AN *IN-SITU* INVESTIGATION INTO THE BEHAVIOUR OF ELECTRON IRRADIATED GRAPHITE IN HELIUM GAS

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INTRODUCTION

Following the discovery of fullerenes [1], a vast amount of research has focused on understanding the mechanism of their formation.

A popular method of production of fullerenes and related structures [2,3] is through using an arc-discharge chamber as pioneered by Krätschmer et al [4]. In such an apparatus, graphite electrodes are surrounded by an inert atmosphere like helium and separated by a small distance so that a large heating current strikes an arc across the gap. A variety of conditions have already been investigated, both in terms of the pressure [5,6,7] and the current density [5]. This has shown that fullerene generation is optimised below 100 mbar of helium, and that a typical current density is 200 A cm^{-2} [5].

Ugarte has also reported investigating the behaviour of fullerene-related material in the electron microscope under the influence of high current density electron-beams [8]. In this case, 150 A cm^{-2} was sufficient to transform the sample into continuous concentric fullerene shells in a time-scale of several minutes. Such structures were termed 'bucky-onions' [8] and formed over longer periods of time when the electron-beam current density was as low as 30 - 50 A cm^{-2} .

Although the high electric fields and high temperatures [9] present during arc-discharge are also expected to be of importance, it is possible to model some of the parameters discussed above in a modified electron microscope equipped with a gas reaction cell. It is also possible that the effect of the beam interacting with the gas around the sample may closely resemble the conditions in a plasma near the electrodes of an arc-discharge chamber [10]. If this assumption is correct, it is hoped that any structural changes that may lead to fullerene formation can actually be observed in real-time, and hence an understanding of the formation mechanism and optimum conditions gained.

EXPERIMENTAL

A suspension of KS10 graphite particles (nominal size 10μm, obtained from Lonza G+T Ltd) 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 continuos silicon monoxide.

The sample was investigated in a modified JEOL JEM 4000 EX HREM fitted with a differential pumping Gas Reaction Cell [11] 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 were easily imaged by phase contrast high resolution microscopy at Scherzer defocus.

The samples were immersed in approximately 25 mbar helium gas. 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 beam current density was measured to be typically 4 - 6.4 A cm^{-2}. This was suitable for recording images with a 1 second exposure of a photographic plate, or by using the S-VHS video equipment and closed circuit television.

Another sample was also investigated at an elevated temperature of 500 °C. This required an increased time for stabilisation as thermal drift had to be reduced to virtually zero.

RESULTS AND DISCUSSION

At ambient temperature, the graphite particles underwent rapid morphological and microstructural changes when the electron beam irradiated the sample. The change was more rapid with higher electron beam current densities (and hence when investigated at higher magnification). The crystalline graphite was seen to

transform into amorphous spherical particles of approximately 10 - 100 nm in diameter.

Despite the presence of a gas, it was possible to image the (0002) planes of graphite particles, and directly follow the microstructural changes that occurred. Figure 1a illustrates the bending of such planes away from the surface, after which they appear to 'vaporise' into the neighbouring spherical amorphous material. This photomicrograph was taken after less than 60 s of irradiation.

At 500 °C the crystalline graphite was much more stable. This enabled the sample to be investigated for longer periods without the morphology of the particle departing greatly from its original form. Figure 1b shows the preserved crystalline structure after approximately 900 seconds of irradiation, and no amorphous spheres can be seen. Analysis of the surface after 1500 seconds (figure 1c) revealed 10 Å diameter features that can be interpreted as closed fullerene shells [12]. These were seen to form from highly distorted and bent graphitic planes, observed several minutes earlier.

CONCLUSION

Some of the conditions found in an arc-discharge apparatus have been simulated *in-situ* in a modified High Resolution Electron Microscope. It is believed this has led to the first real-time observation of fullerene shells forming at the surface of previously untreated graphite particles. Hence, the fullerene material is seen to originate from intact but damaged sheets of graphite rather than condensing from an amorphous carbon vapour.

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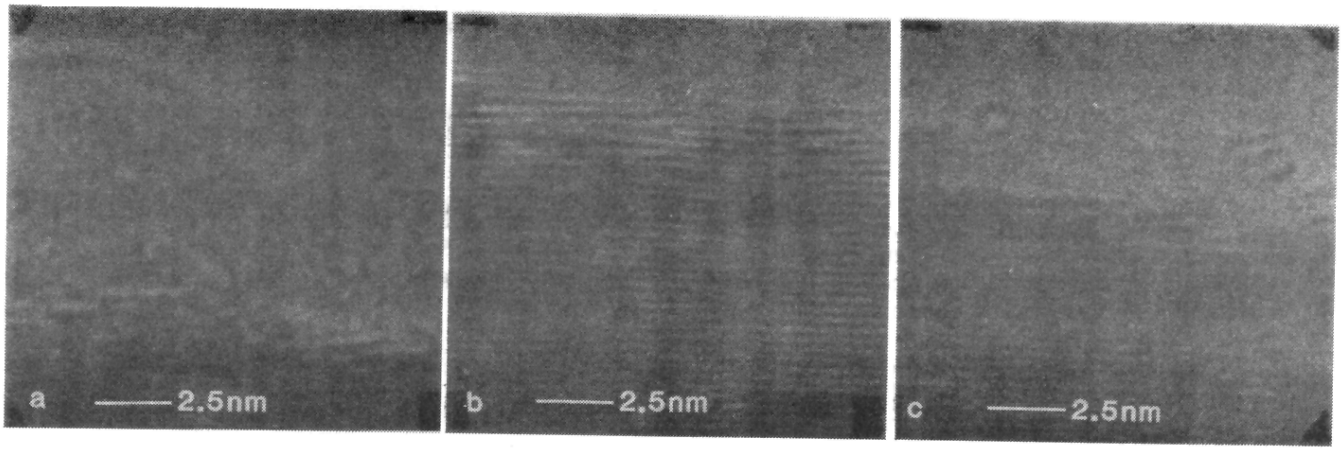

Figure 1 - Projected surfaces of graphite while immersed in 23-25 mbar helium gas and irradiated with an electron-beam current density of 4 - 6.5 cm^{-2} .a: Treatment at ambient temperature reveals the formation of amorphous carbonaceous spheres after less than 60 s. b: A particle at 500 °C after 900 s appears relatively stable. c: After 1500 s the same edge exhibits evidence of fullerene generation.