Synthetic Graphite Advanced Topics; Morphology

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2006

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Synthetic Graphite: Advanced Topics

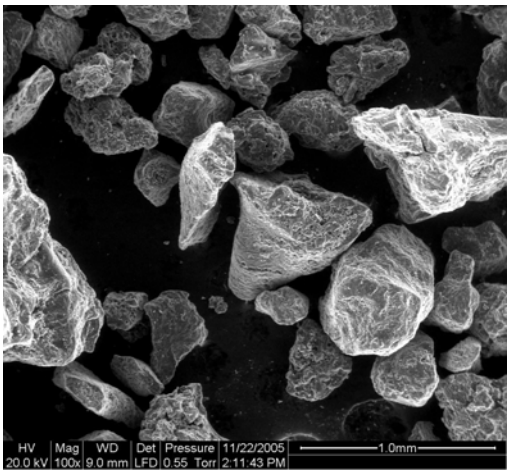
Readers of this section are urged to read the articles in the main heading "A Rigorous Introduction to Graphite" presented on the Asbury Carbons Technical Services page to learn more about the basic structure and properties of graphite materials in general. All of the topics detailed there apply to synthetic graphite.

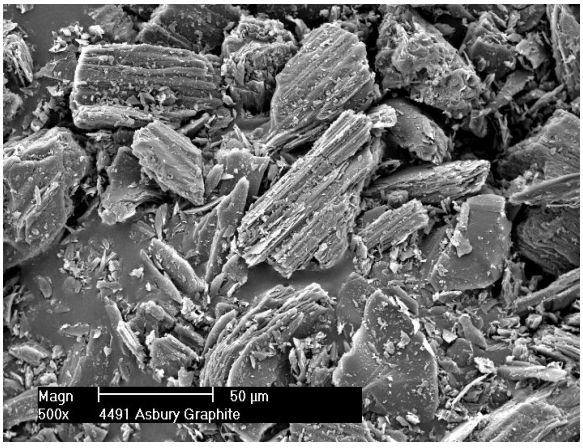
The Morphology of Synthetic Graphite:

Synthetic graphite is a man made material. Manufacturing methods rely on the heat treatment of specially selected precursor carbons that have been shown to be graphitizing carbons. As described elsewhere in these pages, the precursors are typically carbonaceous materials that have passed through the mesophase state and have, more or less, some degree of pre-graphitic crystalline orientation.

The gross morphology of these graphitizable, but not yet graphitized materials can vary from irregular, isotropic grains to elongated acicular anisotropic grains. Large grains of such materials can appear to be cementations of irregular grains, acicular grains, or both. In some cases even large grains show a preferred orientation. However, in no instance do these pre-graphitic carbons exhibit any macroscopic indication of the hexagonal morphology typical of graphite.

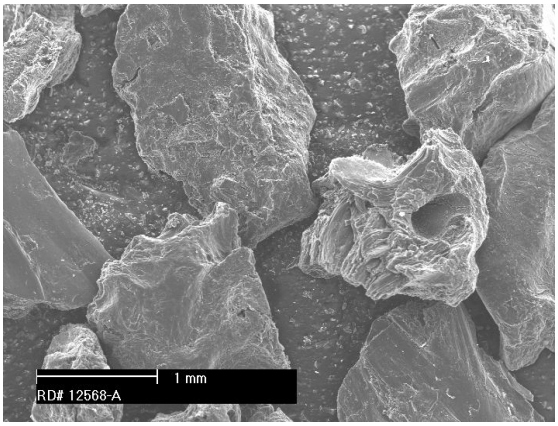
Below are a number of scanning electron micrographs that illustrate the morphology of graphitizable calcined petroleum coke materials. The SEM on the left illustrates coke with granular isotropic morphology with no preferred orientation apparent. The SEM on the right shows a coke with acicular, anisotropic morphology with obvious preferred orientation.

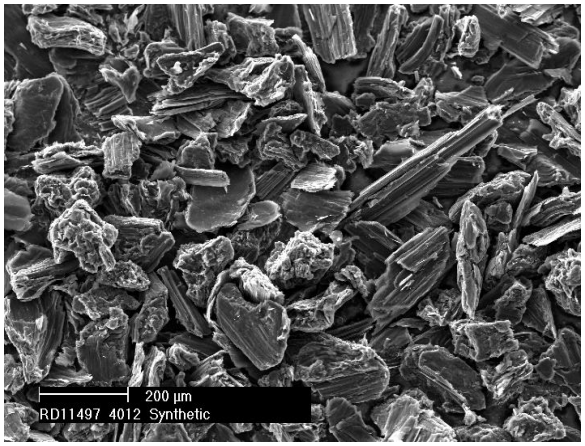




During the graphitization process the materials illustrated in these SEM images do not melt or become plastic. Therefore no apparent gross changes in macro-morphology occur. A piece of calcined petroleum coke that starts out looking like a vesicular, irregular grain, looks much the same after being graphitized (except reflectance will typically increase). An acicular coke will graphitize to acicular-form graphite. The two SEM images below illustrate this. The SEM labeled RD12568-A is a graphitized coke

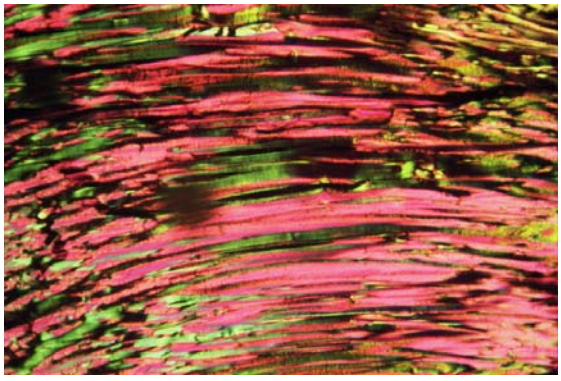
which has irregular grain, nearly isotropic macro-morphology. The SEM labeled RD11497 is a graphitized coke with acicular macro-morphology.

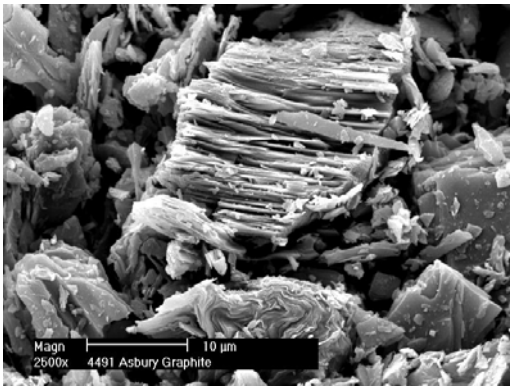




The key descriptive word in the above text is *macro-morphology*. On a macro or gross scale there is no apparent morphological distinction between carbon that is amorphous, and that same carbon in the graphitized state. This is because the graphitization process occurs on a microscopic rather than macroscopic level. Some degree of euhedral morphology is visible to the trained eye in certain highly graphitized synthetic graphite materials when viewed under low power magnification (approx 100X); however crystal forms or faces are typically identifiable only under high magnification or by inference through polarized light microscopy or X-ray diffraction techniques.

Some insight into the semi-ordered state of pre-graphitic carbon: Soft carbon materials can be further divided into their ability to form graphite. Some soft carbon graphitizes more readily or thoroughly than other soft carbon. Some types of soft carbon enter the graphitization process in a highly ordered pre-crystalline state with well ordered layers that, more or less, require only C axis indexing. One such carbon is known as *needle coke*. The accompanying micrographs of needle coke illustrate this concept.

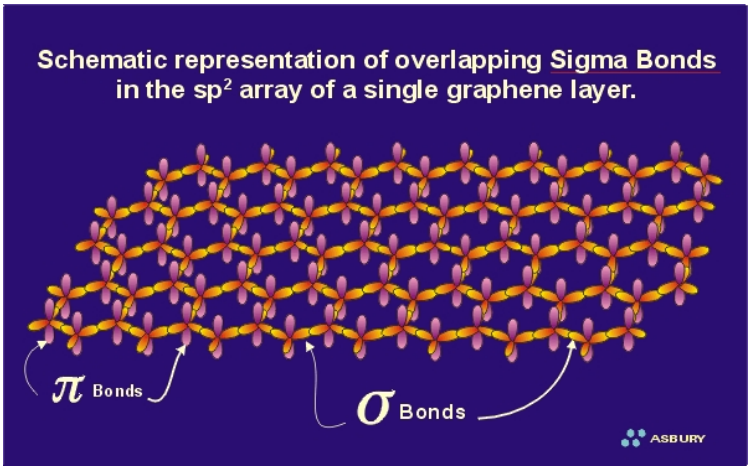




The term *needle coke* comes from the highly developed acicular or needle-like macro-morphology exhibited by this type of coke. These micrographs show the highly anisotropic morphology of needle coke at two levels. The photo on the left is a polarized light micrograph of a polished section of needle coke showing the anisotropic flow domains (image courtesy of Prof. John Crelling, SIU). The two colors indicate the orientation or direction of the carbon structural units that make up the flow regions. The

color banded regions shown can be thought of as layers that extend into and out of the page (notice that the micrograph shows a material that has obviously gone through a fluid phase during its heat treatment history). These layers are actually pseudo-graphene layers that are made up of sp2 carbon atoms arranged in hexagonal ring structures contained in large arrays.

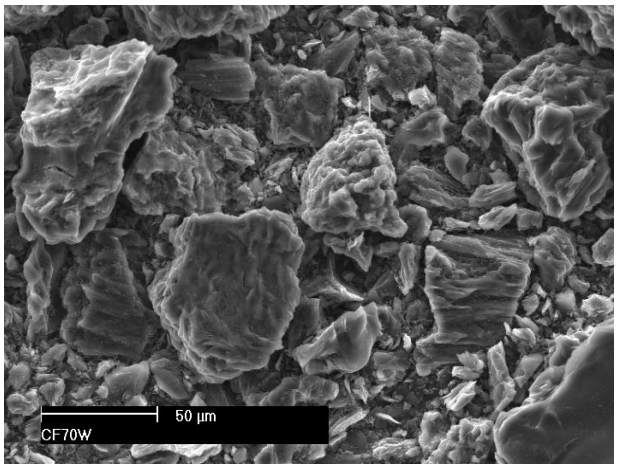
The right hand micrograph above is an SEM of a similar needle coke material that has not been prepared in any way. The layers visible are another view of the same type of layers visible in the polarized light micrograph. If it were possible to optically resolve these layers individually they would resemble the illustration below, which is a schematic representation of a single graphene layer.

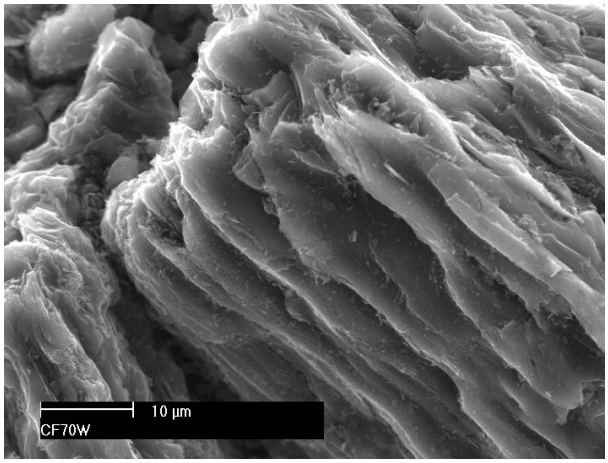


During the coking process (described elsewhere in this article) these layers form as the mesophase forms, grows, and organizes. These layer structures begin their existence as discotic (disk shaped) liquid crystals that coalesce into the mesophase.

Prior to the final heat treatment that results in the formation of graphitic carbon a high degree of two-dimensional (A) axis ordering already exists in these carbons. All that remains to complete the graphitization process is the indexing of graphene layers along the (C) axis. The relationship between the microscopic arrangement of carbon atoms and the macroscopic expression of that arrangement is well illustrated here.

Although not clearly visible in graphitizing isotropic cokes the same layer structures clearly apparent in needle cokes are present, however they are not as well developed. Below are two SEM images of an isotropic coke at low and high magnification.





The micrograph on the left gives the viewer an indication of the gross morphology. The concentration of acicular coke visible in this material is very low, indicating an isotropic

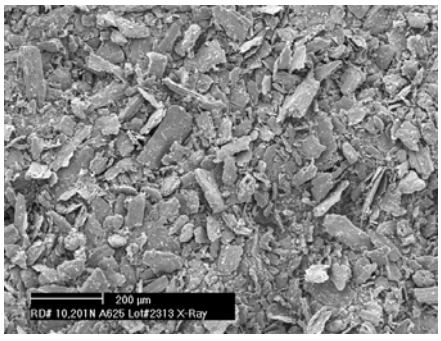
rather than anisotropic microstructure. However, at higher magnification (right hand image) the same coke product clearly exhibits a layered structure similar to the needle coke shown above. Although this coke will form graphite it is apparent that the graphite may not be the same as that formed from the needle coke precursor. Since during the graphitization process no gross changes in morphology will occur the gross morphology of the resulting graphite of these two different materials will differ in the same way that the macro-morphology of the cokes differ. The microstructure of the graphite, however, will differ in the size and extent of the crystals that make up the polycrystalline structure of synthetic graphite. It is beyond the scope of this article to expound on this topic. Suffice it to say, however, that a precursor carbon with well developed layer structures prior to graphitization may have larger, better developed graphite domains after graphitization.

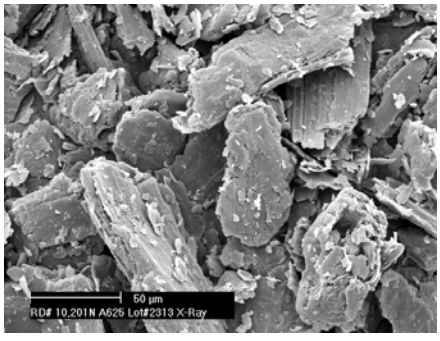
Morphology of Synthetic Graphite-Advanced Concepts; Convergence to Flake Morphology:

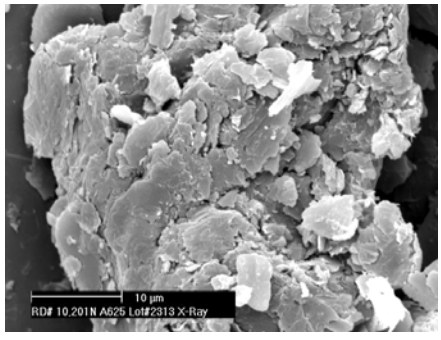
Due to the anisotropic atomic and molecular bonding of carbon atoms in the graphite structure (described in detail elsewhere in these pages), graphite is built on a system of stacked layers. These layers are present because although there are strong covalent bonds holding adjacent, in-plane, carbon atoms together there are no such bonds between planes.

The precursor carbons illustrated and described in the previous section of this article are themselves based on layered structures albeit some have larger, better developed layers than others. Regardless of the size or orientation of the layered structure of a graphitized carbon, at some point (or level of magnification) this morphology will show itself to the observer. This statement is true regardless of the precursor carbon. Graphite will always revert to a layered or flaky morphology as all graphite has the same molecular structure that fits the same hexagonal crystallography. The next series of scanning electron micrographs will be used to illustrate this concept.

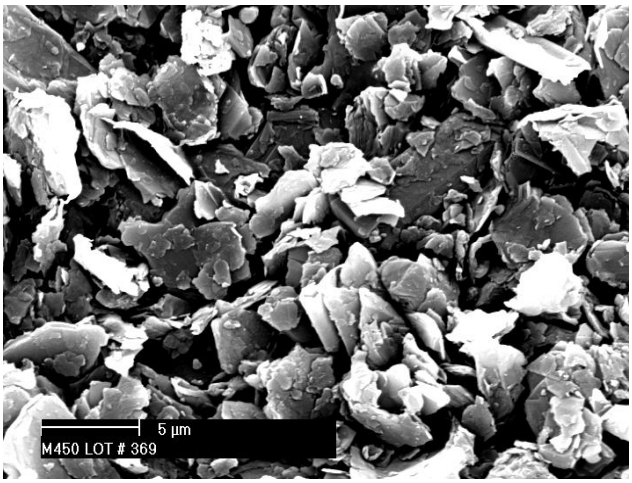
The following images are of Asbury A625 synthetic graphite. A625 is manufactured from a petroleum coke precursor carbon. All three images are of the same sample and differ only in magnification. The image on the far left shows that this graphite has a gross or macro-morphology that is somewhat acicular but does not appear flaky especially if compared to natural flake graphite. The center image is the same view field at a higher magnification. Note that at this level of magnifacation the needle structure inherent to the precursor coke becomes more apparent. In the final image of the series, to the extreme right, the flaky morphology is clearly visible under high power. If this product were ground to a fine powder (10-20micrometers or less) the resultant particles would be all flakes and be very difficult to distinguish even from natural flake graphite.

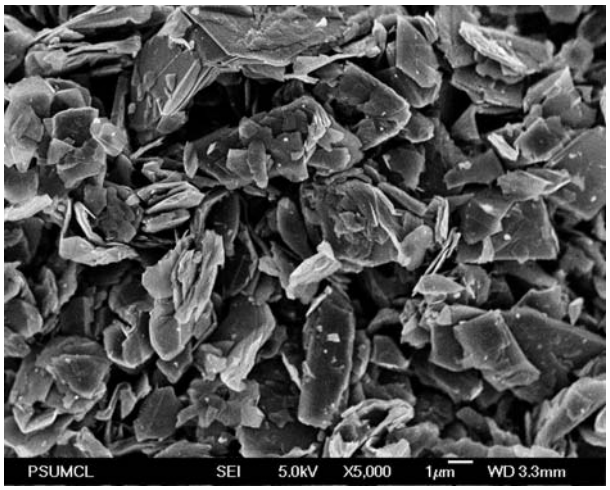






Below are two SEM images that illustrate the similarity between the micro-morphology of highly crystalline, naturally occurring flake graphite and finely ground synthetic graphite.





The micrograph on the left is Asbury Micro-450, a nominal 5-micrometer synthetic graphite powder. The micrograph on the right is Asbury Micro-850, a nominal 5-micrometer natural flake graphite powder. At this magnification it becomes difficult if not impossible to distinguish which of these powders originate from the graphitization of petroleum coke by artificial means, and which one is formed from natural geologic graphitization of pre-historic organic remains. Although methods are available which allow these substances to easily be distinguished from one anther, particle morphology at this level is not one of them.

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