CONF-680620--1

MICROSCOPY STUDIES OF GRAPHITIZATION^(a)

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INTRODUCTION

The structure of graphite, as revealed by replica electron microscopy, is now a familiar sight in the literature. For a wide variety of graphites, the characteristic lamellar features revealed have many similarities; however, to fully utilize the interpretive capabilities of replica electron microscopy it is necessary to recognize variations in basic structural patterns and their causes. The purpose of the work presented here has been to review a broad range of graphites derived from graphitizable carbons and to identify similarities which could then be related to common processes of structural development. With better knowledge of the basic pattern, deviations become recognizable and may be related to raw materials or other process variables.

We will first look briefly at several methods of preparing graphite surfaces for replication, then examine in detail the basic structure common to all polycrystalline graphites, and finally, illustrate the development and modification of this structure.

DISCUSSION

The interpretation of electron micrographs is critically influenced by techniques used to prepare surfaces for replication. In Figure 1a, a replica from an as-polished sample reveals the mechanically worked surface which must be removed to examine undisturbed structure. Polishing does not grossly alter the orientation of graphite at the surface but leaves small broken platelets which mask subtle structural differences. Cathodic

(a) This paper is based on work performed under United States Atomic Energy Commission Contract AT(45-1)-1830.

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vacuum etching is commonly used to remove this worked surface; however, insufficient etching could result in misinterpretation (Figure 1b). The broad featureless areas represent regions in which the etch rate is lowered, probably by localized variations in electrical conductivity, which perturb ion bombardment. Etching in hydrogen (Figure 1c) results in the formation of "fish-scale" features in areas where layer planes intercept the surface at low angles. Chemical reactions apparently cause the uneven stripping of layer planes and also produces pits where layers intercept the surface at high angles. Krypton etching gives a uniform etch and with sufficient time reveals the lamellar features in Figure 1d. The groove networks are often interpreted as microcracks or "Mrozowski" cracks; however, light oxidation etching (Figure 2) after a cathodic etch adds detail indicating the grooves are not all associated with open microcracks. Close examination suggests that the grooves develop on slip zones from which disordered carbon is etched more rapidly. Microcracks do appear in these grooves and in many cases may have existed at some earlier stage in processing; however, categorically identifying all such grooves as microcracks is inaccurate.

Figure 2 illustrates a basic structure found in most graphites which we will explore further. For the purpose of discussion, a subgranular structural unit may be defined as material bounded by slip zones or microcracks parallel to layer planes and low angle tilt boundaries or high angle interfaces intercepting layer planes. Within these boundaries many smaller lamella approximating the thickness of crystallites lie parallel to the subgrain boundaries. Subgrain dimensions range from 0.5 to 5 microns thick ("c" direction) with lengths ("ab" directions) from 1 to 50 microns. No limit in length has been established for highly aligned graphites.

In studying the development of subgrains we find the earliest evidence for the formation of basal boundaries in baked carbon derived from a petroleum coke-coal tar pitch mix (Figure 3). The

filler coke was precalcined to 1300°C and the mix baked at 900°C. Subgrain basal boundaries appear in the filler coke in the upper half of Figure 3a. Basal boundaries are etched deeper in material graphitized to 2450°C (Figure 3b); however, no evidence for the development of boundaries crossing layer planes is found.

In comparing pyrolytic carbons annealed without external stress to 2700°C and 3150°C (Figure 4), additional basal boundaries appear at the higher temperature indicating subgrain thicknesses may reach a maximum at low or intermediate processing temperatures and then decline at very high temperatures as new slip lines develop. This observation also suggests that bonding and disordered layer planes associated with basal subgrain boundaries have a strengthening effect which causes new slip zones to develop to accommodate shear.

Other subgrain modifications can be identified with early stages of processing. The patterns of orientation which subgrains follow are, of course, fixed while the raw material is still in a plastic state. The complexity of folding which may be established during mesophase development (Figure 5) is well known and was discussed earlier in papers given during the First Session.

Disturbances which can modify or even prevent subgrain development can also be traced to the plastic state. Graphites prepared from uncalcined or "raw" coke show little evidence of subgrains (Figure 6). The fracture surface of such a graphite (Figure 6b) reveals warped and kinked structures apparently caused by stresses introduced during reforming in the low temperature state. Another low temperature effect is found in coal tar pitch which has been graphitized en masse (Figure 7). Free carbon inclusions are concentrated in disordered clusters and the remaining material is well aligned. Subgrains develop in the aligned regions but do not appear where inclusions are concentrated. When coal tar pitch is used as a binder, inclusions remain dispersed and reduce subgrain development.

Final development of subgrains appears at 2700°C (Figure 8) with the appearance of boundaries normal to layer planes. Polygonization of curved lamella creates low angle tilt boundaries which in many cases become microcracks. Other high temperature modifications in the form of kink bands are found in graphites subjected to stress at high temperature (Figure 9). It is of interest to note the absence of polygonization in this material and the degree of distortion accommodated without the formation of microcracks normal to layer planes.

Although subgranular structures are common in polycrystalline graphites, it is difficult to define larger structures corresponding to grains in metals. In the presence of certain metals however, grains do develop as shown in Figure 10. In Figure 10a, 7% B₄C in graphite processed above 2600°C resulted in almost total conversion of filler-binder structures to granular structures. Subgrains are again a prominent structural characteristic in this graphite. In Figure 10b, uranium migration at a temperature above 2450°C proceeded from right to left causing complete recrystallization including carbon blacks which can be seen in the partially altered matrix at the extreme left.

A somewhat different grain structure is found in graphite formed from liquid carbon. Figure 11 is an optical micrograph of a portion of a globule of graphite formed by self-resistance heating pyrolytic graphite in an argon atmosphere at 1900 psi. Characteristic structures include acicular graphite needles interlocked with intragranular penetrations, many intergranular voids, and small crystal growths protruding from basal surfaces. The results of electron microscopy will be forthcoming soon; however, there is some optical evidence that subgrains were also formed.

SUMMARY AND CONCLUSIONS

A subgranular structure has been identified in graphites representing a broad range of morphological characteristics.

Subgrains have been defined as lamellar features bounded on basal sides by slip zones and at the edges by tilt boundaries. Subgrains may be distinguished from crystallites by size and by the continuous nature of their boundaries. Basal subgrain boundaries begin to develop during calcining or baking while edge boundaries do not appear until polygonization occurs at about 2700°C. Modifications of subgrain structures are introduced at low temperatures by stresses and inclusions and at high temperatures by external stress and interactions with metals. Internal stresses apparently cause a reduction of subgrain thicknesses above 3000°C by the creation of new slip zones. Studies of granular forms of graphite have been extended to include new variations found in graphite crystallized from the liquid phase.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11