THE APPLICATION OF CARBON MATERIALS IN ADVANCED TECHNOLOGIES

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Abstract. Innovation, often, takes the form of replacing a component made of one material (a metal, say) with one made of another (a polymer, perhaps), and then redesigning the product to exploit, to the maximum, the potential offered by the change. The engineer must compare and weigh the properties of competing materials with precision: the balance, often, is a delicate one. It involves an understanding of the basic properties of materials; of how these are controlled by processing; of how materials are formed, joined and finished; and of the chain of reasoning that leads to a successful choice.

Keywords: material, properties, redesigning

1. Introduction

Carbon is a truly remarkable element which can exist as one of several allotropes. It is found abundantly in nature as coal or as natural graphite, and much less abundantly as diamond. Moreover, it is readily obtained from the pyrolysis of hydrocarbons such as resins and pitches, and can be deposited from the vapor phase by cracking hydrocarbon rich gases. In its various allotropic forms carbon has quite remarkable properties. Diamond possesses the highest thermal conductivity known to man and is prized as a gem stone. Both of these attributes result from the high degree of crystal perfection and bond strength in the diamond lattice. Graphite possesses extreme anisotropy in the bond energies of its crystal lattice, resulting in highly anisotropic physical properties. The most recently discovered allotrope of carbon, C_{60} or Buckminsterfullerene, has been the subject of extensive research, as have the related carbon nanotubes and nanostructures.

Engineered carbons take many forms. For example, cokes, graphites, carbon and graphite fibers, carbon fiber - carbon matrix composites, adsorbent carbons and monoliths, glassy carbons, carbon blacks, carbon films and diamond like films.

There are many applications for diamonds and related materials, e.g., diamond-like carbon films, and there are potential applications for Fullerenes and carbon nanotubes that have not yet been realized. However, the great majority of engineering carbons, including most of those described in this article, have graphitic micro-structures or disordered graphitic microstructures. Also, most engineering carbon materials are derived from organic precursors by heat treatment in inert atmospheres (carbonisation). A selection of technically important carbons obtained from solid, liquid and gaseous organic precursors is presented in table 1.

Table 1. Precursors for engineering carbons [2]

Primary precursor	Secondary precursor	Example products
Hydrocarbon gases		pyrocarbons, carbon blacks, vapor grown carbon fibers, matrix carbon
Petroleum	petroleum pitch mesophase pitch	delayed coke, calcined coke needle coke, carbon fibers, binder and matrix carbon mesocarbon microbeads, carbon fibers
Coals	coal chars coal tar pitch mesophase pitch	semi-coke, calcined coke activated carbons premium cokes, carbon fibers, binder and matrix carbons mesocarbon microbeads, carbon fibers
Polymers	polyacrylonitrile phenolic and furan resins polyimides	PAN-based carbon fibers glassy carbons, binder and matrix carbons" graphite films and monoliths
Biomass		activated carbons

Modern day applications of carbon materials are numerous. Indeed, the diversity of carbon applications are truly astounding, and range from the mundane (e.g., commodity adsorbent carbons or carbon black), to the exotic (e.g., high modulus carbon fibers that enable the lightweight stiff composite structures used in airframes and spacecraft).

2. Crystalline forms of carbon

The commonest crystalline forms of carbon, cubic diamond and hexagonal graphite, are classical examples of allotropy that are found in every chemistry textbook. Both diamond and graphite also exist in two minor crystallographic forms: hexagonal diamond and rhombohedral graphite. To these must be added carbynes and Fullerenes, both of which are crystalline carbon forms. Fullerenes are sometimes referred to as the third allotrope of carbon. However, since Fullerenes were discovered more recently than carbynes, they are chronologically the fourth crystalline allotrope of carbon. Crystalline Fullerenes are now commercially-available chemicals and their crystal structures and properties have been extensively studied. By contrast, convenient methods for mass production of pure carbynes have not yet been discovered. Consequently, carbynes have not been as extensively characterized as other forms of carbon.

a) Diamonds

- Natural Diamonds

Natural diamonds are classified by the type and quantity of impurities found within them.

- Type Ia - This is the most common type of natural diamond, containing up to 0.3% nitrogen.
- Type Ib - Very few natural diamonds are this type (~0.1%), but nearly all synthetic industrial diamonds are. Type Ib diamonds contain up to 500 ppm nitrogen.
- Type IIa - This type is very rare in nature. Type IIa diamonds contain so little nitrogen that it isn't readily detected using infrared or ultraviolet absorption methods.
- Type IIb - This type is also very rare in nature. Type IIb diamonds contain so little nitrogen (even lower than type IIa) that the crystal is a p-type semiconductor.

- Synthetic Industrial Diamonds

Synthetic industrial diamonds are produced the process of High Pressure High Temperature Synthesis (HPHT). In HPHT synthesis, graphite and a metallic catalyst are placed in a hydraulic press under high temperatures and pressures. Over the period of a few hours the graphite converts to diamond. The resulting diamonds are usually a few millimeters in size and too flawed for use as gemstones, but they are extremely useful as edges on cutting tools and drill-bits and for being compressed to generate very high pressures. (Interesting side note: Although used to cut, grind, and polish many materials, diamonds aren't used to machine alloys of iron because the diamond abrades very quickly, due to a high-temperature reaction between iron and carbon.)

- Polycrystalline Diamond (PCD), is a synthetic diamond product that is produced by sintering together selected diamond particles with a metal matrix using very sophisticated high temperature and high pressure technology. The PCD is by its nature, high in uniform hardness, and also more abrasive and shock resistant in all directions as compared to natural diamonds because of its random-orientation structure of the diamond particles.

Polycrystalline diamond (PCD) is generally recommended [2, 3, 5] for the machining of non ferrous workpiece materials where high abrasion resistance is required. Typical metal and plastic applications machined with PCD would be aluminum engine blocks, gearbox components, transmission components and body panels. Typical wood working applications would be furniture, laminated flooring, ceiling/wall cladding.

Examples of typical workpiece materials are as follows:

- Chipboard, fiberboard, particle boards and hard natural woods
- Metal matrix composite
- Aluminum alloys
- Copper, brass, bronze, magnesium alloy
- Ceramics, fiber glass, carbon fiber
- Plastic, rubber
- Pre-sintered (green) and sintered tungsten carbide
- Mineral material

Polycrystalline diamond cutting tools (figure 1) are highly sought by customers worldwide from the aircraft industry, auto industry, iron and steel industry, precision watch industry, and electric and electronic industries.

Polycrystalline diamond (PCD), although hard and highly abrasion resistant, has one limitation in respect to its use in application. That is the machining of ferrous workpiece materials. This is due to a chemical reaction between diamond and the iron in ferrous workpiece materials that can occur when heat is generated during cutting.

Figure 1. Polycrystalline diamond cutting tools

- Thin Film Diamonds

A process called Chemical Vapor Deposition (CVD) may be used to deposit thin films of polycrystalline diamond. CVD technology makes it possible to put 'zero-wear' coatings on machine parts, use diamond coatings to draw the heat away from electronic components, fashion windows that are transparent over a broad wavelength range, and take advantage of other properties of diamonds.

b) Graphite

The flat sheets of carbon atoms are bonded into hexagonal structures (figure 2).

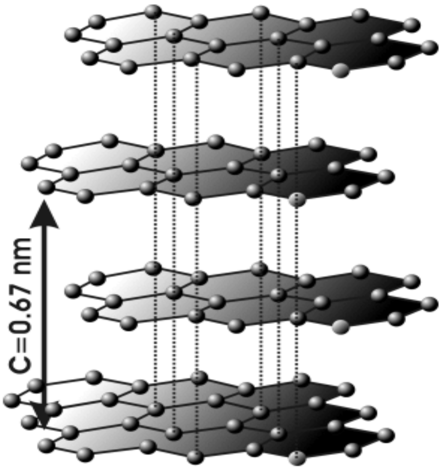

Figure 2. Graphite crystal system

Natural graphites occur widely around the world, although the quality of the ores varies widely. Principal uses of natural graphites are in the foundry and steel industries and in the refractory and electrical industries. Intumescent or expandable graphites are used in firestops, particularly plastic pipes and gaskets, fitted around the perimeter of a fire door. During a fire, the graphite expands and chars to resist fire penetration and reduce the likelihood of the spread of fire and fumes. A typical start expansion temperature (SET) is between 150 and 300 degrees Celsius.

Graphite also finds use as a matrix and neutron moderator within nuclear reactors. Its low neutron cross section also recommends it for use in proposed fusion reactors.

Most synthetic graphites used for engineering applications are granular composites consisting of a filler (usually a coke) and a binder carbon formed from pitch. The graphitic order in most engineering grade synthetic graphites is less well-developed than in natural graphite. Well-graphitised synthetic graphites are produced by hot-pressing pyrolytic graphite (HOPG grade); recently, well-graphitised carbons have been formed by heat-treatment of compacted polyimide films [8].

c) Carbynes

The different forms of carbynes were assumed to be polytypes with different numbers of carbon atoms in the chains lying parallel to the hexagonal axis and different packing arrangements of the chains within the crystallite.

Despite many publications on carbynes, their existence has not been universally accepted and the literature has been characterised by conflicting claims and counter claims.

Despite the scepticism in some quarters, a large number of chemical and physical methods have been developed for producing carbynoid materials. These include: dehydropolymerisation of acetylene, dehydrohalogenation of polyvinylidene halides and reductive dehalogenation of poly(tetra-fluoroethylene) and related compounds, condensation of carbon vapor produced by various means, e.g., laser ablation and arc discharge, shock compression of graphite and other solid forms of carbon.

d) Fullerenes and nanotubes

The large value measured for the elastic modulus [≈ 1 TPa (terapascal)] accounts for the straightness of small diameter nanotubes in TEM micrographs [2]. As a consequence of the elastic limit model, the thermal conductivity of carbon nanotubes along the nanotube axis is expected to be high, based on observations on carbon fibers, while the thermal conductivity between shells of a multi-wall nanotube or between single-wall nanotubes within a single rope is expected to be very low. Very low expansion coefficients are also expected tangential to the nanotube surface, consistent with the anisotropic and anomalous thermal expansion coefficient for graphite which is small and negative in-plane, and large and positive along the e-axis.

Extreme hardness was also found for bundles of carbon nanotubes, exceeding that of the toughest alloys used as substrates. Thus single-wall carbon nanotubes are believed to possess many of the desirable mechanical properties of carbon fibers, but, in addition, single-wall carbon nanotubes have a number of other desirable properties with regard to bending into loops, cross-sectional distortions, twisting distortions, elongation and compression without fracture.

Although research on solid C60 (figure 3), carbon nanotubes, and related materials is still at an early stage, these materials are already beginning to show many exceptional properties, some of which may lead to practical applications. Large scale production of C60 and C70 has already occurred. However, the production of significant quantities of reasonably pure carbon nanotubes has yet to occur.

Figure 3. Fullerene C_{60}

One promising application for C_{60} is as an optical limiter. Optical limiters are used to protect people and materials from damage by high light intensities usually associated with intense pulsed sources. Optical limiting is accomplished through a saturation of the transmitted light intensity with increasing incident intensity.

Another interesting applications area for Fullerenes is based on materials that can be fabricated using fullerene-doped polymers. Fullerene-doped polymers also have significant potential for use in applications, such as photo-diodes, photo-voltaic devices and as photo-refractive materials.

Fullerenes have been shown to benefit the synthesis of Sic and diamond. By fragmentation of individual of C_{60} molecules, diamond films of very small grain size can be synthesized, yielding superior wear resistance, and lubrication properties.

In other materials synthesis applications, the utilization of the strong bonding of fullerenes to clean silicon surfaces, has led to the application of a monolayer of C_{60} as a bonding agent between thin silicon wafers. These strong bonding properties, together with the low chemical reactivity of fullerenes, have been utilized in the passivation of reactive surfaces by the adsorption of monolayers of C_{60} on aluminum and silicon surfaces.

Because carbon nanotubes are conductive, they can provide a signal each time a target substance binds to the enzyme attached to the nanotube (figure 4).

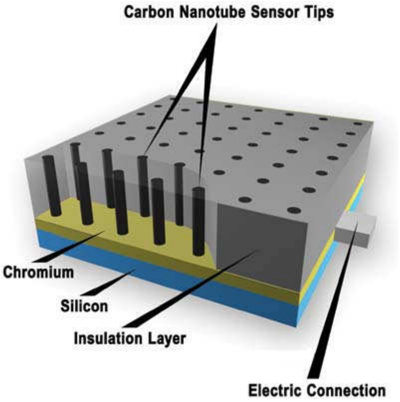

Figure 4. Carbon nanotubes offer specificity and electrical conductivity

The researchers are putting nano-tubes to work as biosensors and improving the way they can be chemically customized to form the basis for a wide variety of devices, including atmospheric and blood sensors [6]. They fashioned carbon nanotubes into a portable, automated sensor system for organophosphate (OP) detection. Besides posing a serious environmental hazard, OP compounds are the raw materials for nerve agents. Detecting these compounds could give emergency personnel a head start in responding to a terrorist attack in which such agents are used.

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