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## Introduction

Each year, large volumes of high-purity graphite powders are used worldwide in many applications. These applications include electrochemical storage systems, like batteries and fuel cells, friction materials, carbon brushes for electric motors, refractory, lubricants and iron powder metallurgy.

Within graphite powders, one can distinguish two main families of commercial products: natural and synthetic graphite. Natural graphite is produced by extracting and concentrating ore that presents sufficient graphite content. The graphite powders so obtained can have different grain sizes and purity. Higher purity can be obtained by a subsequent chemical or thermal purification step. Synthetic graphite, also called artificial graphite, is obtained by transformation of a carbonaceous precursor into graphite through an industrial process, called graphitization.

In this paper, after briefly pointing out the physical and chemical properties of graphite, we will describe the main stages of the different production processes, which lead to high-performance finished products. We will show then, how these main categories of powders intervene in various applications and outline the main application-related properties, that are achieved in nowadays commercially available products.

## Graphite, Its Structure and Its Basic Properties

Graphite is a crystalline solid of black-grey colour with a metallic sheen, whose structure, described by Hull [1], corresponds to a stacking of planes of carbon atoms, that are bonded to each other by covalent bonds with  $sp^2$  hybridization. In a layer or plane, the atoms are arranged according to a hexagonal pattern and thus constitute what is called a "graphene sheet". On the other hand, the interactions between the planes of graphite are weak, due only to Van der Waals forces. This facilitates the "slip" of the planes onto each other, when mechanical pressure is applied. This property of graphite, of being easily cleaved along the graphene sheets, is mainly responsible for its lubricating properties.

Due to its electronic structure, graphite shows a high electrical conductivity. It can reach 25'000 S/cm [2] in the plane of a single-crystal. In dense polycrystalline graphite materials, conductivity is in the range of 1'000 S/cm [3] and the anisotropy factor is reduced to a few units at the most.

Thanks to its chemical (layered) and electronic band structure, graphite is an ideal host for the intercalation of certain atoms. Depending on the type of atoms, i.e. reducing metals [4] or acid-oxidizing molecules [5], one speaks of "intercalation compounds" or "graphite salts", respectively. On the other hand, graphite is generally very stable in corrosive environments and also exhibits a good oxidation resistance. At high temperature and in oxidizing atmosphere, graphite "burns" primarily at the edges of the layers, where the most reactive sites are located [6].

## Natural Graphite: from Mine to Finished Product

Natural graphite results from the transformation of organic matter deposits subjected to the effect of very strong metamorphic pressures combined with high temperature, over millions of years. Some deposits are sufficiently rich to allow a profitable exploitation by selective mining. Operations like rock drilling and blasting by explosives can be necessary to the extraction of the ore, whose graphite content generally varies between 3 and 20%, depending on the deposit. Basically, the graphite flakes are liberated by successive phases of mechanical grinding in wet phase. The purpose of this stage is to release the maximum of graphite flakes, while trying as well as possible to preserve the integrity of the large-sized flakes, which yield the highest market value. Subsequently, the flakes released are separated from the impurities (gangue) by flotation. This process, repeated several times, makes it possible to reach purity levels as high as 99.0% carbon. The flakes collected are then dried and

classified in different particle size ranges by sieving, according to the needs of the various applications.

To reach higher purity, treatments by chemical purification are necessary. The two methods used are: leaching with hydrofluoric and hydrochloric acid, or the hydration of graphite by caustic soda followed by leaching with hydrochloric acid. Thermal treatment at high temperature (> 2000 °C) also allows the purification of natural graphite.

Different types of natural graphite have different denominations: for example, microcrystalline graphite (erroneously called “amorphous” graphite) corresponds to a product, whose flakes and crystallites have relatively small size. Macrocrystalline graphite refers to graphite products with bigger flake and crystallite size. The name “vein” or “lump” graphite is strictly reserved for a special type of graphite, mainly sourced in Sri Lanka.

## Primary Synthetic Graphite: Precursors and Graphitization

Primary synthetic graphite is synthesized specifically for the desired application, whereas secondary synthetic graphite (also called “scrap”) is a by-product of the electrode industry. Secondary synthetic is produced by milling turnings recovered from machining operations or from spent or defective graphite electrodes, mainly produced for aluminum or steel production [7,8]. It usually has a lower level of crystallinity than primary and also shows much bigger property variations (ash, density, crystallinity, etc) between different production lots.

Primary synthetic graphite powders are obtained from mixtures of selected carbon precursors, like petroleum and coal tar-based cokes. These cokes are graphitized by heat treatment at temperatures above 2500 °C under exclusion of oxygen. During the heat treatment process, the amorphous coke material is purified and transformed into crystalline carbon. Various continuous and batch graphitization processes are possible for this heat treatment. A traditional batch process is the Acheson furnace technology [7]. In this process, the carbon raw material is positioned between two electrodes and covered by refractory powder material to protect it from oxidation. Electric current is passed through the carbon bulk, which acts as an electric resistance between the electrodes. In this way, based on the Joule effect, temperatures above 3000 °C can be generated inside the furnace. Of course, in this case electrical power is the main cost factor for the production of synthetic graphite. At the end of the graphitization process, bulk agglomerated graphite is unloaded from the furnace (see Fig. 1), sampled and analyzed. In this way, crystallinity, impurities and all relevant properties can be controlled before further processing of the raw graphite takes place.

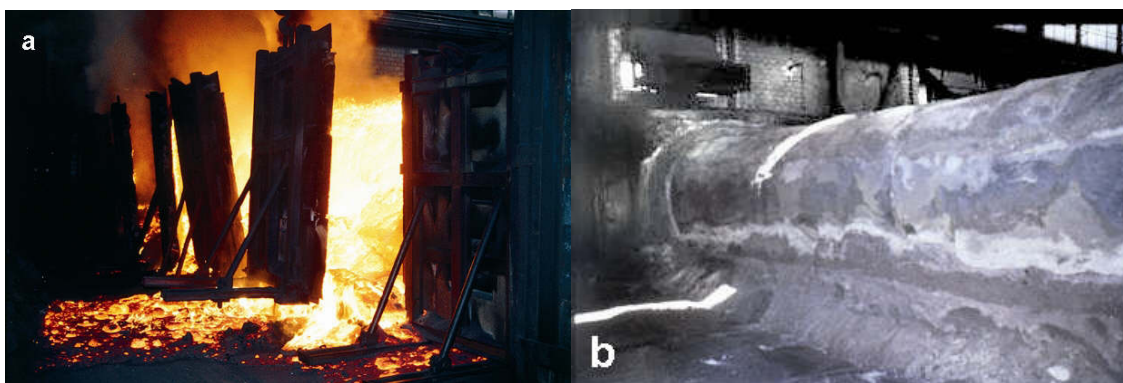


Figure 1 - Beginning a) and end b) of the cooling phase after the graphitization process.

By using high-purity cokes as starting material in the graphitization process, purity levels above 99.9 % can be achieved routinely. The final properties of synthetic graphite result from the choice of the precursor materials and from the process parameters, combined with strict quality control of the starting materials.

## Primary Synthetic and Natural Graphite Powders: Milling and Conditioning of the End Products

Graphite has a relatively low value of hardness (0.5-1 in Mohs [9]). However, due to its flaky shape and the strength of the covalent bonds within the graphene sheets, milling of graphite to fine particle size is very difficult. For sizes above 100 microns, any type of hammer mill and industrial sieving equipment will do the job, with low energy input and low contamination level. On the other hand, for fine particle size ( $d_{90} < 44$  microns), the process becomes very energy-consuming and the level of contamination by metal increases sharply. Therefore, the choice of the mill to be used takes into account the desired particle size distribution and the production cost, but also several other criteria, like maximum impurity level, and even preferred shape of grain (aspect ratio). The latter can be modified to some extent during the milling process or by an extra conditioning step after milling.

Among the milling techniques used, one can distinguish:

- **Ball mills:** grinding media (metal, ceramic, etc,..) and graphite powder are put into motion inside a closed vessel by rotational or vibration energy. This allows very drastic size reduction of the particles in a very short time and can be operated in wet or dry conditions. Depending on the mill geometry and on the parameters chosen, the milling effect is mainly due to shear stress or to impact energy, thus influencing the final particle size distribution (PSD) and shape of the powder product.
- **Mechanical or hammer mills:** the milling energy comes from a rotor with blades, pins etc, moving at high peripheral speed (around 100 m/s). Graphite particles are ground by the impact with the blades and by collisions between each other and with the inner jacket of the mill.
- **Air-jet mills:** particles are accelerated by air jets and comminution is achieved by collisions between the particles (autogeneous milling) or against a target.
- **Final PSD control:** for very fine products, sieving cannot be used at industrial level, so the final particle size and the amount of fines are controlled by means of air classifiers with a rotating wheel. In the case of hammer or jet mills, such devices are integrated in the mill. Quite often, a reduced fraction of fines can be of advantage for the final application, like in carbon brush and batteries. In this case, special classifiers adapted to the fine particle size range (0-10  $\mu\text{m}$ ) have to be used in a separate processing step after milling.
- **Shape-surface modification:** some applications require modifications of the surface morphology or particle shape. In these cases, an extra mechanical process can be applied after the milling process. An example of this is the manufacture of products with increased bulk density by a patented process (potato-shaped™ graphite [10]).

As a special case, expanded graphite deserves being mentioned, in view of its quite unique properties. The production process is based on the expansion, occurring during thermal shock, of intercalated natural graphite flakes. First, large flakes of high-purity natural graphite are intercalated with a strong acid. Subsequently, by applying a thermal shock at optimized conditions, it is possible to produce expanded graphite with very low density (5-10 g/liter) and with coarse “worm-like” shaped grains. These grains are extremely anisometric particles formed by stacks of graphene sheets. By a special milling technique it is possible to manufacture products with fine particle size ( $d_{90} = 40\text{-}100 \mu\text{m}$ ), that are extremely effective as conductive additives at low loading (see “mobile energy, alkaline batteries”).

Summarizing, based on this wide portfolio of raw materials and processes, it is possible to manufacture graphite powders, designed to provide high performance in many specific applications. This is achieved by controlling all relevant powder properties like crystallinity, ash, impurities, spring back, specific surface area, surface texture and particle size distribution. Moreover, the application of very strict quality control criteria to all processing steps, from the mine to the graphitization, to the final milling and conditioning, allows manufacturing of powder products with very high purity and very high consistency of properties.

## Fields of Application for Graphite Powders

We classified the main applications of graphite by the market segments, where the powders are supplied to, namely mobile energy, tribology-lubricants, automotive industry, thermally conductive polymers and the metallurgy sector.

### Mobile Energy

*Alkaline Batteries:* Graphite is used as conductive additive in the cathode, together with electrolytic manganese dioxide (EMD). For this application, both synthetic and natural graphite grades are used (see Fig. 2). High-purity powders with very high crystallinity, good compaction properties and fine particle size ( $d_{90} < 44 \mu\text{m}$ ), ensure the high conductivity level required at low graphite loading. At the same time, graphite gives lubricity and thus reduces tool wear in production, during pressing of the cathode rings. Corrosion resistance plays a key role in this application, being related to cell gassing and leakage. Strict control of the metallic impurity residues (few ppm) of the graphite material allows to minimize such effects, while keeping cell performance at maximum.

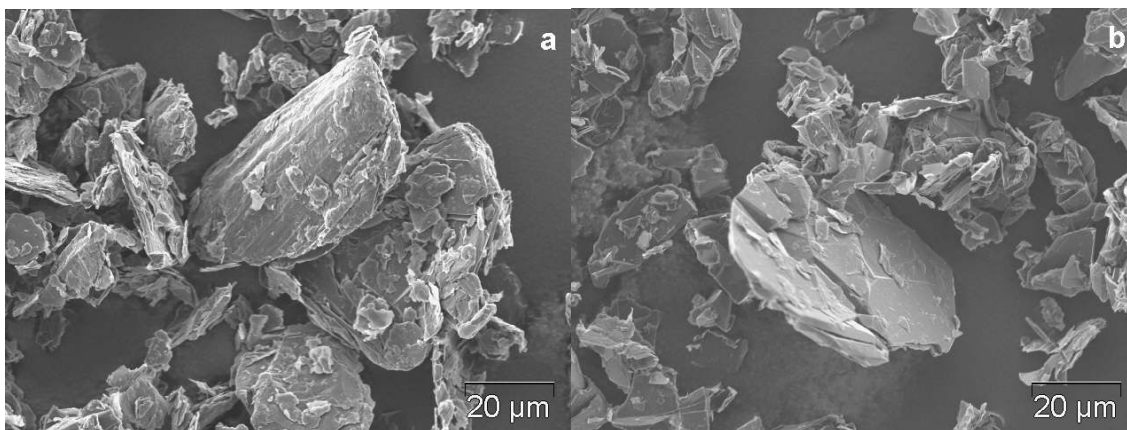


Fig.2 - Grains of synthetic a) and natural b) graphite powders.

Various types of hammer and jet mills with customized features allow to manufacture a complete range of products with different price/performance ratios and different morphologies, that ensure maximum effectiveness at reduced weight loading. For high-end batteries expanded graphite [11,12] can be used. Due to the very high anisometry of its particles, this particular graphite material can be used at lower loading than non-expanded powders, thus boosting the cell performance. On the other hand, expanded graphite is difficult to mix with electrolytic manganese dioxide, due to the very big difference of apparent density of the two powders. This problem can be solved by using “composites” made of non-expanded and expanded graphite materials [13].

Rechargeable Lithium-ion Batteries: graphite is widely used as active material in the negative electrode, due to its ability to reversibly insert lithium ions between the graphite layers. In batteries with optimized electrodes, the reversible electrochemical capacity is maintained over several thousands cycles.

Powders with high apparent density allow to pack more grains in the electrodes and this results in batteries with higher energy and power density, as requested by the market. Such powders with high apparent density can be obtained by “round-shaping” of both natural and synthetic graphite grains [10].

Another key requirement for this application is that the graphite surface should be compatible with the chemistry of lithium-ion batteries (salts, solvents and binders).

Fuel Cells-Bipolar Plates: most bipolar plates today are manufactured by compression moulding of a graphite/polymer (or resin) compound with graphite loading in the range 75-85 wt%. The plates so obtained have a surface with built-in flow fields, are lightweight, gas tight, corrosion resistant, mechanically stable and have high electrical conductivity in the through-plane direction. High purity, medium-coarse graphite ( $d_{90} = 44-200 \mu\text{m}$ ) with very low anisotropy are the preferred choice, but very often a graphite mixture is used. This can include a small fraction of very fine graphite grades or conductive carbon blacks and carbon fibers.

As an alternative, bipolar plates can be made with flexible expanded graphite, manufactured by a process similar to the one used for foil and gasket production (see “graphite seals” below). In this case the raw material is medium-fine flaky natural graphite.

Fuel Cells-GDL and MEA: the manufacturing of electrode components like Gas Diffusion Layers (GDLs) or Membrane Electrode Assembly (MEA) with low thickness, controlled porosity and low electrical resistance, requires very fine powders with controlled PSD and good corrosion resistance. Both graphite and carbon black are used for this purpose. For catalyst support, an extra requirement is a very high surface area, to ensure high catalytic activity at low loading. High surface area graphite (HSAG) shows excellent corrosion resistance, whereas high surface blacks and carbons enable higher catalytic activity.

## Automotive Applications

Friction Materials: graphite powders are used in the manufacture of brake pads or drums and clutch facings. Graphite has to provide the required level of friction coefficient at different operating conditions. It also contributes to temperature, vibration and noise control, while keeping wear rate and cost within acceptable limits. The spectrum of products and technical requirements is huge. It covers OEM parts and aftermarket, small vehicles like motorbikes, ATV, snowmobiles or small cars and heavy-duty vehicles like trucks, trains, airplanes and racing cars. To cover all these applications, medium-to-coarse powders ( $d_{90} = 44$  to  $1000 \mu\text{m}$ ) of synthetic graphite, both primary and secondary, and natural graphite, are mainly used. Graphite is very often used in combination with different cokes. All these friction grades are typically manufactured by means of mechanical grinding and sieving. A key issue is the consistency of the powder properties, especially PSD, density, ash level and ash composition.

Carbon Brush: graphite powder is a main component for the majority of the carbon brushes used in electrical motors. Its properties make it possible to adjust the lubricity, the density, the hardness, the wear and the electrical conductivity of the brushes. Medium-to-fine powders ( $d_{90} = 44-150 \mu\text{m}$ ) of primary synthetic graphite are widely used in resin-bonded carbon brushes of small size. Key parameters are tight PSD control, and very often a reduced amount of fines is essential to control resin absorption. Fine powders are manufactured mainly by means of hammer or air-jet mills with classifier, whereas natural graphite grades with medium PSD are obtained mainly by hammer mills in combination with sieving. High-purity natural graphite gives an optimum level of performance in

metallic or semi-metallic carbon brush for low-voltage, high-current applications, like automotive 12V systems.

In order to comply with the variety of technical specifications existing on electrical systems, powder products from electrographite, scrap and carbon black are also used in this field.

Graphite Seals: expanded natural graphite is processed by compression in sheets or foils by means of roll systems. These sheets of variable thickness are used for the manufacture of cylinder head gaskets for car engines and of valve or pipe joints in the chemical industry. The advantages of this type of graphite joints lie in their flexibility, thermal stability and excellent resistance to chemicals and to aging. Graphite foils are also finding use in thermal management for various electronic devices like plasma screen displays, portable computers, etc.

## **Tribology-Lubricants**

Graphite can be used as solid powder lubricant. As an example, it ensures lubrication of the brake shoes of the train wheels. Its lubricity is also exploited in oil- or grease-based suspensions. Water-based dispersions of graphite, including various additives (surfactants), are sprayed on hot steel mandrels at high temperature to ensure lubrication during the production of seamless tubes for oil drilling. Mixed as an additive in drilling mud, graphite "seals" the wall of the drilling well, thus decreasing the loss of mud pumped to evacuate the drilled rock fragments from the bottom of the hole. In addition, it also acts as lubricant for the drilling equipment, reducing wear of the drilling head and rods.

## **Thermally Conductive Polymers**

Carbon black is the additive of choice for plastics and rubber, both for reinforcement and for imparting electrical conductivity at low loading. The use of graphite powders in polymers or rubber is limited by the degradation of the mechanical properties that it implies. This effect can be somewhat reduced by use of finer powders ( $d_{90} < 44 \mu\text{m}$ ). On the other hand, if thermal properties are required, carbon black does not bring much and graphite, thanks to its crystallinity, becomes the additive of choice, as an alternative to metal flakes or powders. Typically, fine-to-medium high-purity powders of highly crystalline natural or synthetic graphite bring the best results for this application.

## **Applications Related to Metallurgical Industry**

Refractory industry is probably the largest existing natural graphite powder consumer. Over the years, graphite has become an essential additive, thanks to its excellent thermal properties and lubricity, combined with its inertness and hydrophobicity. The addition of graphite in certain refractory products significantly increases thermal shock and corrosion resistance. The most widespread application in iron and steel industry is undoubtedly the use of magnesia-carbon bricks, which can resist the corrosion caused by the impurity layer (slag), which occurs on top of the molten metal.

Graphite powder is also used as protective layer during melting of copper and other non-ferrous alloys. This layer prevents the molten metal bath to be in contact with the ambient air, thus avoiding the oxidation of the most reactive metals.

The list of applications of graphite powders mentioned above is not exhaustive, since it would be necessary to quote other applications, like pencils, iron powder metallurgy, synthetic diamonds, hard metals, etc. Nevertheless, it shows the diversity of the markets served, each one imposing its own technical and economical specifications. Thus, a graphite manufacturer has to position itself to respect at all time these contingencies and should always aim to develop products for technological applications with high added-value. It is only by offering performing and innovative products as profitable solutions to these markets, that it will be able to ensure its economical survival.



## References

- [1] A. W. Hull, Phys. Rev., **1917**, 10, p. 661.
- [2] W. Primak, L.H. Fuchs, Phys. Rev., **1954**, 95, p. 22.
- [3] T. Ishigawa, T. Nagaoki (Eds.), Recent Carbon Technology, ch. 2, JEC Press Inc., (1983)
- [4] A. Hérold, Bull. Soc. Chim., **1955**, 187, p. 999.
- [5] H. Thiele, Z. Elektrochem., **1934**, 40, p. 26.
- [6] L. Bonnetain, G. Hoynant, Les carbones Volume 2, Masson and Co (editors), (1965), chapter XVII, pp. 298-306.
- [7] M.B. Redmount, E.A. Heintz, in: Introduction to Carbon Technologies, H. Marsh, E.A. Heintz, F. Rodriguez-Reinoso (Eds.), ch. 11, Alicante: Universidad (1997).
- [8] H. Marsh, K. Fiorino, in: Introduction to Carbon Technologies, H. Marsch, E.A. Heintz, F. Rodriguez-Reinoso (Eds.), ch. 12, Alicante: Universidad (1997).
- [9] Handbook of Chemistry & Physics, ED. R.C. Weast, 70<sup>th</sup> Edition, 1899-1990, CRC Close Inc, Florida.
- [10] Mr. E. Spahr, D. Cattaneo, K. Streb, Method for producing graphite powder with an increased bulk density, Patent WO 01/38220, Timcal Ltd., (2001).
- [11] Y.Mototani, J. Asaoka, H. Tanaka, Alkaline manganese battery, patent EP 0'675'556, Matsushita Electric Ind. Co Ltd., (1995).
- [12] G. Furdin, J-F Marêché, A. Hérold, Flat micronic graphite, process for its preparation and its applications, patent WO 93/08123, (1993).
- [13] Mr. E. Spahr, H. Wilhelm, Electrochemical cell, Patent WO 03/032415, Timcal Ltd. (2003).

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