Letters

Effect of Substrate Structure on Deposition of Evaporated Carbon

Lewis and Floyd [1] have reported the formation of an oriented graphite "skin" on pyrolytic (PC) and glassy (GC) carbon surfaces heated in contact with conventional synthetic graphite to temperatures $\geq 2600°$ C in inert gas by RF induction. They have interpreted their observations in terms of reorientation of the substrate, perhaps induced by the anisotropic surface free energy of graphite. It is the purpose of this note to report on some observations on a similar carbon deposition effect which requires a different explanation.

In the course of tensile creep studies on PC and GC (also called vitreous carbon), it was found that carbon deposits built up on the exposed gauge section surfaces of the specimens during tests lasting several hours at temperatures in the range 2700 to 2900° C. The creep tests were carried out in helium at one atmosphere in a tubular resistance furnace with a single-spiral element of coke-pitch graphite. The equipment and techniques have been described in detail elsewhere [2, 3]. The most prominent carbon deposits formed on the layer-plane edge "a" surfaces of pyrolytic carbon specimens. As shown in fig. 1a, deposition was concentrated near the ends of the gauge section, terminating abruptly where the grips (GC inserts in coke-pitch graphite bodies) made intimate contact with the specimen and tapering off rapidly toward the centre of the specimen. These "a" surface deposits were quite adherent, and differential thermal expansion stresses which developed during cooling from the test temperature resulted in kink deformation of the specimen corners, and finally cracking and flaking of the deposit. The drawing-ink fiducial marks were placed on the specimen before testing. Almost no deposition occurred on the layer-plane face "c" surfaces of the pyrolytic specimens, as can be seen in fig. 1a. Thin, powdery, poorly adherent deposits formed on the surfaces of the GC specimens.

Flakes of the deposit removed from pyrolytic "a" surfaces were examined by X-ray diffraction and found to be well graphitised and randomly oriented. Examination of metallographically polished sections of the deposit in polarised
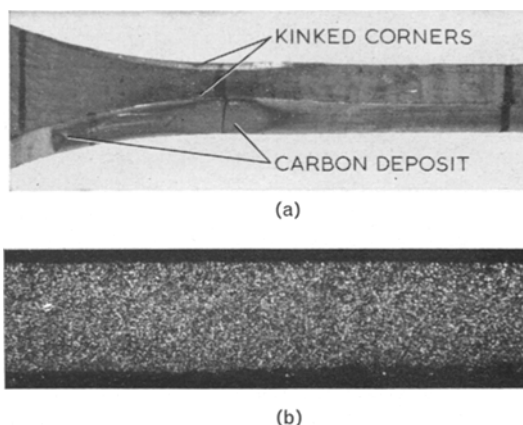

(a)

(b)

Figure 1 (a) Carbon deposit on layer-plane edge surface of pyrolytic carbon tensile specimen (× 4). (b) Cross-section of carbon deposit. Polarised light (× 120).

light confirmed that the texture was random. As shown in fig. 1b, there was no growth-cone structure, and the particle size was a few microns in diameter. The source of the deposit was traced to evaporation of carbon from the graphite heating element. By shielding the gauge section with a wrapping of flexible graphite foil, deposition on the specimen was greatly reduced. A sheet of foil, wrapped snugly around the grips and tied with carbon yarn to completely shield the specimen from the heating element, eliminated deposition on the specimen entirely. However, considerable distortion and deposition, which reproduced the spiral geometry of the element, occurred on the outer surface of the shield. Examination of the heating element showed extensive loss of material from the edges of the spiral turns. The evaporated carbon evidently originated there and was carried to the specimen, partly by flow of helium gas admitted through the viewing ports, and partly by diffusion and convection. Considerable deposition also occurred on the conventional graphite specimen grips, especially the cooler outer ends, making them difficult to disassemble after prolonged high-temperature tests. The distinctive deposition pattern on the specimen (fig. 1a) can be understood in terms of the distribution of deformation and temperature along the specimen. Continuing plastic strain in the uniform gauge section prevented the build-up

559

of adherent deposits there; but in the throat regions at each end, the strain fell off rapidly because of the increasing cross-section. Near the gripped portion, the specimen was partially shielded by the grip body, reducing the deposit thickness. Micropyrometer measurements showed a small negative temperature gradient from the centre to the ends of the uniform gauge section, and the temperature fell rapidly in the grips due to conduction and radiation losses out of the ends of the furnace. The heating element was, of course, hotter than the specimen.

The deposition phenomena reported here differ in several respects from those reported by Lewis and Floyd (L & F) [1]. They found pyrolytic-like deposits adjacent to and growing towards the PC or GC specimen surfaces, and of mass comparable with the specimen mass loss. In a number of years' experience in high-temperature treatment and deformation of PC and GC in various graphite resistance furnaces at temperatures up to 3200° C in both helium and argon atmospheres, no effects of this type have been observed by the author (nor, apparently, reported in the literature). This suggests that the particular experimental arrangement employed by L & F may have had a fundamental influence on their results, a possibility which they also noted. The difference in deposit structure can be understood on this basis. In the apparatus used by L & F, the distance from the probable source of the evaporated carbon to the substrate was quite short, in general much less than a centimetre. In this case it is reasonable to suppose that the carbon would deposit as graphitic platelets, producing the pyrolytic-like texture they observed. In the present experiments, the distance from source to substrate was several centimetres, allowing aggregation into larger soot-like particles before deposition. Other aspects of their observations, which led them to a surface-reorientation interpretation, are more difficult to reconcile with the author's experience.

Two conclusions are drawn from the present observations.
(i) The deposited carbon was evaporated from the coke-pitch graphite heating element. It did not come from the pyrolytic or glassy carbon specimens.
(ii) The nucleation, growth and adherence of evaporated carbon films at high temperatures is strongly dependent on the nature of the substrate surface. Deposits form readily on pyrolytic "a" surfaces, while glassy carbon surfaces are much less effective substrates, and virtually no deposition occurs on pyrolytic "c" faces. The low sticking probability for carbon atoms on layer plane surfaces has previously been noted by Diefendorf [4]. The pyrolytic carbon used here was deposited at 2200° C from methane by a commercial producer (Super-Temp Corporation*). It was well graphitised (interlayer spacing $d \simeq 3.36$ Å) and highly oriented (average layer plane misorientation $\leq 2°$) in the gauge and throat regions as a result of the high temperature tensile deformation. The glassy carbon (Tokai Electrode Co† GC-30) was isotropic and disordered ($d \simeq 3.42$ Å). Consideration of the structural characteristics of these different surfaces suggests that free carbon bonds on the edges of graphitic layer planes may play an important role in the deposition phenomena. The pyrolytic "a" surfaces on which deposition was most pronounced consist entirely of layer-plane edges. On the pyrolytic "c" faces where no deposition occurred, edge atoms are exposed only at imperfections such as cleavage steps. On the glassy carbon surfaces, a uniform but dilute distribution of edge sites would be expected because of the isotropy and small crystallite size ($\simeq 100$ Å), but the number of free bonds might be further reduced by the suspected high incidence of cross-link bonding in this type of material. The porosity and structural heterogeneity of coke-pitch graphite surfaces undoubtedly affected both the evaporation source and substrate characteristics of this material. The influence of chemical bonding at exposed layer-plane edge sites on deposit nucleation and adherence could account qualitatively for most of the deposition phenomena reported here, and may also have played a role in the results of Lewis and Floyd.

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References

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Fracture Studies in Glass-Reinforced Gypsum Plaster using the Scanning Electron Microscope

Fractographs of fibre-reinforced composites are seldom published, for the simple reason that so far it has been virtually impossible to take meaningful pictures by existing techniques. With the development of the scanning electron microscope [1] many of these difficulties have been overcome and the mode of fracture of composite specimens can now be studied with high resolution. The high depth of field which this instrument provides imparts to the micrographs a marked three-dimensional quality. This is particularly important in research on fibrous materials as it enables the investigator to focus along the entire length and depth of a fibre. The ease with which fractured composite surfaces can be prepared and subsequently examined with the scanning microscope must add substantially to the attractiveness of this technique when compared to other microscope methods.

It has been shown recently [2] that a structural composite material for indoor applications in buildings can be produced by reinforcing gypsum plaster ($CaSO_4$, $2H_2O$) with glass fibres. Either α or β hemihydrate plaster ($CaSO_4$, $\frac{1}{2} H_2O$) can be used as the starting material in the form of a thin slurry which can be sprayed simultaneously with a stream of chopped glass fibre roving on to a vacuum mould of any desired shape and size [3]. After dewatering, the material is allowed to set, and during this period the conversion of the hemihydrate to the dihydrate takes place. The resulting composite material is found to have appreciable structural strength and excellent impact strength and fibre resistance. Work is in progress to assess the suitability and economic viability of this composite material for various components in buildings such as partitions, floor-deck, staircase etc. It is foreseen that in some applications this composite material may be used as a substitute for timber.

Numerous photographs have already been taken with the scanning electron microscope (Stereoscan manufactured by the Cambridge Instrument Company) of fracture surfaces of set gypsum plaster with or without fibre-reinforcement, broken in uniaxial tension and compression, in flexure and by impact. The few micrographs presented in this communication were selected to bring out particular features. In general, the microscope was operated at 30 kV and the freshly fractured surfaces of the specimens were coated with a thin layer of carbon to make them electrically conducting.

Fig. 1 shows evidence of failure by shear in an unreinforced set gypsum plaster specimen which was broken in compression. The fault plane is clearly visible and it appears that pow-
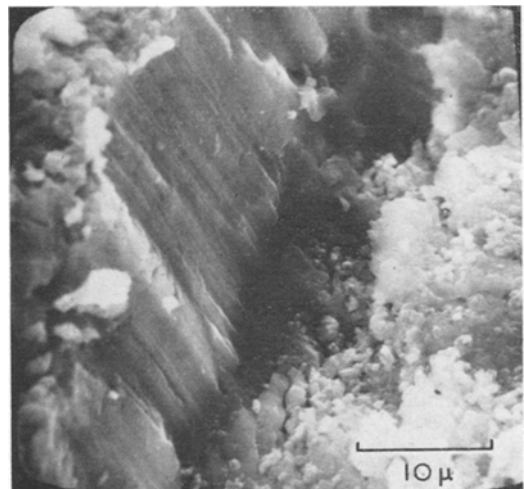

Figure 1 Shear failure in set gypsum plaster.