CHARACTERIZATION OF ELECTRODE DEPOSITS FORMED DURING THE CARBON-ARC EVAPORATION OF GRAPHITE

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INTRODUCTION

Since the discovery of the bulk synthesis of fullerenes by the resistive heating of graphite[1], there has been a great deal of interest in the mechanism of formation and the characterization of the materials formed. It is now well established that the generation of a carbon arc across two graphite rods results in the formation of a number of different materials. The soot produced contains C_{60}, C_{70}, higher fullerenes[1] and disordered carbon, while the deposit, which grows on the cathode, has been shown to contain nanotubes[2]. This cathode deposit is graphitic in nature[3] and contains concentric layers of highly ordered sheets which are aligned with the basal planes parallel to the rod axis. High yields of nanotubes have been found within these layers when the arcing occurs in He pressures of 300-500 torr[4].

In experiments to synthesise nanotubes in a carbon coating unit we have observed the formation of a small anode deposit. This paper discusses the characterization of this deposit.

EXPERIMENTAL

The carbon arc experiments were conducted in an Edwards 12 E 6/512 coating unit in a helium atmosphere. High purity graphite rods were used. The cathode was sharpened to a point and the anode was polished flat The rods were initially just touching and a voltage (10-30 V) applied across them. Once arcing was initiated, the voltage was decreased so that the current was constant at approximately 60 A. Since the instrument has no means of controlling the separation of the rods, the run time was usually of the order of 5 min.

Raman spectra were recorded using a Spex 1401 double monochromator fitted with a Spectr Acq spectrometer computer control system. The sample illumination and collection system was a BGSC microscope system. The spectra were curve resolved using Microcal 'Origin' software to obtain peak widths and integrated areas.

RESULTS AND DISCUSSION

A number of different atmospheres, He, Ar and N_2, at different pressures were used for the carbon arc experiments. In agreement with previous researchers[4], helium pressures of 300 and 500 torr were found to give the most stable arc. This is thought to be because the most effective momentum transfer during a collision between carbon species and a third molecule, is when the third molecule is monatomic and close in mass to the carbon species (probably C^+), i.e. He.

The distribution of carbon between the three products formed during arcing, i.e. cathode deposit, anode deposit, and soot, was approximately 40%, 10% and 50%, respectively. Both the cathode and anode deposits had a silver appearance on their outsides and the insides were a matt black.

Raman microprobe studies indicated that both the cathode and the anode deposit were highly ordered. Two main bands were apparent, the D band (indicative of disorder) at approximately 1360 cm^{-1} and the G band (indicative of graphitic order) at approximately 1580 cm^{-1}[5]. Thus, the intensity ratio I_D/I_G gives an indication of the order within the deposit structure. These are listed in Table 1. The inside of the deposits were more graphitic than the outside which probably reflects the higher temperature experienced on the inside of the deposits as compared to the outside.

Polarised optical microscopy indicated that both deposits were highly anisotropic with the basal planes aligned parallel to the rod axes. This has been observed previously for the cathode deposit[3] and is considered to arise from the thermoionic current, "electron wind", produced in the DC arc.

Nanotubes were detected by TEM in both the anode and the cathode deposits (see Figure 1(a)) although they appeared to be far less abundant in the anode deposit. The nanotubes in the cathode deposit were of the order of 10 nm in diameter and 1μm in length. The nanotubes in the anode deposit appeared to be much shorter.

Scanning electron microscopic examination of the anode deposit indicated that the silvery material on the outside of the deposit consisted of close-packed spherical surface structures as shown in Figure 1(b). In contrast, tubular carbon structures were found on the inside of the deposit as shown in Figure 1(c). Both the spherical structures and the "carbon spaghetti" are reminiscent of the cathode deposit studied by SEM[6].

During the carbon arc process it is thought that low molar mass cations (C_n^+, $n < 3$) will migrate to the cathode resulting in the observed isotopic enrichment in ^{12}C of this deposit[3]. Similarly, small carbon species which reside within the arc long enough, collide with other species and grow, ultimately to form fullerenes isotopically enriched in ^{13}C. The observation of a deposit growing on the anode during the carbon arc process necessarily implies the presence of anionic carbon species. Such species are expected to be far less stable than their positively charged counterparts and therefore it is not surprising that the anode deposit is not formed in large amounts. We suspect that this deposit has not been detected previously because in most arcing experiments the cathode deposit is allowed to grow extremely large so that it covers the end of the anode. The question arises as to whether the anode deposit is formed from small or large C_n^- fragments. Isotopic measurements are listed in Table 1. It is clear that the anode deposit is also depleted in ^{13}C, indicating that, like the cathode deposit, it grows from small carbon species.

CONCLUSIONS

During the carbon arc evaporation of graphite deposits are formed on both the anode and the cathode. Characterization of the anode deposit indicates that it is very similar in composition and structure as the cathode deposit. The formation of a deposit on the anode implies the presence of C_n^- fragments within the arc. These are expected to be much less stable than the C_n^+ fragments

which is corroborated by the fact that approximately four times as much material is deposited on the cathode compared to the anode. Both the anode and the cathode are depleted in ^{13}C, relative to the graphite rod, indicating that they are formed from C_n^- and C_n^+ ($n < 3$) respectively.

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Table1: Raman band intensity ratios and ^{13}C contents for carbon materials

Material	I_D/I_G	Δ_{GR} ^{13}C (‰ PDB scale)*
Graphite rod	0.49*	0
Cathode deposit		-1.82
Outside	0.88	
Inside	0.27	
Anode deposit		-1.26
Outside	0.33	
Inside	0.25	
Soot	1.61*	+3.09

*Referenced to the graphite rod for 500 torr He run. *From ref. 3.
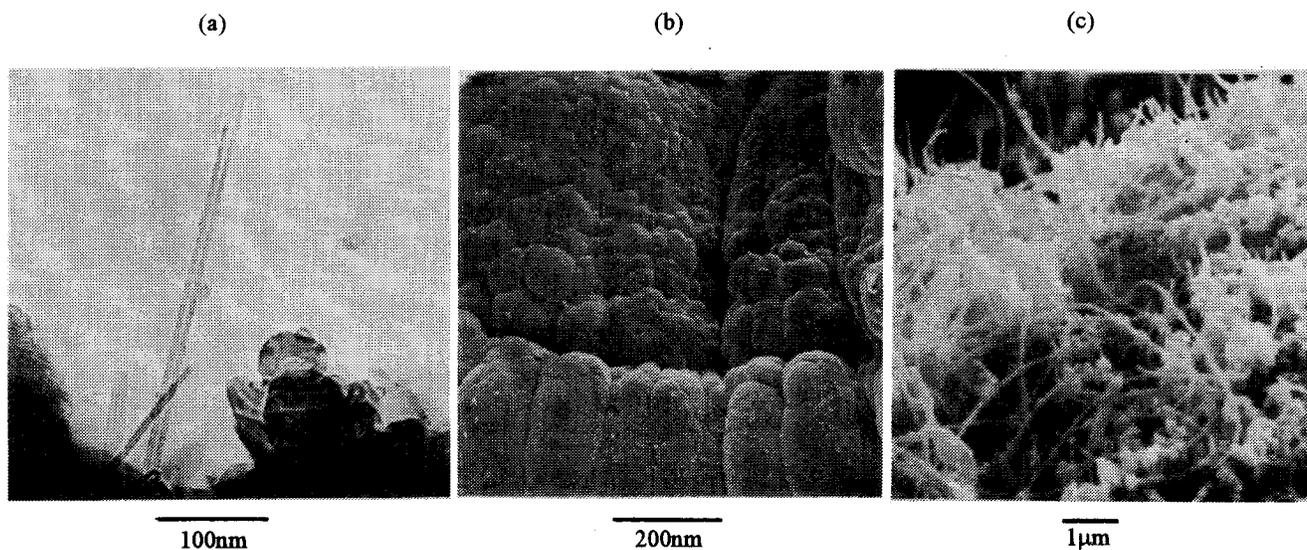
(a) (b) (c)

100nm   200nm   1μm

Fig. 1: (a) TEM of nanotube located in cathode deposit formed in 300 torr He. SEM of (b) outside and (c) inside of anode deposit formed under 500 torr He.