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Structural variations of the cathode deposit in the carbon arc

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ABSTRACT

Synthesis of various carbon nanostructures, including fullerenes, single-walled and multi-walled nanotubes and nanoparticles, by arc discharges relies on ablation of the graphite anode and deposition of synthesized carbonaceous products on the cathode surface and on the reactor chamber walls. For backbone all-carbon system, the cathode deposit plays a critical role in sustaining the arc discharge and thereby, the synthesis processes. This deposit usually exhibits spatially distinct structural variations with three different axially symmetrical morphologies. In particular, a rim of pyrolytic carbon separates the innermost core consisting of multi-walled carbon nanotubes from the outmost ring with powdery amorphous carbon soot. Experiments revealed a strong correlation between the current conducting arc attachment to the cathode deposit and the nanotube forming area in the deposit. Results suggest that particle and heat fluxes from the plasma are responsible for purity of nanotubes in this deposit core area. It appears that a better synthesis selectivity can be obtained in low ablation regime which is characterized by a nearly constant arc current density independent on the anode diameter.

1. Introduction

DC and AC arc discharges at moderate (1–100 Torr) and atmospheric pressure levels are commonly used for synthesis of carbon nanostructures, including fullerenes, nanotubes and nanoparticles [1–4], and other nanomaterials such as ZnO [5], SiC [6], and gallium oxide [7], *etc.* In a typical synthesis by a DC arc discharge (so-called anodic arc), the anode electrode is consumed by ablation to provide a feedstock of atoms and molecules to sustain nucleation and growth of nanostructures. Ablated and synthesized products are then deposited on the electrodes and the reactor chamber wall. Independent of the material of interest, the cathode deposit is a common feature for all anodic arc discharges. This plasma facing deposit plays an important role in sustaining the arc discharge as it acts as an effective cathode electrode. For carbon arc discharges, the deposit has usually a complex morphology with various synthesized structures including fullerenes, multi-walled nanotubes, and amorphous carbon soot [2,8–11]. In this paper, we demonstrate that these structural variations of the cathode deposit are associated with spatial variations of plasma, particle, and heat fluxes at the arc attachment to the deposit. These results can be generalized for low and high anode ablation modes, which are usually observed for synthesis arcs [12–15]. Recent theoretical models attributed these ablation modes to the formation of the negative and positive anode sheath regimes of the arc, respectively. It was also shown that power flux from the plasma to the cathode depends strongly on the anode sheath regimes [12,16]. We show now that structural variations of the cathode deposit depend also on the anode ablation mode.

The measured correlation between arc properties and carbon structures on the cathode deposit is a key result of this paper, which goes beyond previous studies of structural variations of the arc deposit on the cathode [13]. The paper is organized as follows: in Section 2, we describe the experimental setup for the characterization of the current and the surface temperature distributions at the cathode. Experimental results are described and analyzed in Section 3. Conclusions of this study of synergetic plasma and material processes and practical implications of the results are summarized in Section 4.

2. Experimental

The experimental arc synthesis setup (Fig. 1) employed in the present study was described elsewhere [13]. The anode (A) and cathode (C) are set up in a vertical configuration in order to avoid

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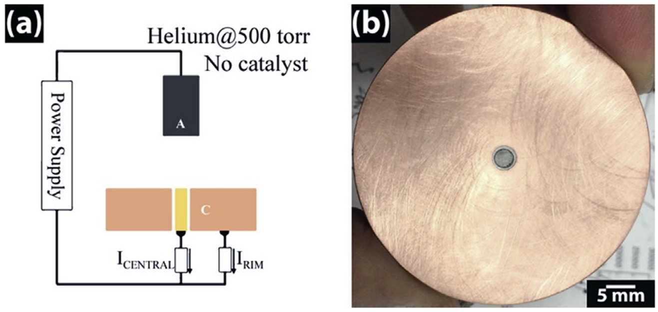

Fig. 1. (a) A schematic of the arc setup with a graphite anode (A) and the segmented cathode (C). (b) Photograph of the segmented cathode. (A colour version of this figure can be viewed online.)

asymmetrical effects on the arc and deposition brought by convective flow. In order to measure the arc current distribution, a segmented cathode composed of a graphite central electrode (diameter d = 3.2 mm) and a copper rim electrode (d = 50.8 mm) is used. In order to allow a better measurement resolution of the current distribution and its correlation with the deposit morphology, the diameter of the central electrode is almost twice smaller than in Ref. [13]. The rim electrode is insulated from the central electrode by a thin layer of boron nitride with a thickness of 0.5 mm in order to minimize the disturbance to the arc. The central and rim electrodes are connected electrically to the arc power supply through separate shunt resistors of 2 mOhm and 1 mOhm, respectively. In arc operation, these resistors are used to measure the currents the segmented electrodes.

The carbon arc discharge experiments were conducted in a reactor chamber filled with helium gas at 500 Torr. The arc was initiated by bringing the anode into contact with the cathode, after which the current was maintained at 65 A. An external control system increased the electrode gap until the specified discharge voltage was reached. The gap was about 2 mm wide. Throughout all experiments described in this paper, the voltage measured across the two electrodes was maintained about 20 V. This voltage includes the voltage drop across the arc and along the electrodes [12].

After the arc initiation, it usually took about 10 s for the arc current to stabilize and for the anode to reach the specified inter-electrode gap. During the arc operation, the graphite anode is ablated, producing flux of carbon atoms, molecules and clusters. The arc plasma is mainly generated from these carbon species some of which are ionized producing positive atomic and molecular ions [17]. The fluxes of charged and neutral plasma particles to the cathode form a carbonaceous deposit (Fig. 2). In present experiments, the arc was operated with segmented and non-segmented cathodes made from graphite and copper. We found no difference in structures and properties of the cathode deposits formed with these different cathodes.

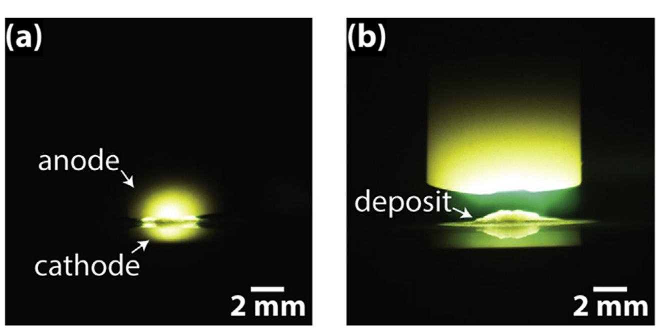

Fig. 2. Unfiltered images of (a) the onset of the arc and (b) the arc steady state. The top and bottom electrodes are the anode and the cathode, respectively. The small hump of the material on the cathode is the carbonaceous deposit. (A colour version of this figure can be viewed online.)

Reliable measurements of the current distribution using the segmented cathode were feasible only for a steady-state arc operation in the low ablation mode. In this mode, the deposit grows relatively slowly (about 30 s) before it completely electrically shorts the segmented electrodes. In the high ablation mode, the deposit was large enough to short the electrodes while arc was still reaching a steady state operation (i.e. less than 10 s). From previous arc studies [12,14], an arc current of 65 A and an anode diameter of 9 mm were selected to facilitate the low ablation mode. From the measurements of the anode weight and the cathode deposit thickness before and after arc operation, an ablation of 0.56 ± 0.03 mg/s and a deposit thickness of about 1 mm were determined. This is consistent and comparable with ablation rates measured for this regime in Refs. [12,13].

In addition, a set of arc experiments was also conducted in the high ablation mode, using a 6 mm diameter graphite anode and the same operation conditions (arc current, voltage, and helium gas pressure) as for the low ablation mode. The main purpose of these experiments was to study the effect of the anode ablation mode on the morphology of the cathode deposit.

The distribution of the surface temperature of the cathode deposit was also measured during the arc discharge. For these measurements, a calibrated FLIR tau 2640 infrared camera together with a 3.2% transmittance neutral density filter were placed to acquire the side view of the electrodes and cathode deposit. Similar to the measurement procedure reported earlier [13,14], C-type thermocouples inserted into the anode and cathode were used to calibrated this IR camera. The temperature measured by the IR camera had an uncertainty of about 100 °C. Moreover, the same thermocouples were used in order to determine the heat flux to the electrodes.

The cathode deposits produced in arc experiments were carefully studied via electron microscopy. The cathode deposit from each run was kept on the cathode without disturbance and first surveyed by an FEI Quanta 200 field emission SEM operated at 10 kV. This survey allowed us to identify characteristic parts of the deposit with distinguished appearances. After that, these parts were separately collected, sonicated in an acetone bath for about 3 min, and dispersed onto a TEM grid. The TEM samples were studied by a Philip CM200 field emission TEM at 200 kV. Structural analysis of the deposit was carried out using a Rigaku MiniFlex XRD with Cu Kα as the X-ray source.

3. Results and discussion

3.1. Cathode deposit

3.1.1. Microscopic evaluation

A cathode deposit occupies usually a large area with an effective diameter larger but comparable with the anode diameter. For example, for a 9 mm diameter anode, including the outer soot formation the deposit is about 14 mm. Fig. 3 demonstrates three typical regions of the cathode deposits collected in the experiments. Each region features distinctive structures com-pared to one another. Starting from the innermost region to the outermost region, the deposit consists of (1) a fibrous core that contains loosely entangled and randomly oriented multi-walled carbon nanotubes and polyhedral nanoparticles, (2) a particulate rim that contains curvy pyrolytic carbon sheets, and (3) amorphous carbon soot. Nanotubes were found only in the core area of the deposit which is typically much smaller than the total deposit area. For example, for