Cathodic Arc Carbon Plasma-Gas Interaction Effects at Low Pressures of He, Ar and N_2 in Fullerenes Synthesis

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Abstract

Cathodic arc pasma show similar characteristics compared to the fullerene producing laser ablated plasmas. Experimental and theoretical knowledge of cathodic arc systems are applied here to study the possibility of fullerence nucleation in these systems. Predictions of the nucleation zone are given using a model of the plasma expansion and compared to spectroscopic observation of C_2 molecular radiation.

1. Introduction

Fullerenes are currently produced using the graphite electrodes arc technique in a pressure range typically varying between 50-500 Torr. Helium is generally used as the background gas, the yield being larger than with argon and nitrogen. In the graphite arc system, the anode is the electrode being eroded and generating the strong carbon vapour flux expanding in the gas at low pressure. The cathode for this thermionically emitting material in fact shows a mass gain; it grows in size as a result of the incoming carbon flux from the anode. This cathode growth is the site of nanotubes formation.

This behaviour is very different from typical vacuum arcs (thereafter called cathodic arcs) even in the transition region between 1 Torr to atmospheric pressure. Cathodic arcs are primarily governed by field emission at the cathode, with mobile micron-size cathode spots generating a very strong ion flux. The anode in this case is the passive electrode, receiving the carbon vapour and ion flux emitted by the cathode spots. This discharge mode is used for example in the arc ion-plating technique to generate diamond-like films. The carbon plasma energies involved in cathodic arc systems (typical ion energies between 10-100 eV) are much higher than those produced by the thermionically emitting carbon arcs in fullerene production. These energies and the expanding plasma behaviour are however very similar to the laser produced carbon plasma such as the fullerene producing experiments of Smalley and Kroto [1]. Hence cathodic plasmas could possibly be the source of some fraction of fullerene. Our interest in this type of discharge is twofold. First, experimental and theoretical studies were performed on the cathodic plasma expansion characteristics in various gases including He, Ar, N_2 and SF_6 in the context of understanding the electrode erosion and arc spot movement phenomena [2,3]. These studies indicate the very strong influence of the background gas on the local plasma parameters in the same pressure range as fullerene synthesis is observed. They also show important differences in the plasma structure between the expansion in helium compared to argon and nitrogen. Cathodic arcs could hence constitute interesting tools to measure and understand the necessary local conditions for fullerene formation. The second interest is related to the very strong erosion rate properties of cathodic arc systems (typically around 10^{-5} grams/Coulomb for vacuum carbon arcs [4,]), possibly resulting in larger fullerene production rates.

This paper presents the plasma expansion model applied to carbon cathodes in helium, argon and nitrogen. Preliminary experimental results on the spatial distribution of the fullerene synthesis zone are also presented using the C_2 Swan band emission in the expanding plasma.

Plasma expansion model

Time resolved measurements of the velocity and position of cathodic vapours in expansion in various gases were performed using the experimental setup shown in Figure 1 for pulsed arc discharges [2,3]. As pressure in the chamber is increased pass a given threshold, a sharp boundary is observed separating the supersonic cathode plasma expansion from the background gas. This boundary attains rapidly a stable position in the first 10-50 μs of the expansion. The discharge volume above the threshold pressure can be schematically separated in three zones (Figure 2): a cathode plasma region close to the cathode spot, a stationary boundary zone (shock wave) through which vapours emitted by the cathode spot are diffusing, and the relatively unaffected background gas.

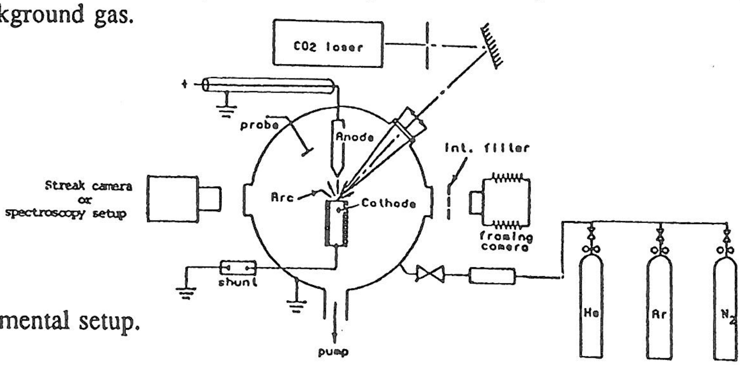

Fig. 1: Experimental setup.

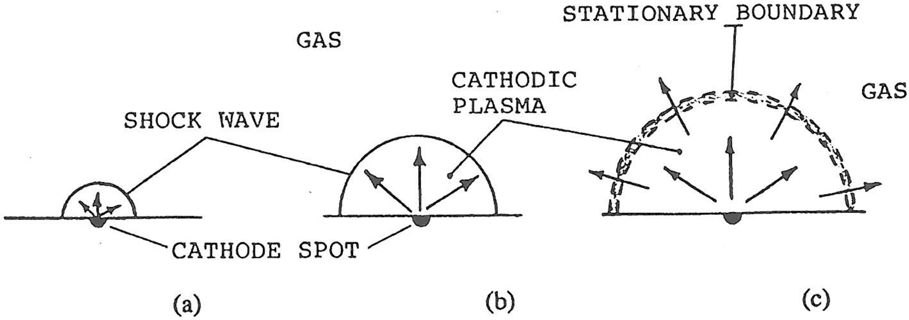

Fig. 2: Initial stages of the plasma expansion (a,b) and stationary shock wave geometry attained (c).

The radial position of the boundary from the cathode spot was found to be governed essentially by two important parameters. First, similar plasma expansion velocities were observed for different gases provided the gas mass density in the chamber was kept constant. Second, the final stable position of the boundary was found highly dependent on the sonic velocity C of the gas being used, i.e. expansion stops once the boundary velocity reaches the velocity of sound in the gas. An analogy of this phenomena would be to consider an inflating balloon that attains a stable size once pores in the membrane open to let through the continuously incoming flux. For example with initial expansion velocity typically of 10^4 m/s, a given gas mass density of helium (C_{He}=1019 m/s) or argon (C_{Ar}=323 m/s) in the chamber will lead to plasma sizes inside the boundary that are much smaller in helium compared to argon, the sound velocity of helium being attained first in the expansion. These phenomena were thoroughly investigated experimentally and modeled using a self-similar snowplow hemispherical expansion [3]. It is interesting to note that the erosion rate of the cathode correlates with the pressure range of these phenomena, indicating that the resulting plasma density above the spot plays an important role. Results of this model yielded the evolution of the boundary velocity and equilibrium radius of the boundary R_c as a function of the gas parameters, and the material dependent vacuum cathode erosion rate E_r and plasma expansion velocity V_o:

$$\frac{R_c^3\, \rho_g}{\tau_c\, I}\left(\frac{C^2 + (2\,kT)/M_g}{V_o^2 - C^2/3}\right) = \frac{3}{2\pi}\, E_r \qquad (1)$$

where kT, M_g, ρ_g are the temperature, atomic mass and mass density of the background gas, respectively. The parameter τ_c is the time necessary for the boundary to reach the sound velocity C at a given arc current I, evaluated by integrating the boundary velocity in the initial stage of the discharge. Figure 3 shows a comparison of this model with experimental measurements on copper cathodes in

He, Ar and SF_6 gases [3]. A good agreement is observed over five orders of magnitude of the gas related parameters, covering two orders of magnitude of the boundary radius. A summary of the model can be written using the following simple expression:

$$R_c^{\beta} f = E_r \tag{2}$$

where R_c is the critical radius reached by the plasma expansion, f a function characteristic of the background gas, and exponent β varying slowly between 2.1 and 2.5 over the five orders of magnitude of parameter f.

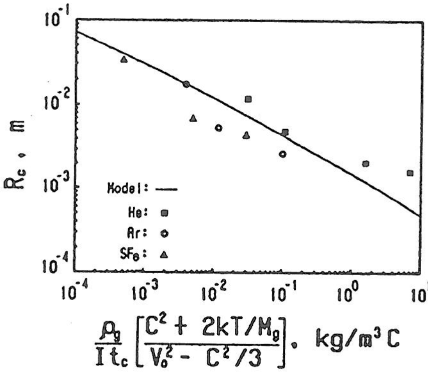

Fig. 3: Steady-state radius attained by the plasma/gas boundary versus gas properties using equation (1) (solid line). The points refer to experimental values.

3. Link with fullerenes - case of carbon cathodes

Cathodic arc plasmas yield expansion characteristics very similar to the fullerene producing laser ablation experiments. The fullerene synthesis pressures also correspond to the pressure range cathodic arc expansion is strongly affected by the gas. Very specific regions of the plasma or neutral gas volume could possibly satisfy the necessary local conditions of carbon density and temperature for fullerene synthesis. These regions can be identified from the above model and observations. It is extremely unlikely that the very high density (typically 10^{25} m^{-3} at the cathode spot, decreasing as r^{-2} [5]) and temperature (above 1 eV) could give rise to large C_{60} molecules in the carbon plasma region inside the boundary. Similarly, the neutral carbon vapour diffusing away from the boundary in the gas zone is expected to attain rapidly temperatures and carbon-carbon collision frequencies that are too low to generate the large molecules. We can hence estimate the boundary volume and the volume located shortly after this boundary to be regions where synthesis of C_{60} may occur. If true, this should result in differences in yield between He, Ar and N_2. Helium provides a synthesis region of much larger carbon plasma density compared to argon and nitrogen.

To verify this hypothesis, the expansion model was used to evaluate the critical radius of cathodic carbon plasma expanding in He, Ar and N_2 at different pressures, and preliminary experimental measurements were made in helium.

4. Results

The calculated critical radius R_c attained by a 100 A carbon cathodic arc plasma is given in Figure 4 as a function of pressure for helium, argon and nitrogen backgrounds. It can be seen that a helium background generates much smaller plasma volumes compared to both argon and nitrogen. These last two gases in turn give rise to very similar expansion, yielding similar local plasma properties in the vicinity of the transition boundary. This curve also predicts that, if fullerenes are effectively produced in cathodic carbon arcs at some optimal pressure in helium, argon and nitrogen should provide their maximum yield at a higher pressures.

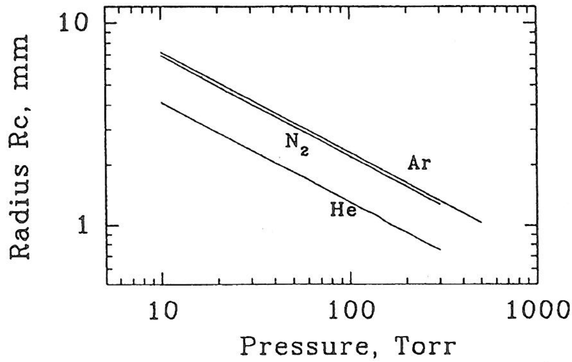

Fig. 4: Critical radius R_c evaluated from the hemispherical self-similar model versus pressure in helium, argon and nitrogen.

Spectroscopic observation of the cathodic arc plasma was used in order to evaluate if the plasma-gas transition zone effectively corresponds to a nucleation zone of larger carbon clusters. Laser triggering of the discharge (Figure 1), small electrodes (6 mm in diameter) and short arc pulse durations (250 μs) ensured relatively stable cathode spot position to provide reliable spatial distributions. The monochromator was set on the C_2 molecule Swan band as an indicator of larger carbon clusters nucleation zones. Intensities were recorded using a photomultiplier connected to a digital oscilloscope. The image from a given position in front of the cathode was focused on the entrance slit of the monochromator with a 200 μm spatial resolution. Intensities were recorded 200 μs after the beginning of each discharge. This delay enabled to eliminate the initial expansion stage and yielded reproducible results, it corresponds to at least twice the time necessary to reach the equilibrium plasma-gas interaction geometry with boundary radius R_c. An arc current of 120 A and pressure of 55 Torr He was used for this test in order to increase the value of R_c and facilitate measurement of the position of this transition region. Model predictions using these values yield a critical radius R_c close to 3 mm.

Results of the measurements are shown in Figure 5. One can see the total intensity of the C_2 Swan band showing a maximum between 2 and 4 mm from the cathode. Such a result indicate this zone could effectively provide conditions for fullerene nucleation. At this point however, too little carbon soot is produced by the 250 µs pulse discharges to enable fullerene yield analysis. This is now the object of further studies in pulsed and continuous cathodic arc discharges.

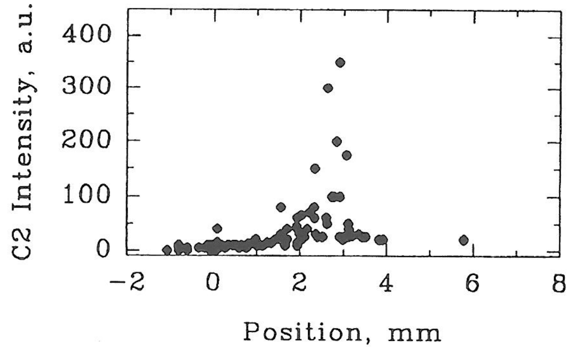

Fig. 5: Total intensity of the C_2 Swan band at various distances to the cathode in 5 Torr He, I = 120 A.

5. Conclusion

Cathodic arc plasmas show similar properties compared to fullerene producing laser plasmas. Experimental and theoretical knowledge of cathodic arc systems were applied to study the possibility of fullerene nucleation in this type of discharge. Predictions of expected nucleation zones in He, Ar and N_2 were given. A preliminary experimental study on the spatial distribution of the C_2 molecule emission correlates with the expected zone of nucleation. Further studies however are needed to evaluate if fullerenes are effectively produced by these discharges. If confirmed, cathodic arc systems could prove to be very useful tools in the analysis of local conditions necessary for fullerene synthesis.

References

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