IN-SITU FULLERENE FORMATION - THE EVIDENCE PRESENTED

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INTRODUCTION

Controlled environment transmission electron microscopy [1] is *not* a new technique to be applied to the study of carbonaceous material; it was pioneered by Baker and co-workers for the study of the gasification of graphite and the catalytic growth of carbon filaments [2,3]. However, it is only relatively recently that high resolution instruments have become available, enabling gas-immersed specimens to be investigated at near-atomic resolution [4].

It was expected that such equipment would quickly advance the understanding of carbonaceous material during a variety of gas reactions, providing real-time in-situ information on a microstructural level.

However, it soon became clear that the behaviour of a carbonaceous specimen immersed in a gas and *simultaneously* observed with the electron-beam of the microscope could not be explained *solely* by chemical reactions. As a result, it was suspected that the moderate electron-beam current density (required to provide bright high resolution images) was interacting with the gas and creating a localised plasma environment in which a high flux of low energy gas ions impinged on the illuminated region of the sample. Calculations suggested that the energies involved were sufficient to physically sputter-damage the specimen and complicate the results in the manner observed.

A serendipitous outcome was that the proposed plasma environment closely matched aspects of the conditions used to generate fullerenes [5] in the arc-discharge apparatus [6], and eventually we were able to provide the first images of single-shell fullerenes forming on the surface of previously untreated graphite crystals [7].

This paper aims to summarise the results of our recent work, describing a mechanism for the formation of fullerene molecules, and providing evidence that the features observed were closed shells similar to C_{60} or C_{70} bucky-balls.

EXPERIMENTAL

The samples investigated were KS10 graphite particles (obtained from Lonza G+T Ltd.), Raven 430 carbon black particles (obtained from Columbian Corporation), and HCV-grade hexagonal-boron nitride (h-BN, obtained from BNP Ltd.).

A suspension of each was made by ultra-sonification for several minutes in acetone. The material was then deposited on 3 mm gold electron microscopy finder grids coated with either lacy carbon or continuous silicon monoxide films.

Each sample was investigated in a modified JEOL JEM 4000 EX High Resolution Electron Microscope fitted with a differential pumping Gas Reaction Cell [4] and side entry specimen holder with integral heating element. The microscope was operated at 400 kV, with a LaB_6 filament, and provided a point-to-point resolution of better than 2.5 Å. As a result, the (0002) planes of correctly oriented graphite or h-BN were easily imaged by phase contrast high resolution microscopy at Scherzer defocus.

The samples were immersed in up to 25 mbar helium gas and heated to ~500°C. After stabilisation had been achieved, an area was irradiated with the electron-beam and simultaneously observed at 400 000 x. At such a high magnification, the electron-beam current density was measured to be ~6.4 A cm^{-2} and was suitable for recording images with a 1 second exposure of a photographic plate or by using closed-circuit S-VHS video equipment.

RESULTS AND DISCUSSION

After ~1500 s of irradiation, features were observed on the graphite crystals that could be interpreted as single graphene layers bent and curved to eventually form fullerene molecules. Figure 1a indicates two such features at different stages of formation. Although this was evidence of real-time fullerene nucleation, it was

inconclusive as to whether the images were of bucky-balls or end-on bucky-tubes [8].

Figure 1b illustrates similar features seen forming after ~1000 s of irradiation on the surface of a primary particle of the Raven 430 carbon black sample. Because these curved graphene sheets have formed tangential to a sphere of fragmented graphite crystallites, it is good evidence that they are bucky-balls rather than bucky-tubes. The dimensions of the circular fringe in figure 1a would suggest a C_{60}-fullerene, and the slightly elliptical shape in figure 1b closely fits that of a C_{70}-fullerene.

As further evidence, it was found that such features could not be formed on the surfaces of h-BN crystals. Such crystals are iso-electronic and iso-structural to graphite, and although h-BN nanotubes are possible [9], the C_{60}-fullerene analogue is a more highly strained $B_{12}N_{12}$ to avoid similar nearest-neighbours [10]. Therefore, this suggested that the processes occurring in the microscope were promoting the formation of pentagonal defects, and hence bucky-balls, rather than simply rolling up the (0002) layers of the crystals to form bucky-tubes.

CONCLUSION

The controlled environment high resolution transmission electron microscope has been used to provide real-time evidence of fullerene formation. From the consideration of various precursors it has been shown that bucky-balls rather than bucky-tubes are created, and this leads to a mechanism for fullerene nucleation: In the microscope, it is thought that the high flux of low energy ions impinge on the surface graphene layers and sputter carbon atoms. Occasionally the layers rapidly repair with a pentagonal defect, causing curvature and the eventual formation of a bucky-ball.

Hence, it is suspected that in the arc-discharge apparatus the flux of ions in the plasma between the electrodes introduces pentagons into condensing graphene fragments. It follows, therefore, that carbon atoms do not condense as fullerenes, but that fullerenes nucleate from conventional, intact graphene fragments. This insight should lead to improvements in the yield of fullerene material in the future.

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This project was funded by an EPSRC CASE studentship in collaboration with Corporate Technology Europe, Raychem Ltd., Swindon, SN3 5HH, U.K. Ron Doole is acknowledged for his help and advice on the use of the Gas Reaction Cell and Steven Baigrie for his continued scientific interest in the research.

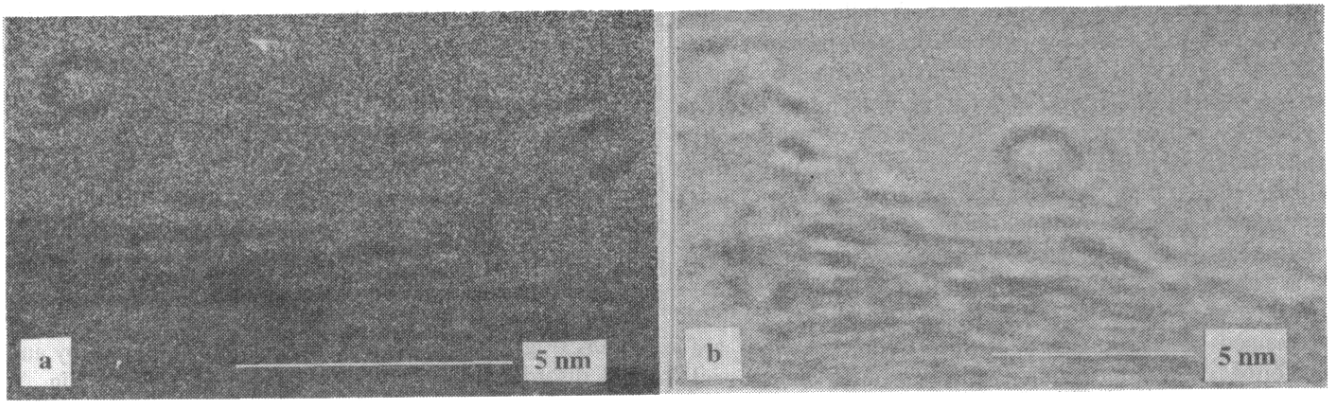

Figure 1 - Features interpretable as single-shell fullerene molecules nucleating during in-situ controlled environment high resolution transmission electron microscopy on the surface of a graphite crystal (a) and a carbon black particle (b).