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Self-organisation processes in the carbon arc for nanosynthesis

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Abstract

The atmospheric pressure carbon arc in inert gases such as helium is an important method for the production of nanomaterials. It has recently been shown that the formation of the carbon deposit on the cathode from gaseous carbon plays a crucial role in the operation of the arc, reaching the high temperatures necessary for thermionic emission to take place even with low melting point cathodes. Based on observed ablation and deposition rates, we explore the implications of deposit formation on the energy balance at the cathode surface, and show how the operation of the arc is self-organised process. Our results suggest that the can arc operate in two different regimes, one of which has an important contribution from latent heat to the cathode energy balance. This regime is characterised by the enhanced ablation rate, which may be favourable for high yield synthesis of nanomaterials. The second regime has a small and approximately constant ablation rate with a negligible contribution from latent heat.

I.   INTRODUCTION

Carbon arcs, first discovered in the early 19th century [1], have had for numerous applications. They have been used as radiation standards [2], in image furnaces [3] and in carbon arc welding among other things. A recent development has been their use as an efficient method for the production of high purity carbon nanotubes [4–6], in which the graphite anode ablates and nanotubes and other fullerines are formed in a deposit on the cathode surface [5, 7]. As nanotubes have unique electrical and mechanical properties [8–10], they could potentially be used for hydrogen storage, nanoelectronics, chemical sensors and many other applications [8, 9, 11].

It has been proposed [12–14] and was recently shown [15] that the carbonaceous deposit formed during the carbon arc discharge plays a crucial role in its operation. The deposit 1) changes the arc from graphite-cathode to graphite-deposit, 2) reaches the high temperatures necessary for thermionic emission to provide the electron current and 3) reduces heat flux to the cathode.

Figure 1 illustrates the self-organisation process, in which the steady-state operation of the carbon arc is treated as a self organised process. Electrons emitted from the carbonaceous deposit heat the graphite anode, which ablates. The carbon ions and atoms travel to the cathode and condense to form the deposit, which is at the high temperature necessary for thermionic emission to support the electron current in the arc.

Electrons heat anode

Anode ablates and ions travel
to the cathode
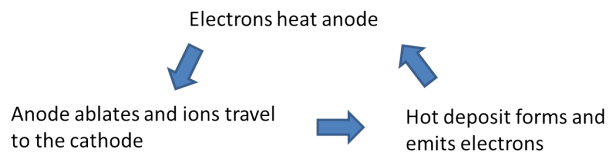
Hot deposit forms and
emits electrons

FIG. 1. Schematic of self-organisation in the carbon arc.

The ablation and deposition during the arc should be accounted for in models as the deposit formation changes the cathode material, which affects the arc-cathode interaction. In our experiments, under the same operating conditions, we show that the arc can operate in two regimes in which the importance of deposition in the energy balance at the cathode changes drastically. In particular, in the regime with enhanced ablation and deposition which is relevant to nanosynthesis, the latent heat is an important term in the energy balance at

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the cathode. Although the focus of this paper is on the carbon arc, the results may be applicable to other anodic arcs (in which the anode evaporates) where a solid deposit is formed on the cathode.

II. EXPERIMENTS AND RESULTS

Using the setup described in previous works [15, 16], experiments were performed with a copper cathode of diameter 5 cm and graphite anodes with diameter between 6 and 12 mm. The duration of each experiment was approximately 1 minute, with discharge current 65 A. Discharge voltage was maintained between 20 and 25 V using a feedback system. With the 6 mm anode the voltage was approximately 25 V while with the 12 mm anode, it was approximately 21 V. Helium at 500 torr was used as a buffer gas.

Ablation and deposition rates were measured by weighing the electrodes before and after arc operation. Deposition rates were between 0.6 and 0.7 of the ablation rate independent of anode diameter. This is likely due to the arc gap of 1-2 mm being much smaller than the electrode diameters, which would reduce the loss of material from the inter-electrode gap.

The ablation rates are shown in Figure 2. Above diameters of 9 mm, the ablation rate was small (< 1 mg/s) and approximately constant, while at smaller diameters, the ablation rate rose abruptly. In addition, there were visible craters on the anodes with diameters > 8 mm, indicating that the arc diameter was smaller than the anode diameter. These observations are consistent with Ref. [16], in which enhanced ablation was observed at smaller anode diameters.

Additionally, the formation of the cathode deposit was shown to play a crucial role in the operation of the arc [15]. From infrared measurements, it was shown that the surface of the deposit reached about 3500 K (Fig. 3), which allows thermionic emission to provide the electron current in the arc. The deposit was also of low enough thermal conductivity so that the copper cathode did not reach its melting temperature.

The differences in behaviour of the ablation rate in the two regions shown in Fig. 2 suggest that the arc can operate in two regimes, and we examine how the energy balance at the cathode changes with anode diameter.
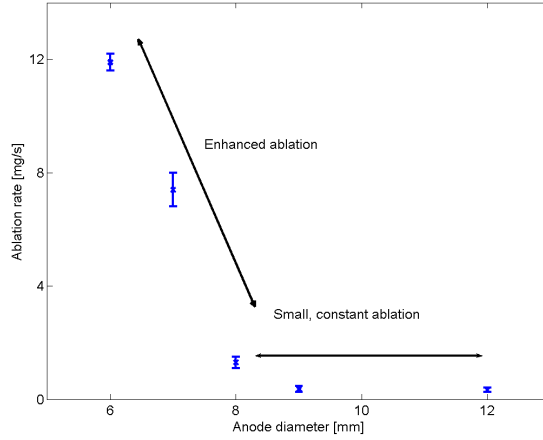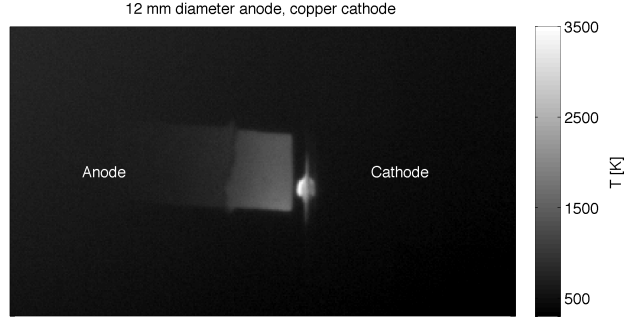
3

FIG. 2. Anode ablation rates.

FIG. 3. Infrared measurements of the cathode deposit.

III. CONTRIBUTION OF DEPOSIT TO CATHODE ENERGY BALANCE

Due to the deposition of the carbon atoms and ions on the cathode, the energy balance at the cathode must account for the latent heat [17] in addition to the standard terms considered in energy balance for cathodic arcs [18]. The thermal conductivity of the cathode should also be that of the deposit rather than the cathode material. Based on our previous results [15], the deposit has a poorer thermal conductivity than graphite (estimated at at least 5x less), which itself has a conductivity more than ten times lower than that of copper. The estimates are supported by our analysis of the deposit, which showed that it had a lower density than graphite and a more amorphous structure.

A full description of the arc-cathode interaction requires numerical simulations and is beyond the scope of this paper. Here we show how the inclusion of deposition affects energy

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balance at the cathode and highlights the existence of two regimes.

In atmospheric pressure arcs, energy flux at the cathode is dominated by ion heating and emission cooling [18], which are given by

$$Q_i = \frac{I_i}{e}(E_i + eV_c - \phi)$$
$$Q_{ee} = \frac{I_{ee}}{e}(2T_e + \phi)$$

(1)

Here I_i and I_{ee} are the ion and electron emission currents respectively, E_i is the ionisation energy, V_c the cathode sheath voltage drop and ϕ the work function.

With the cathode temperature at 3500 K, the thermionic emission current is large enough to account for all of the electron current in the arc and the ion current is estimated using the Bohm sheath condition with a plasma density of 10^{21} m^{-3} and electron temperature of 0.6 eV, giving an ion current of approximately 6 A. The sheath voltage drop is between 3 and 12 V [13, 17]. Heating due to ions is thus between 60 and 110 W. The calculated electron cooling is then approximately 340 W. For reference, the total power dissipated in the arc is between 1300 and 1625 W.

The heating due to deposition is given by

$$Q_{dep} = \dot{m}H/m_C$$

(2)

where H is the latent heat of vapourisation per atom, $\dot{m}$ is the deposition rate and m_C is the mass of a carbon atom. The contribution of deposition varies between 13 W for the 12 mm anode and 414 W for the 6 mm anode. Comparing these values with the total power of the arc and the expected dominant terms in the cathode heat flux, we see that in the case of the 12 mm anode, heating due to deposition is negligible, while with the 6 mm anode, deposition plays a significant role. This suggests that the arc operates in two regimes which are characterised by the ablation rate and depend on the electrode geometry, which could affect the plasma parameters. A more accurate model which can capture these differences, not seen in current models, would require coupling the surface interactions to the sheath and arc plasma as well as two dimensional effects. We also note that evaporation from the deposit is not taken into account here, which would reduce the contribution of latent heat.

IV. SUMMARY

Anodic carbon arc experiments were conducted between graphite anodes of varying diameters and copper cathodes. The ablation rate decreased with increasing anode diameter before becoming small and approximately constant [16], while the formation of the cathode deposit was found to be crucial in the operation of the arc [15]. The evaporation of the graphite anode and formation of the carbon deposit on the cathode are self-organized to maintain the current conduction in the arc. We show that for smaller anodes, the contribution of the deposition to energy balance must be included when modelling the arc-cathode interaction. The differences in the ablation rate when increasing the diameter suggest that the arc can operate in two different regimes, which cannot be captured by current models because of the contribution of latent heat. This should be a subject for further experimental and simulation work.

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