Materials Science and Engineering of Carbon: Fundamentals

(Second Edition)

碳材料科学与工程基础

(第2版)

[日] Michio Inagaki [中] Feiyu Kang

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Preface

One of the authors (M. Inagaki) has been emphasizing the importance of nanotexture, as well as structure, to understand carbon materials. In 1985, he proposed the classification of nanotexture of carbon materials on the basis of preferred orientation schema of anisotropic layers of carbon hexagons, planar, axial, point and random orientation. Nanotexture is formed during carbonization of organic precursor, as well as structure, and governs the structure development during heat treatment at high temperatures, which has been understood as graphitizing and non-graphitizing. Nanotextures can explain the reason why fibrous carbon materials exist, such as carbon fibers and tubes, and the spherical carbons, such as carbon blacks and fullerenes, from strongly anisotropic carbon layers consisting mainly of hexagons. In order to convince of the importance of nanotextures in carbon science and engineering, he published a book in Japanese entitled 'Materials Engineering of Carbons' in 1985, and another book in Japanese entitled 'New Carbon Materials - Structure and Functions' with his friend, Y. Hishiyama in 1994. In 2000, the book in English entitled 'New Carbons - Control of Structure and Functions' from Elsevier added the concept of carbon families, diamond, graphite, fullerene and carbyne, to follow the rapid progress in science, engineering and applications of carbon materials. However, he strongly felt that, even though many young scientists and engineers are interested in and working on nanocarbons, such as carbon nanotubes and graphenes, fundamental knowledge on carbon materials is necessary for them. Most basics of carbon materials were already clarified before 1985. The books, which give such fundamental knowledge on carbon materials, are rather few and also it must be handy and easy to buy. Therefore, he discussed with Prof F. Kang and decided to publish the book from Tsinghua University Press, China, entitled 'Carbon Materials Science and Engineering - From Fundamentals to Applications'. The book aims to give comprehensive information firstly on fundamental science on preparation and characterization of various carbon materials, and secondly on engineering and applications of various carbon materials, on the basis of the same basic concept as published before, i.e., classifications based on carbon families and nanotextures.

Since so many copies have been sold mostly in China, the present authors (M. Inagaki and F. Kang) decided to write advanced science and engineering on carbon materials under the corporation of two more authors (M. Toyoda and H. Konno) by taking in recent developments, and it was published in September, 2013, with the title 'Advanced Science and Engineering on Carbon' by two publishers, Tsinghua University Press and Elsevier. At the same time, the publishers asked the present authors to revise and up-date the previous book 'Carbon Materials Science and Engineering — From Fundamentals to Applications'. Here, the revised version is presented.

In this revised version, the content is largely revised and up-dated, for example, a chapter of nanocarbons is newly added, although fundamentals in carbon science and engineering do not change and the basic concepts, carbon families and nanotextures, are still valid. The authors hope to provide fundamental science and engineering on carbon materials, associated with some applications, to young graduate students who are working on various carbon materials and also engineers whose works are more or less related to carbon materials. It will be a great pleasure for the authors if they will always bring this book with them to discuss their results and to read the scientific papers published. They may find out how the data they got and/or those published either agree or disagree with the general information explained in this book, and also what is missing from this book.

Acknowledgments

The authors would like to express their sincere thanks to the people who kindly provided the data and figures for this book, the names and affiliations of contributed persons being mentioned in the caption of figures and tables. They also thank all of the people who took care of this book in Tsinghua University Press and also in Elsevier.

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Introduction

1

1.1 Carbon materials

Carbon C is one of the abundant elements on the Earth, because almost all organics are composed from carbon networks, and it is very familiar in our daily lives, for example, ink for newspapers, lead for pencils, activated carbons in refrigerators, etc. Carbon materials, which consist mainly of carbon atoms, have been used since prehistoric era as charcoal. In Japan, a large amount of charcoal (about 800 tons) was reported to be used for casting a great image of Buddha in Nara from 747-750. Soft graphite has been used for a long time as lead and carbon blacks as black inks. Diamond crystals are fascinating for all human beings not only as jewels but also the hardest materials were found to consist of carbon atoms, the same atoms as lubricating soft graphite in 1799. Nowadays various carbon materials are used in our daily lives, though many of them are inconspicuous; activated carbon produced from coconut shells for a filter of tobacco, carbon fibers for reinforcement of rackets and fishing rods, leads for automatic pencils, activated carbons for deodorization in refrigerators, membrane switches composed of graphite flakes for keyboards of computers and various instruments, etc. Charcoal may be the first carbon material used practically, as it has been used since the pre-historic age. Carbon materials started to be used as electrodes for batteries around 1800. Since 1878, large-sized carbon rods were used as electrodes for iron refining, which were industrially produced by heat treatment at high temperatures (as high as 3000°C) and called graphite electrodes because crystalline graphite structure was well developed in most of them. Later on, various carbon materials having graphitic structure for various applications were developed, which were called graphite materials, even though the development of graphitic structure is not complete. At the same time, carbon materials without noticeable graphite structure, such as charcoal, were also developed and opened new applications.

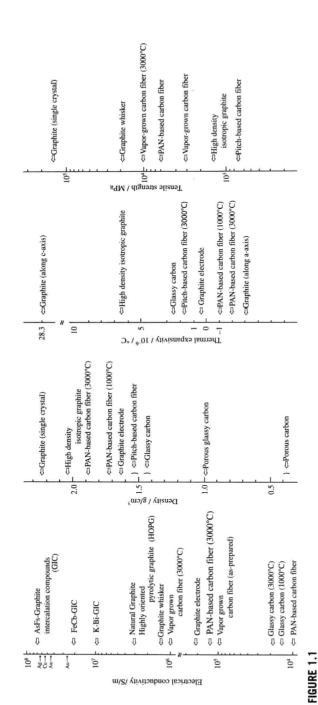
There was no clear definition and no clear-cut classification on what graphite materials are and what carbon materials are. In the present book, however, we will use the term 'carbon materials' for materials composed predominantly of carbon element, irrespective of their structure, so including fullerenes and carbon nanotubes, and also the terms either 'carbon materials' or 'carbons' for the materials without three-dimensional graphite structure. On the other hand, 'graphite materials' and sometimes 'graphites' were used for the materials which have three-dimensional graphite structure, even partly. In industry, the term 'graphite'

and 'graphitized' are often used, even though graphite structure is not developed appreciably; for example PAN-based carbon fibers heat-treated at a high temperature used to be called 'graphite fibers', even though almost no graphite structure was developed, as will be explained later in detail.

Polycrystalline graphite materials have been used in various fields of industries using their different properties. Their characteristics can be summarized as follows; (1) high thermal resistance in non-oxidizing atmosphere, (2) high chemical stability, (3) high electrical and thermal conductivities, (4) small thermal expansion coefficient and, as a consequence, high thermal shock resistance, (5) very light weight, (6) high mechanical strength at high temperatures, (7) high lubricity, (8) highly reductive at high temperatures and easily dissolved into iron, (9) non-toxic, (10) radiation resistance, and (11) low absorption cross-section and high moderating efficiency for neutron.

Since all polycrystalline graphite materials consist of parallel stacking of carbon hexagonal layers, like graphite, which are called crystallites, their properties of a bulk material are strongly governed by different factors, such as how large the crystallites are, how these anisotropic crystallites orient in the bulk, to what temperature they were heat-treated, etc. The preferred orientation of crystallites in bulk graphitic materials depends strongly on the condition of forming process and the heat treatment temperature governs the size and perfection of the structure. Therefore, most of the properties of carbon materials distribute in a wide range. In Fig. 1.1, electrical conductivity, bulk density, thermal expansion coefficient (expansivity), and tensile strength are compared for different carbon materials, including natural graphite, various fibrous carbon materials, and graphite intercalation compounds (GICs).

Polycrystalline graphite is a good electric conductor, but its electrical conductivity of roughly 2×10^5 S/m is inferior to metals. By intercalation of different species into the interlayer spaces of graphite, however, electrical conductivity is much improved and becomes even higher than that of metallic copper. Thermal expansion coefficient of graphite single crystal is very high along the c-axis (perpendicular to the graphite layer plane), but negative (i.e., shrinkage) along the a-axis (parallel to the layer). In polycrystalline graphite materials, this anisotropy in thermal expansion is spaciously averaged, depending strongly on the size and arrangement of crystallites (i.e., structure and texture). In fibrous carbons, it is mainly governed by expansion along the layer planes and so rather small values. In most of physical properties, such as electrical and thermal characteristics, the highest and the lowest values are realized in the directions perpendicular and parallel, respectively, to graphite layers, as shown on the electrical conductivity and thermal expansion coefficient in Fig. 1.1. Mechanical properties, such as tensile strength, and bulk density are texture-sensitive characteristics and so they show a wide range of values, in general. The practical values for various carbon materials including polycrystalline graphite materials (high-density isotropic graphite and graphite electrodes) are inferior to the theoretical values for graphite single crystal, because of their polycrystalline nature.



Range of various properties of carbon materials.

1.2 Short history of carbon materials

Development of carbon materials was discussed by dividing into three periods, before 1960, between 1960 and 1985 and after 1985, as summarized in Table 1.1. The year 1960 may be said to be the beginning of the era of new carbons, because of the inventions of carbon fibers from poly(acrylonitrile), pyrolytic carbons by CVD process, and glass-like carbons from thermosetting resins, which were completely different from the carbon materials used before 1960.

Up to 1960, four carbon materials were known and had practical applications in various fields of industries; artificial graphite blocks mainly used for steel refining, carbon blacks for ink and reinforcement of rubbers, and activated carbons for water purification, in addition to natural diamond. These carbon materials, except diamond because of its very different appearance and properties, were proposed to be called **classic carbons**.

In 1960, three carbon materials, carbon fibers, glass-like carbons, and pyrolytic carbons were developed, which were completely different from classic carbons in their production processes and also properties. Following these three carbon materials, different kinds of carbon materials had been developed under the modifications in precursors, preparation conditions, etc. So, we called these carbon materials **new carbons**, in the contrast to classic carbons. After the finding of graphite intercalation compounds having a high electrical conductivity, higher

Table 1.1 Carbon Periods				
Period	Years	Carbon Materials Developed	Remarks	
1	Pre-1960	Artificial graphite blocks Activated carbons Carbon blacks Natural diamond	Mass production Sale in either tons or kilograms	
II	1960-1985	Various carbon fibers Glass-like carbons Pyrolytic carbons High-density isotropic graphites Intercalation compounds Various composites Synthetic diamond Diamond-like carbons	Introduction of various techniques for the production of carbon materials (e.g., CVD, composite with other materials, etc.). Development of new applications Sale mostly in grams	
III	Post-1985	Fullerenes Carbon nanotubes Graphene	Nano-sized Sale in milligrams	

than copper, a boom in research on intercalation compounds has arisen in a world-wide scale, although it could not open the practical applications.

The year 1985 was another epoch for carbon materials, where a carbon cage consisting of 60 carbon atoms was found, which was named buckminsterfullerene C₆₀ and followed by a series of carbon cages, such as C₇₀, C₈₆, etc. In 1991, multi-walled carbon nanotubes were reported, which was followed by the finding of single-wall carbon nanotubes. In 2004, a single hexagonal carbon layer was reported. Finding of these novel carbons, **nanocarbons**, attracted pronounced attention to nano-scale science and technology, and accelerated the development of the science related to nanotechnology. In the course of nanotechnology development, the word **nanocarbons** came to be often used. Also, structure and texture of most carbon materials were required to be controlled in nanometer scale for all applications.

1.3 Classic carbons, new carbons, and nanocarbons

1.3.1 Classic carbons

The fundamental science and technology on classic carbons, artificial graphite blocks, carbon blacks, and activated carbons, were established before 1960, in the period I (Table 1.1). It has to be emphasized, however, that these carbon materials are principal products and principal incomes for carbon industries world-wide currently.

In Fig. 1.2, photographs of these carbon materials are shown. These three-carbon materials have a wide range of sizes; graphite electrodes representing artificial graphite blocks are used in a size of about 700 mm in diameter and about 3 m in length, carbon blacks are spherical particles with the diameter from 10 to a few hundred nanometers, activated carbons are porous materials with irregular

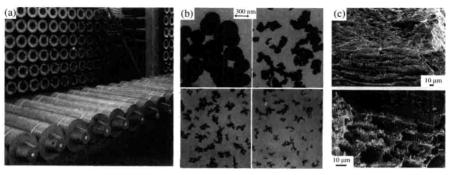


FIGURE 1.2

Classic carbons. (a) Graphite electrodes (b) Carbon blacks (c) Activated carbons.

shapes. Diamond is so rare in nature and expensive as to be measured by using the unit of carat, different from other carbon materials (gram).

1.3.2 New carbons

The important developments related to carbon materials since 1960, in the periods of II and III, are listed in Table 1.2. The period II started with the developments of PAN-based carbon fiber, pyrolytic carbon, and glass-like carbon, all three of them being completely different from classic carbons.

Carbon fibers [1], which were produced by carbonization of poly(acrylonitrile) fibers after oxidation (PAN-based carbon fibers; Fig. 1.3), fascinated people by their high strength and flexibility and many demonstrative pictures, for example, hanging an automobile by a thin string of carbon fibers, were published in various journals. The developments of other kinds of carbon fiber followed in the 1970s, including pitch-based and vapor-grown carbon fibers. In contrast to carbon fibers, glass-like carbon was very hard and brittle, and its gas impermeability which had never been realized in classic carbons was amazing [2]. It was named from its conchoidal fracture surface, similar to soda-lime glass. Now different products of glass-like carbon were industrially developed, as shown in Fig. 1.4. Pyrolytic

Table 1.2 Topics Related with Carbon Materials				
Year	Basic Science	Materials Development	Technology Development	
1960		PAN-based carbon fibers Pyrolytic carbons Glass-like carbons	Electrodes for electric discharge machining	
1965	Mesophase spheres in pitch	Needle-like cokes Mesophase-pitch-based carbon fibers		
1970	Biocompatibility of carbon materials	Vapor-grown carbon fibers	Carbon prostheses	
1975	High conductivity of GICs		Mesocarbon microbeads	
1980	Diamond-like carbon films	Isotropic high-density graphites Carbon-fiber-reinforced concrete	Carbon electrode for fuel cell	
1985		Buckminsterfullerene C ₆₀ , followed by various fullerenes	First wall for fusion reactor	
1990	Superconductivity of K ₃ C ₆₀	Carbon nanotubes, single- wall and multi-walled		
1995			Carbon anode for lithium ion rechargeable batteries	

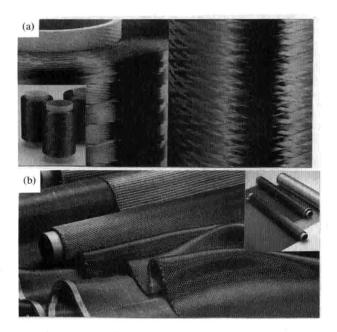


FIGURE 1.3

Carbon fibers.

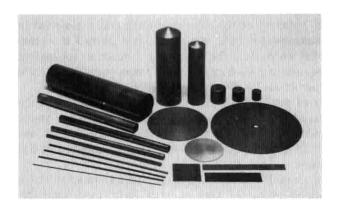


FIGURE 1.4

Products of glass-like carbon.

carbons were produced by a completely different technique from conventional ones, chemical vapor deposition (CVD) [3], though it is very common in material production nowadays. Their strong anisotropy in various properties, such as electrical and thermal conductivities, gave a quite new aspect for the application of