films with a thickness estimated at around 1 Å are almost certainly patchy in the sense that not all the fibers may be coated, or the coating may be patchy with uncoated fibers exposed. Thicker films with a thickness estimated at around 8 Å probably have no exposed fiber. Table 1 also lists the C 1s/metal atom atomic ratio based upon the highly approximate assumption that the surface is completely homogeneous over the depth of sample being studied. Thus if the surface were entirely

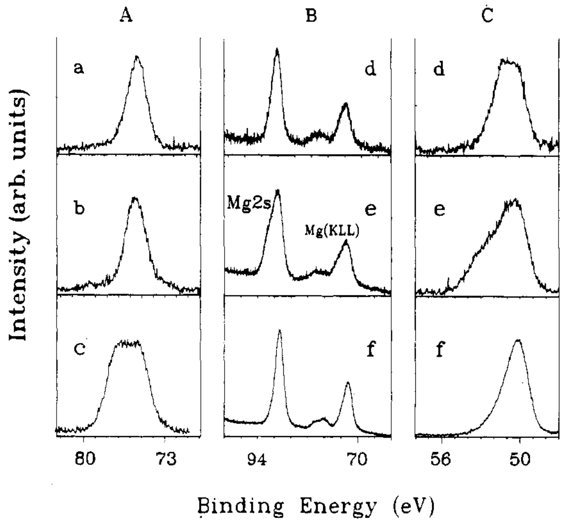

Figure 4. XPS spectra of E120 carbon fibers coated with oxidized aluminum and oxidized magnesium thin films. (A) Al 2p core region. (B) Mg 2s and Mg($KL_{23}L_{23}$) Auger regions. (C) Mg 2p. (a) Coated with oxidized aluminum in ~10^{-4} Torr of pure O_2 at 1300 °C for 2 min; (b) as (a), but heated to 1300 °C for 20 min at 10^{-7} Torr of pressure; (c) as (a) but using 1.5 × 10^{-3} Torr of pure O_2; (d) coated with oxidized magnesium in 10^{-3} Torr of pure O_2 at 1300 °C for 2 min; (e) as (d) but using more magnesium metal; (f) as (e), but heated to 1300 °C for 10 min at 10^{-7} Torr of pressure.

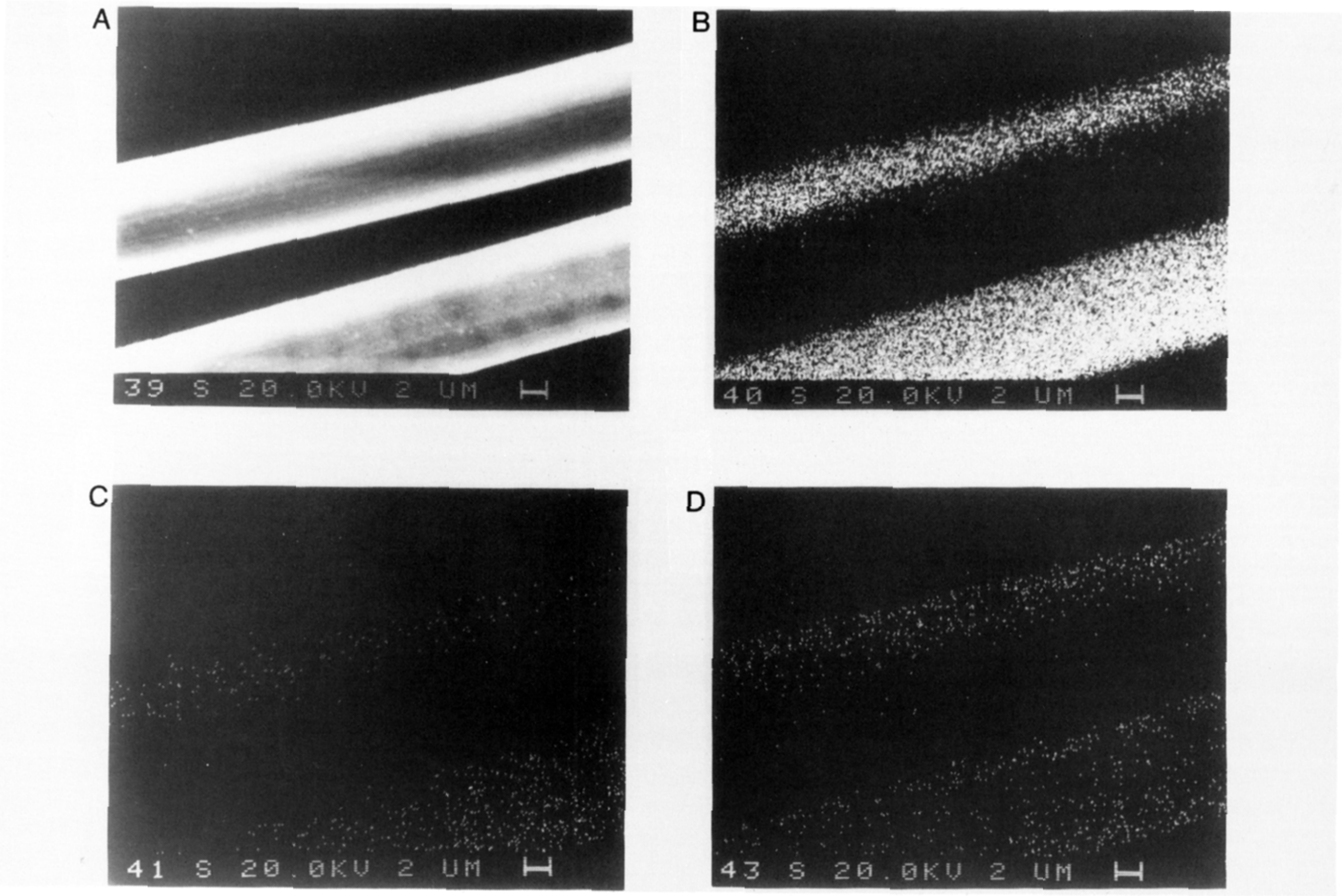

Figure 5. Scanning electron microscopy and wavelength-dispersive X-ray emission maps of E120 carbon fibers coated with oxidized magnesium in 10^{-4} Torr of oxygen at 1300 °C for 2 min. Note the 2-μm scale marker on all the pictures. (A) SEM micrograph. X-ray *micrographs (B) for carbon, (C) for oxygen, and (D) for magnesium.*

Al_2O_3 this ratio would be 1.5, and if the surface were entirely MgO this ratio would be 1.0. The observed ratios for aluminum oxide coated fibers are higher than magnesium oxide coated fibers, as expected, and the values observed are reasonable bearing in mind the extremely approximate nature of the model.

Wavelength-dispersive X-ray emission spectra in the aluminum or magnesium X-ray region were used to give an idea of the surface topography of the film as well as the relative amount of a particular element. This method gives a map of the surface with an intensity proportional to the concentration of the atom whose X-ray emission is being mapped. The most intense and most uniform X-ray emission maps (e.g., Figure 5) were obtained for the thicker films (around 8 Å).

Aluminum Oxide Coated Fibers. The overall spectrum (Figure 3a,A) of the carbon fiber sample coated with a thinner aluminum oxide thin film clearly showed a new intense O 1s feature at 532 eV and weaker features corresponding to O(KVV) Auger, Al 2s, and Al 2p at about 745, 120, and 75 eV, respectively. The O 1s spectrum (Figure 3a,C) has a very intense peak at about 532.2 eV, and the valence band (Figure 3a,D) showed an intense O 2s peak at 24 eV. However, the C 1s (Figure 3a,B) spectra did not show much difference than that of the untreated carbon fiber (Figure 2a,B), which indicated that the oxygen on the carbon fiber surface was not bonded directly to the graphitic carbon atoms. The sharp and narrow O 2s peak shape in the valence band spectrum is consistent with that of oxidized aluminum.[15] We have shown[15] that aluminum oxides can be distinguished by their valence band spectra especially in the region at a binding energy below 16 eV, but the overlap of the carbon features with those of the oxidized aluminum make it difficult to make any clear distinction between the type of oxidized aluminum for the thin coatings. The spectrum of the thicker coating (Figure 3c,D) indicates oxidized aluminum in the form of γ-Al_2O_3, the spectrum being essentially superimposible with our previously reported data for this compound.[15] The broader C 1s, C 1s, and Al 2p regions are similar to that found for thicker magnesium oxide films, and this is discussed in more detail below.

After the fiber sample coated with aluminum oxide was moved back to the high vacuum chamber and heated to 130 °C at 10^{-7} Torr vacuum for 10 min, the XPS data (Figure 3b) did not show any changes except that the oxygen signals are slightly lower than those before the heating (compare Figure 3b with Fiber 3a). This is in contrast to the fiber sample that was O_2 ion etched at ambient temperature, which lost all its functional groups on heating (see Figure 2e,f). The similarity in the Al 2p spectra of the thinly coated sample (peak at 75.3 eV) before and after the heating (Figure 4a,A and 4b,B), provide further evidence that the oxidized aluminum on the fiber surface was not changed by the heating.

Magnesium Oxide Coated Fibers. Figure 3, parts d and e, show the XPS data for the fiber sample coated with a magnesium oxide film to give a thin and thicker layer, respectively. The extra thickness was achieved by increasing the amount of magnesium metal used in the

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evaporation process. The valence band spectra show features similar to the thinner and thicker aluminum oxide films. The valence band of the thicker films (Figure 3e,D) and O 1s region (Figure 3e,C) both show substantial amounts of oxygen. The O 1s region, as in the thicker aluminum oxide film case, shows multiple features. Thus there is evidence in Figure 3e for three types of oxygen feature (this is especially obvious in the O 1s region (Figure 3e,C), but this result will be discussed in the section below concerned with variations with film thickness. In the thicker film case the C 1s spectrum (Figure 3e,B) shows more oxidation than do the less-coated aluminum oxide and magnesium oxide samples, but again this will be discussed in the section concerned with variation s with film thickness. All the magnesium oxide films show three different types of oxygen in contrast to the thinner aluminum oxide films, where only one type of oxygen is seen. When the thicker magnesium oxide coated sample was heated to 1300 °C for 10 min its C 1s (Figure 3f,B), O 1s (Figure 3f,C), and valence band (Figure 3-f-D) spectra all showed changes, but the amount of oxygen on the surface remained much the same (as indicated by comparison of the O 1s to C 1s intensity ratios in Table 1). The Mg 2p (Figure 4e,C) and Figure 4f,C) spectra and the Mg 2s and Mg ($KL_{23}L_{23}$) Auger spectra (Figure 4e,B and 4f,B) before and after the heating also showed changes in the Mg regions on heating. The valence band spectra of the thicker films (Figures 3e,D and 3f,D) show strong similarities with the valence band of MgO, though not as close as the resemblance of the valence band of thicker film of aluminum oxide to γ-Al_2O_3. This is reasonable bearing in mind that the photoelectric cross sections of aluminum in the valence band are about twice as high as those of magnesium, so that the former will be a more dominant contributor to the spectrum than the latter. We were able to eliminate the possibility that magnesium metal formed on the fiber surface on heating (possibly resulting from a reaction between the magnesium oxide and carbon) by examination of the Mg ($KL_{23}L_{23}$) region, and this study will be discussed further below. Figure 5 shows the SEM and wavelength-dispersive X-ray emission spectra for carbon, magnesium, and oxygen for the magnesium oxide coated fibers after heating. The SEM indicates (within the resolution of the instrument) that the coating does not crack on heating, and the X-ray maps provide further evidence for the uniformity of the coating. We find that fibers coated with 10^{-3} Torr of partial pressure of oxygen seem to have a less uniform film than those coated with an approximately 10^{-4} Torr of partial pressure of oxygen (shown in Figure 5). There appear to be some "clumps" of magnesium oxide at the higher oxygen pressure. SEM and wavelength-dispersive X-ray emission studies similar to those described in Figure 5 were found for the oxidized aluminum coated fibers.

The magnesium oxide coated fibers showed a much lower water partial pressure after 1 min of heating at 1300 °C than the oxygen ion etched uncoated fibers, and the water partial pressure was less than that of most of the residual gases.

Variation Spectral Appearance with Film Thickness. We have repeated these experiments several times and have gone on to cover the fibers that were coated with aluminum or magnesium oxide with phenolic resin and have then subsequently carbonized this resin. This has enabled us to prepare a "microcomposite" inside the special vacuum chamber. We will discuss these results in a separate publication.[16] During these studies we prepared a number of coated fiber samples and were thus able to see the spectral variations that occur with repeating the sample coating experiment. We have also studied other coatings on carbon fiber surfaces including silicon nitride films deposited by chemical vapor deposition (CVD).[17] A common feature of all these studies is that as the film thickness increases (possibly irregularly in the form of thicker islands), there tends to be an increase in the width of the XPS spectra. Thus for the thicker coatings the Al 2p and Mg 2p regions are broadened (Figure 4). Since we know that the Al 2p region shows little variation in binding energy with the type of oxidized aluminum,[15] causes other than chemical differences for this broadening seem likely. We have performed a detailed study of the variations in spectral appearance with sample bias for the fiber coated with silicon nitride,[17] which clearly shows that differential sample charging plays a role in this broadening. We report below the results of a study that allowed us to eliminate the possibility that the narrowing of the Mg spectral regions on heating corresponded to chemical changes.

Possible Fiber Oxidation by the Oxidized Metal Films. A further question of concern to us was whether the oxidized aluminum or magnesium coating on the fibers reacted with the carbon fiber. For example, attempts to intercalate carbon fibers with aluminum chloride followed by subsequent oxidation have led to complete loss of carbon following heating in air.[18] In our case the deposited aluminum oxide films appear to cause little carbon oxidation following deposition and do not appear to cause substantial oxidation of the carbon following heating in vacuum. Figure 3 shows significant graphitic carbon fiber for both thicker and thinner films. Since the experiment probes *both* the surface of the coated fiber, and the fiber–oxide coating interface the spectra represent an addition of the spectroscopic features at both interfaces. The total amount of oxygen is seen to be consistent with the amount of metal oxide (Table 1 and the discussion above). The surface of the oxide coating would be expected to contain oxide and some residual hydrocarbon. The fiber–oxide interface would be expected to contain oxide and carbon. The higher chemically shifted species in the thicker films are clearly visible on the core regions. If the higher chemically shifted species in the C 1s region are due to differential charging on the C 1s region for surface hydrocarbons, then no oxidation of carbon would have been seen. Of course it is not possible to rule any oxidation of carbon out. It is however reasonable to say that the results are consistent with a situation where the carbon is not oxidized. Oxidation of the carbon would lead to magnesium metal formation. If the metal were formed then the need for the metal to diffuse though a magnesium oxide film into a substantial oxygen partial pressure (10^{-3} Torr) would be likely to inhibit its formation and if formed lead to oxidation of the metal. However, if significant reaction with the carbon were to occur under these conditions, then significant loss of carbon in the form of CO would be anticipated, with the possible loss of adhesion of the oxide film. Mass spectrometric studies of the magnesium oxide coated fibers during the 20-min heating

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[16] Xie, Y.; Sherwood, P. M. A., to be published.

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[18] McQuillan, B.; Reynolds, G. H., *Extended Abstracts of the 1986 MRS Symposium on Graphite Intercalation Compounds*, Dresselhaus, M. S., Dresselhaus, G., Solin, S. A. Eds.; Boston, 1986; p 138.

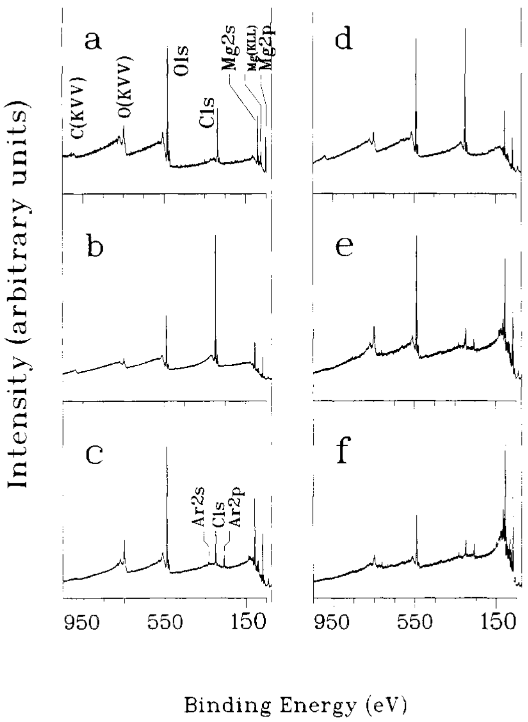

Figure 6. XPS overall scan spectra. (a) MgO powder; (b) magnesium metal ribbon; (c) as (b) but argon ion etched for 1 h; (d) magnesium metal rod; (e) as (d) but argon is etched for 1 h; (f) as (d) but argon ion etched for 2 h.

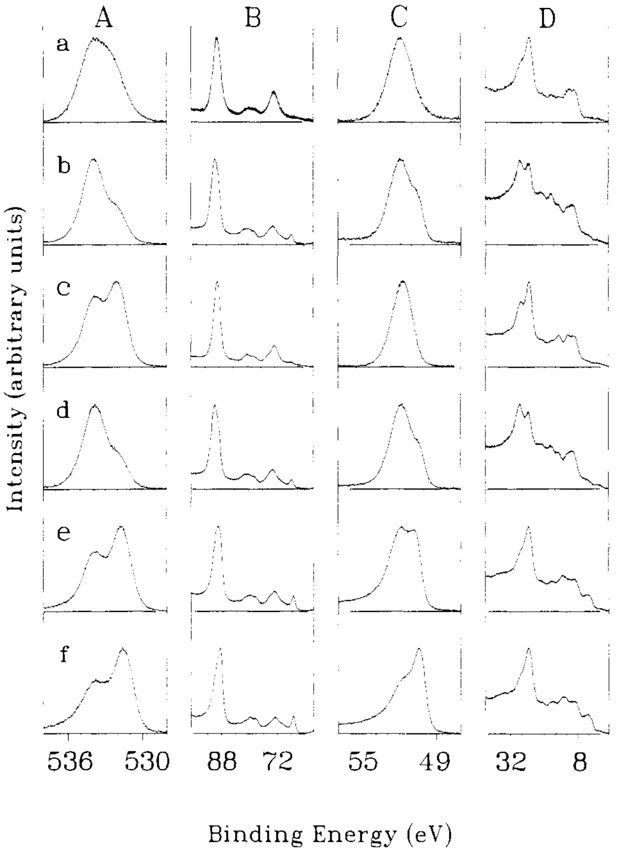

Figure 7. XPS spectra of MgO powder, magnesium metal ribbon and rod. (A) O 1s core region. (B) Mg 2s and Mg($KL_{23}L_{23}$) Auger regions. (C) Mg 2p region. (D) Valence band. (a) MgO powder; (b) magnesium metal ribbon; (c) as (b) but argon ion etched for 1 h; (d) magnesium metal rod; (e) as (d) but argon ion etched for 1 h; (f) as (d) but argon ion etched for 2 h.

period at 1300 °C showed a CO(+N_2) partial pressure that never exceeded 5×10^{-7} Torr. It is important to note that we find no evidence of any metal formation resulting from oxide reduction in either the core or valence band XPS data for aluminum or magnesium oxide films. This observation now discussed in more detail.

Magnesium Metal and Compound Studies. We performed a number of studies to try to understand the variations that we observed in the magnesium XPS data following heating of the oxidized magnesium coated fibers. These studies included XPS studies of magnesium oxide (MgO) powder, magnesium metal ribbon, and magnesium metal rod samples. Figure 6 shows the overall scan spectra of the MgO powder, magnesium metal ribbon, and rod samples. Figure 7, columns A–D, shows XPS spectra for the O 1s, Mg 2s, and Mg($KL_{23}L_{23}$) Auger, Mg 2p, and valence band spectra, respectively.

The XPS spectra of the MgO powder sample ("a" spectra in Figures 6 and 7) gave the expected spectrum for a powder sample showing some carbon and adsorbed water contamination. An O 1s oxide feature was found at 530 eV, with a corresponding O 2s feature at about 24 eV. The feature at 532 eV in the O 1s spectrum (Figure 7a,A) and the feature at 28 eV in the valence band (Figure 7a,D) were due to the oxygen signals of chemisorbed moisture on the powder surface. The Mg 2p, Mg 2s, and Mg($KL_{23}L_{23}$) features of MgO appeared at 50.8, 87.2, and 71.2 eV, respectively.

The magnesium metal ribbon and rod samples had even more chemisorbed moisture (as evidenced by O 1s core region spectra (Figure 7b,A and Figure 7d,A) and valence band spectra (Figure 7b,D and Figure 7d,D) and much more carbon contamination (as evidenced by overall scan spectra (Figure 6b and Figure 6d on their surfaces than the MgO powder sample. As expected, both samples showed considerable surface magnesium oxide. The O 1s peak at 529.8 eV in Figure 7b,A and Figure 7d,A, and the O 2s peak at 24 eV in Figure 7b,D and Figure 7d,D were the oxide signals from the MgO. The Mg 2p peak at 50.8 eV in Figure 7b,C and Figure 7d,C, the Mg 2s peak at 87.2 eV and the Mg($KL_{23}L_{23}$) Auger peak at 71.2 eV in Figure 7b,B and Figure 7d,B were the magnesium signals from the MgO. The discrete Auger peak at 68.8 eV in both Figure 7b,B and Figure 7d,B is indicative of metallic magnesium. The presence of metallic magnesium was also confirmed by the clear shoulder feature at 49.4 eV in Figure 7b,C and Figure 7d,C and the shoulder feature at about 4 eV in the valence band spectra (Figure 7b,D and 7d,D). The Mg 2s spectra (Figure 7b,B and 7d,B) also showed a very weak shoulder feature at 87.0 eV, which was due to metal magnesium. *It is the absence of the metal feature in the $MgK_{23}K_{23}$ Auger spectrum of the magnesium oxide coated fiber after heating that allows us to discount the formation of magnesium metal on the fiber surface.* The spectral narrowing in Figure 4C does not correspond to a shift in peak position but rather gives a single peak with a position and width similar to that of MgO (see Figure 7C) with a Mg 2p binding energy of 50.5 eV. The high binding energy shoulder on the peak Figure 4e,C at about 53 eV is at far too high a binding energy to correspond to any known magnesium oxygen compound. We thus conclude that this peak is due to differential charging, probably arising from some locally thicker islanding of the MgO film. This thicker island formation may be lost on heating leading to an elimination in differential charging and thus the expected MgO peak width and position. See the discussion of the variation of spectral appearance with film thickness above.

Figure 7 also shows the effect of argon ion etching of the metal ribbon (Figure 7c) and rod (Figure 7e,f). In the case of the ribbon further oxidation seemed to occur, presumably due to underlying oxidation throughout the ribbon. Etching of the rod caused an increase in the intensity of the metal features which slowly increased as the etch time increase from 1 h (Figure 7e) to 2 h (Figure 7f). One also notes signals due to implanted argon in the etched samples (Figure 6c,e,f). Etching leads to reduction in the higher binding energy O 1s and O 2s features associated with chemisorbed water and/or the presence of hydroxide.

Conclusion

This work shows that the approach of preparing potentially oxidation inhibiting coatings in a vacuum system attached to a surface analytical instrument allows the coatings to be studied and their effectiveness to be monitored, within an integrated vacuum system. The simple oxygen ion etching process provides a useful test of oxidation conditions, and *in situ* heating provides an effective means for investigating the stability of the fiber and coatings at typical composite operating conditions. Oxygen ion etching is seen to oxidize carbon fiber surfaces, with the oxygen functionality so formed being removed by heating to temperatures of 1300 °C.

Aluminum and magnesium oxides can be easily coated onto the carbon fiber surface in the specially designed vacuum chamber, and the coating can be controlled so that no aluminum or magnesium metal is formed on the fiber surface. These coatings cannot be removed by heating the fiber to high temperature, and they appear stable to cracking after such treatment. We believe that they may prove useful in protecting carbon fiber surfaces in carbon–carbon composites operating at high temperatures.

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