A Graphite Primer

Graphite is one of the three readily occurring solid forms of carbon. It exhibits very unique properties which make it an attractive material for use in several industrial applications. Some of these unique properties include high electrical and thermal conductivity, good compressive and flexural strength, machinability to complex configurations, and stability at ultra high temperatures. Graphite has no known melting point at normal pressures and sublimes (changes phase from a solid directly to a gas similar to dry ice) at temperatures in excess of 3000°C. These unique physical properties often make graphite the material of choice for EDM electrode applications.

Graphite exists as a naturally occurring mineral and is mined in such countries as China, India, Brazil, and Canada. However, naturally occurring graphite does not necessarily possess the properties necessary for its successful application to our industry.

Artificial graphite is a crystalline material (See Fig #1) which is inherently anisotropic in nature. That is, it has a grain direction resulting in physical property differences depending on with and against grain directions much like wood. This anisotropy can be controlled by the choice of raw materials, the graphite particle size, and the molding method used in the production of the material. Of these three, the molding method has the most pronounced effect.

There are two primary molding methods used to produce graphite: The extrusion process which results in a high degree of grain directionality, and the isostatic process which minimizes grain direction by pressing the billet equally in all directions simultaneously. This article will deal exclusively with the isostatically molded graphite materials typically used in the EDM process.

A Brief History of Graphite

The graphite industry evolved from the previously fledgling carbon industry, which involved blending highly carbonaceous particles with various binders, molding to a desired shape, and baking to form a solid carbon material. Some of the early carbon products included dry cell battery carbons and early arc projector electrodes. These products were followed with the development of carbon brushes to support the growing electric motor industry.

The artificial graphite industry followed when it was discovered that some carbon materials could be converted to a graphite-like material through an ultra high temperature graphitization process. In fact, this graphitization process was developed and patented in France in 1893 by Charles Street, an engineer working for Le Carbone, one of the forerunners of the current Mersen Group. However, it would be many years before this process would be utilized to manufacture industrial quantities of graphite.
**Raw Materials**

Artificial graphite is manufactured from two basic raw materials: petroleum coke particles as the filler and coal tar pitch as the binder.

The predominant filler used in the manufacture of graphite is calcined petroleum coke (See Fig #2). This material is a by-product of the distillation and coking of crude oil from the petroleum industry’s manufacture of gasoline products. Coking is a thermal treatment process applied to the petroleum residuals to bring about a thermal decomposition, or removal of its volatile fractions. The resultant petroleum coke is a solid, porous carbon material and is normally calcined at temperatures in excess of 1000°C prior to use by the graphite industry. (Calcining is a thermal treatment process similar to coking, but it is performed at a much higher temperature than coking in order to remove any residual volatile that may not have been driven off during the coking process.) Not all petroleum coke can be used in the manufacture of graphite, and graphite manufacturers go to great lengths to select only the best of these cokes for their use.

The coal tar pitch (See Fig #3) binder is a glass-like super-cooled liquid, which is obtained as a by-product of the destructive distillation of coking coal. Although this is also a very large tonnage industry, only very select fractions of coal tar pitch are applicable in the manufacture of artificial graphite.

Graphite Manufacturers specify very discreet softening point ranges and chemical compositions for the coal tar pitches they intend to use.

The process for manufacturing graphite is shown in Figure #4 and explained in the following text.

**Milling**

After inspection and property verification of the incoming raw materials, the initial step in the graphite process is to mill the coke filler to the prescribed particle or grain size. The tiny dust-like particles produced in this step are captured by what is essentially a large dust collector and deposited in a bag. (See Fig #5) For the purpose of this article, we will limit our discussion to artificial graphite with typical filler sizes ranging from 4 to 20 microns in cross section. These are the graphite materials most often used in the EDM process and represent the great majority of isostatically molded specialty graphite grades.
Mixing
After milling, the coke particles and coal tar pitch, along with trace additives to facilitate processing, are combined in a heated mixer (See Fig #6) which melts the pitch and intimately mixes the pitch binder and coke filler. Various mixing times and conditions are utilized, with parameters dictated by the process specification for the particular grade being manufactured. Once the mixing cycle has been completed, the mix is allowed to cool and re-solidify into “mix balls” as they are sometimes referred.

Crushing & Milling
These “mix balls” are then crushed and milled into “flour” using a pulverizing process.

Screening
At this point, the graphite grade is determined, although its form remains as coke particles coated by the coal tar pitch binder. This “green mix,” as it is referred to in the industry, is then staged for molding. A rough screening operation is sometimes performed on the molding flour to remove any particles that may not have been properly pulverized by the prior operations.

Pressing
Cold isostatic pressing is the preferred method for molding fine grain specialty graphite materials. In this process, the “molding flour” is loaded into a rubber bag supported by rigid, perforated tooling that provides size and shape. This tooling assembly is then loaded into the isostatic press (See Fig #7) and pressed to shape at pressures as high as 20,000 psi. The isostatic press (See Fig #8) is

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a large pressure vessel and the pressure is applied equally in all directions through a hydraulic fluid. For this reason, the resultant pressed billet exhibits nearly no grain direction and will have nearly equal properties in all directions when converted into graphite.

**Baking**

The next step in the manufacturing process is baking the “green” billet. In reality, the billets at this stage are shades of black in color and are only referred to as “green” in that they have not yet been fired. In the baking process, the molded billets are raised to temperatures approaching 1000°C at a prescribed ramp rate. This is accomplished in very large, micro-processor controlled, natural gas fired kilns (See Fig #9). During this process the coal tar pitch binder is converted into a solid carbon binder. It is imperative that temperature ramp rates be accurately controlled during this process to avoid cracking. In practice, for the fine grain graphite materials we are discussing, total baking times can range from one to two months. After baking, the material is now a true solid baked carbon that is very hard, abrasive, and exhibits poor electrical and thermal conductivity. With the exception of a few mechanical carbon applications, the material in this state has little commercial value and should be considered as just an intermediate step in the manufacture of graphite.

**Graphitizing**

Now that the billet is a true solid, it can be subjected to the ultra high temperature treatment widely known in the industry as graphitization. The graphitizing process involves electrical resistance heating of the carbon material to temperatures approaching 3000°C. The graphitizing process consumes enormous amounts of electricity. (As a result, Mersen has its own sub station tied directly to the grid.) Because resistance heating is used to reach graphitizing temperatures, the heating time is fairly short. However, a much longer time is required to allow the now graphite material to cool sufficiently to be unloaded. In practice, this process normally takes from one to three weeks to complete.

During this ultra high temperature graphitizing process, the amorphous carbon undergoes a radical change. The small crystallites seen in amorphous carbon grow and realign into much larger continuous benzene ring layer planes normally associated with the theoretical graphite lattice. It is this transformation that provides the artificial graphite material with the high thermal and electrical conductivity as well as machinability that are required in its use.
Testing
Physical testing to verify properties and removal of the outer mold skin are all that remain to be done before the graphite billet is ready for sale. The typical physical properties tested to characterize the graphite for quality assurance include apparent density, electrical resistivity, flexural strength, hardness and residual ash. For specific applications, additional testing is often done prior to approval, including EDM wear ratio, CTE, compressive strength, and oxidation rate. After QA approval of the graphite billet, it often undergoes a cleaning operation in which the outer surfaces of the billet are machined (See Fig #10) away to remove any contamination that may be present on the billet surface.

History of Mersen USA
Mersen’s European roots began with the Le Carbone Company in France in the 1890s. As noted earlier, the original graphitization patent was actually assigned to Carbone in 1893. Carbone became one of the leading graphite producers in Europe.

Mersen USA's roots begin near the turn of the 20th Century. Its life in North America began in 1906 as the Stackpole Battery Co., later renamed Stackpole Carbon Co. The early products manufactured by Stackpole included dry cell batteries, battery carbons, and electric motor brushes. By the 1960s, Stackpole was manufacturing a very large tonnage of graphite chlorine cell anodes and was beginning development of isostatically molded fine grain graphite materials. Through the 1970s and into the 1980s, Stackpole continued to refine the isomolded graphite process and became a significant player in the fine grain graphite markets including EDM, Continuous Casting of metals, the manufacture of advanced ceramics, the new semiconductor market, and others.

Carbone acquired the Stackpole Carbon Co. in 1991. The acquisition resulted in the synergistic combination of Carbone Europe’s unique knowledge of raw materials and an advanced graphitizing process with Stackpole's expertise in mixing, isostatic pressing, and baking, along with their ability to manufacture large size billets. Recognizing these strengths, Carbone's management approved almost continuous plant expansions throughout the ‘90s continuing to present, making the current plant in St. Marys, PA one of the largest isomolded graphite facilities in the world. In addition, by utilizing the efforts of the R&D and Engineering groups in both St Marys and France, Carbone continued to advance their technologies and asserted itself as a leader in the fine grain graphite industry worldwide.

In 2010, management decided to restructure the entire organization under the new Mersen name. This reorganization was done to bring all companies worldwide under a common focus and unify their worldwide capabilities toward the endeavor of becoming the world leader in all their focus markets.

This in no way changed the commitment of the former companies to the fine grain graphite market but rather provides the opportunity to utilize their strong capabilities in the more than 40 countries and beyond where Mersen has a presence.

Mersen recently commissioned the largest cold isostatic press in the world at their St Marys, PA facility with an inside diameter of more than 86” and capable of 20,000 psi molding pressures. This new press and a planned further expansion of the St. Marys, PA facility will ensure Mersen has the ability to supply the growing graphite market with a variety of sizes and forecasted tonnage.
The DarkStar Particle

In conjunction with the aforementioned expansion, Mersen has continued to expand its product offerings to the marketplace. 10 years ago Mersen (Carbone of America at the time) began a program to develop an ultra-fine grain graphite that not only performed in the EDM process equivalent to anything currently available, but also was readily machinable. Based on years of experience, Mersen recognized that simply milling existing grades finer was never going to get the results desired. In order to obtain the desired material characteristics, a new raw material and new process would have to be developed. After several years of research, it was determined that this new raw material would have to be specially made to satisfy the unique property requirements, and Mersen would likely have to manufacture this special raw material in-house. Mersen recognized that the new raw material would need to be synthesized from a readily available, highly carbonaceous, raw material. Utilizing various thermal and mechanical processes, engineers refined several potential raw materials until they found the answer to their needs. The result was a raw material which provided outstanding adhesion when processed at the ultra high temperatures required to obtain the quasi-graphitic state of an EDM graphite electrode, while maintaining the single phase characteristics required to facilitate machining. Thus, the DarkStar particle was born.

Mersen quickly recognized that the new DarkStar material could not be processed using traditional graphite manufacturing techniques. A pilot plant line was set up and after considerable tweaks to the process and product testing, a manufacturing plant was constructed. The end result of this ten year endeavor is the new DS-4 ultra-fine grain EDM graphite.

Mersen EDM Grades

Mersen USA produces all of its graphite in its St. Marys, PA facility. Mersen manufactures a complete line of EDM grades from the coarser grain E+18 material used for its high metal removal rate at an economical price to the ultra-fine grain DS-4 material, which performs equal to or superior to any other readily available graphite in the most demanding EDM applications. The complete Mersen EDM graphite lineup includes:

### Mersen EDM Graphite Grades

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<th>Grade</th>
<th>Grain Size (microns)</th>
<th>Bulk Density (g / cc)</th>
<th>Flexural Strength (psi)</th>
<th>Hardness (Shore)</th>
<th>Resistivity (ohm - inch)</th>
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Now you can confidently handle your most challenging EDM machining operations while saving money! Top-performing DS4, featuring the DarkStar ultra-fine carbon particle, is the result of years of intense R&D and field testing/usage. DS4 is the latest EDM graphite innovation from the United State’s largest producer of specialty graphite, Mersen. It’s time to give DS4 a try… we’re confident you’ll like the results.

Our proven ultra-fine grain EDM graphite delivers an unmatched performance/value package!

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DS4 Delivers:
• Excellent surface finish
• Intricate detail
• Easy to machine
• Exceptionally strong

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