THE EFFECT OF MICROPOROSITY ON GRAPHITIZABILITY OF GLASSY CARBON

By J. L. Kaae, General Atomic Company, San Diego, Calif.

Introduction

The glassy carbons obtained by pyrolysis of thermosetting resins are well known for their resistance to crystallite growth during high-temperature exposure. Phase-contrast observations with transmission electron microscopy have shown that these carbons are composed of interweaved crystallites in a tangled geometrical arrangement (1). It has been suggested that the resistance to crystallite growth is due to this tangled microstructure (2). That considerable microporosity is present in the glassy-carbon microstructure is obvious from the relatively low density of this material. The role which the microporosity plays in the resistance to crystallite growth is the subject of this paper.

It is known from studies of isotropic pyrolytic carbons with microstructures similar to those of glassy carbons that high-temperature fast-neutron irradiation causes considerable densification of the tangled microstructure, obviously resulting in removal of much of the microporosity (3). The mechanism of this densification is thought to result from the expansion of individual carbon crystallites perpendicular to the layer planes and the shrinkage of the crystallites parallel to the layer planes. Thus, high-temperature irradiation of a glassy carbon should produce the tangled microstructure with greatly reduced microporosity and annealing of irradiated and unirradiated material should allow a study of the effect of the microporosity on crystallite growth.

Experimental

The carbon investigated was obtained from the Beckwith Carbon Company and was designated 1800 Grade indicating heat treatment to 1800°C. Small pieces of this material were irradiated in a series of capsules used primarily to study the behavior of graphites during irradiation, a program supported by the U.S. Energy Research and Development Administration (Contract E(04-3)-167, Proj. Agrmt. 17). Following irradiation, specimens were heated to either 1200°C, 1900°C or 2200°C and held for one hour at these temperatures in a graphite-resistance furnace.

Measurements of the apparent crystallite size, L_c, were obtained from x-ray diffractometer traces of the (002) reflection using copper Kα radiation. L_c was calculated from the formula: $L_c=0.89\lambda/\beta \cos\theta$. where λ is the wave length of the radiation, β is the half-heigh peak width, and θ is the Bragg angle.

Specimens were also examined with transmission electron microscopy. To prepare specimens for this examination, they were first mechanically polished to a thickness of about 50μm and then were thinned by sputtering with 6 Kev argon ions until they were sufficiently thin for transmission with 100 Kev electrons.

Results and Conclusions

The variation of density with fast-neutron exposure at 1100°C is shown in Fig. 1. As expected, fast-neutron irradiation did cause densification of the material. The specimen selected for subsequent examination was one exposed to a fast-neutron fluence of 10.3×10^{21} n/cm^2, E>0.18 Mev. As can be seen from the figure, this specimen had a density of 2.04g/cm^3.

The apparent crystallite size calculated from broadening of the (002) x-ray diffraction peak is shown in Fig. 2 as a function of the annealing temperature. Because of the very broad nature of the diffraction peak and because lattice strains also can contribute to broadening, these values should not be taken literally as a crystallite size, but they can be considered as a measure of the crystalline perfection.

Irradiation produced some increase in the apparent crystallite size, but on subsequent annealing there was very little increase up to the maximum temperature employed (2200°C). On the other hand, the unirradiated material showed significant increases in the apparent crystallite size when it was annealed at temperatures above 1900°C. Thus, it seems that removal of the microporosity from glassy carbon produces a material which is more stable on subsequent annealing than the carbon with microporosity.

A transmission electron micrograph of the unirradiated carbon after annealing at 2200°C is shown in Fig. 3. The magnification is not sufficiently high that layer planes can be resolved, but if the magnification was increased, planes could be resolved in each of the small bands in the micrograph. Several of these bands indicated by arrows. Thus, these bands are images of regions within the specimen where curved and/or twisted ribbons or sheets of parallel layer planes are perpendicular to the specimen surface.These microstructural observations are consistent with those made previously on fragmented specimens(1).

A similar micrograph of the irradiated specimen after annealing at 2200°C is shown in Fig. 4. Not surprisingly, it does not appear the same as the unirradiated material. Bands are no longer visible. However, very small diffraction-contrast fringes are now present. Several are marked by arrows. Although slightly smaller, these fringes appear identical to those observed in isotropic pyrolytic carbons where it was shown that the fringes always appeared in regions where the layer planes were perpendicular to the surface of the foil and that the fringes were perpendicular to the layer planes (4,5). Assuming this to be the case in Fig. 4, the orientations of the diffraction-contrast fringes suggest that the tangled microstructure is still present since the fringes frequently fall in a series which apparently defines a band similar to those of the unirradiated material. (See the fringes marked by arrows in Fig. 4.) Also, within small regions fringes are oriented in many different directions. Thus, irradiation apparently did not destroy the tangled microstructure.

These results indicate that the microporosity in the tangled microstructure of glassy carbon is not the structural feature responsible for its resistance to crystallite growth during annealing. Rather they show that removal of the microporosity enhances the stability of the material. The high resistance to crystallite growth in glassy carbon probably lies in the tangled nature of the microstructure. Since increases in the average crystallite size most probably occur through growth of one crystallite at the expense of others and since interstitial mobility in the crystallites is high in directions parallel to the layer planes (6), easy transfer of atoms to one crystallite would require that adjoining crystallites have nearly the same orientation. This is not the situation in glassy carbon. Densification of the structure through irradiation apparently does not change this arrangement, but "tightening up" of the structure would accentuate the

misalignment of neighboring crystallites and thereby make crystallite growth more difficult.

References

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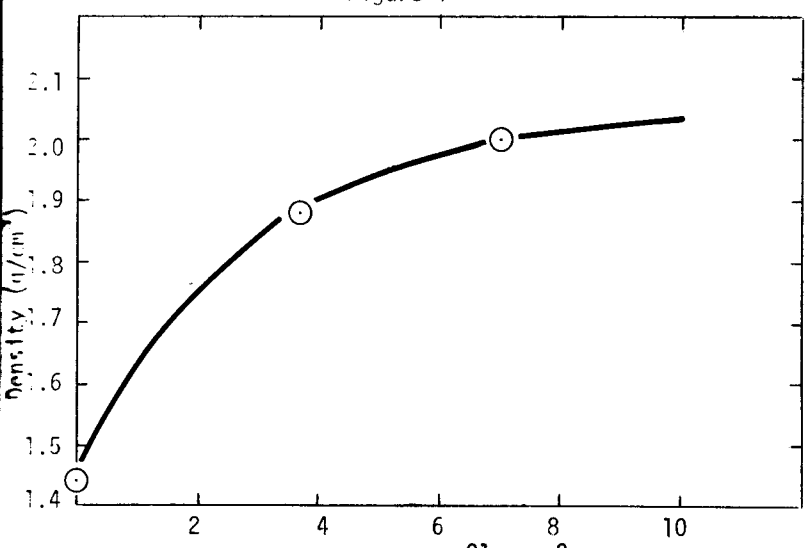
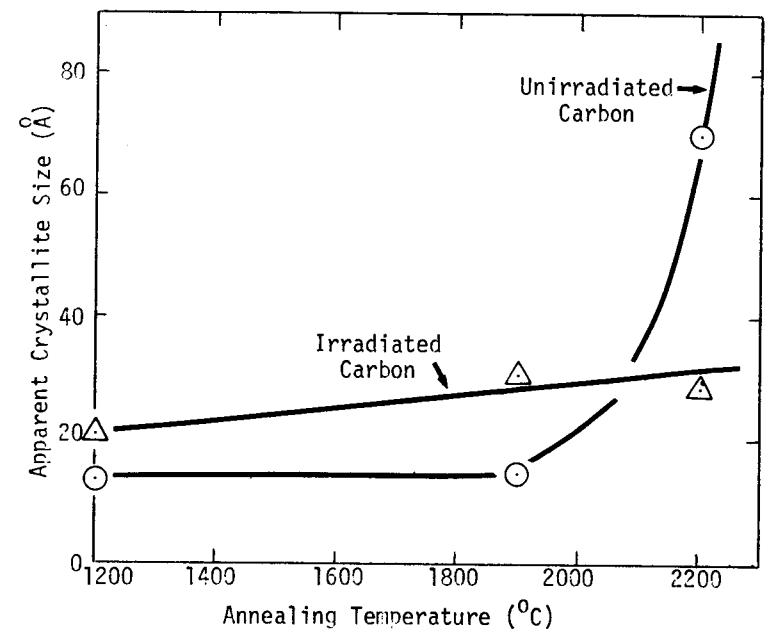
Figure 1



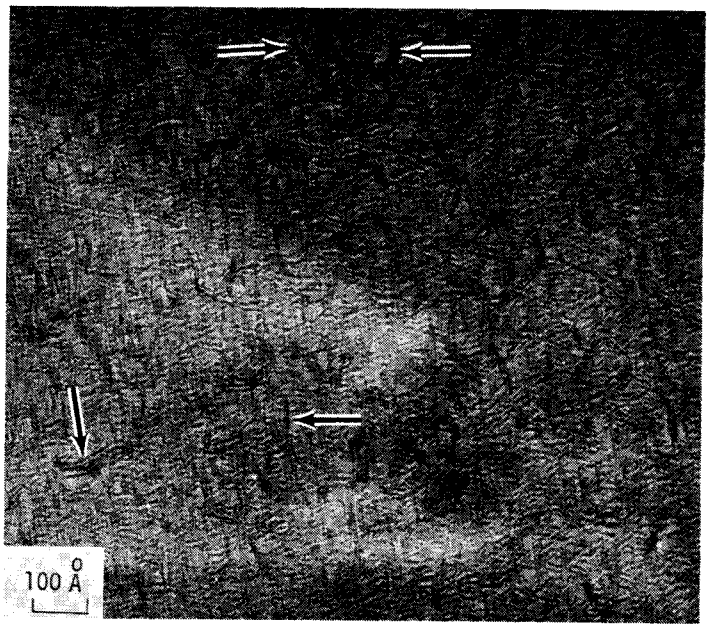
Variation of density during irradiation at 1100°C.

Figure 2



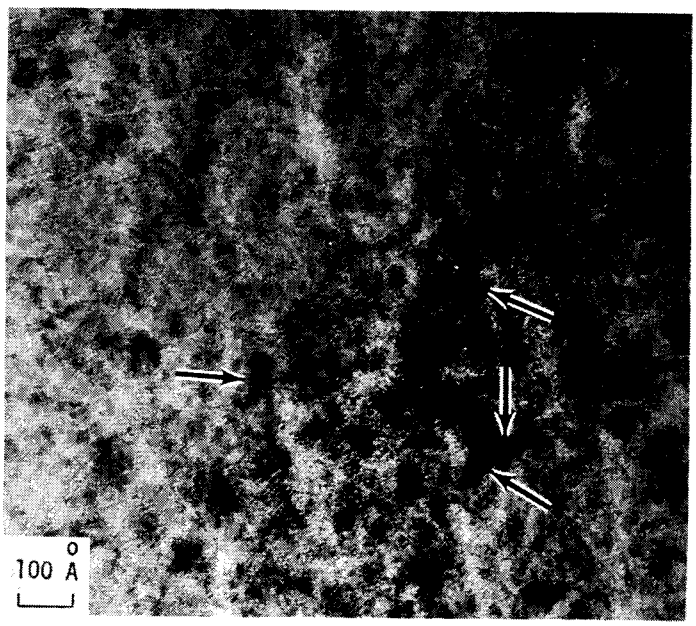
Apparent crystallite size (L_c) as a function of annealing temperature.

Figure 3



Microstructure of unirradiated carbon after annealing at 2200°C. Arrows indicate bands which are images of crystallites whose layer lanes are perpendicular to the surface of the specimen.

Figure 4



Microstructure of irradiated carbon after annealing at 2200°C. Arrows indicate diffraction contrast fringes similar to those observed in isotropic pyrocarbons.