Springer Series in Materials Science 5

M. S. Dresselhaus · G. Dresselhaus
K. Sugihara · I. L. Spain · H. A. Goldberg

Graphite Fibers and Filaments

Springer-Verlag

M. S. Dresselhaus · G. Dresselhaus
K. Sugihara · I. L. Spain · H. A. Goldberg

Graphite Fibers and Filaments

With 226 Figures

Springer-Verlag Berlin Heidelberg New York
London Paris Tokyo

Professor Dr. Mildred S. Dresselhaus
Dr. Gene Dresselhaus
Dr. Ko Sugihara
Massachusetts Institute of Technology,
Cambridge, MA 02139, USA

Professor Dr. Ian L. Spain
Colorado State University,
Fort Collins, CO 80523, USA

Dr. Harris A. Goldberg
Celanese Hoechst Corp.,
Summit, NJ 07901, USA

Guest Editor: Professor Dr., Dres. h. c. Manuel Cardona
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1
D-7000 Stuttgart 80, Fed. Rep. of Germany

Series Editors:

Prof. Dr. *U. Gonser*
Fachbereich 12/1
Werkstoffwissenschaften
Universität des Saarlandes
D-6600 Saarbrücken, FRG

Dr. *A. Mooradian*
Leader of the Quantum Electronics Group, MIT,
Lincoln Laboratory, P.O. Box 73,
Lexington, MA 02173, USA

Prof. Dr. *K. A. Müller*
IBM, Zürich Research Lab.
CH-8803 Rüschlikon, Switzerland

Dr. *M. B. Panish*
AT&T Bell Laboratories,
600 Mountain Avenue,
Murray Hill, NJ 07974, USA

Prof. *H. Sakaki*
Institute of Industrial Science,
University of Tokyo,
7-22-1 Roppongi Minato-ku,
Tokyo 106, Japan

ISBN 3-540-18938-6 Springer-Verlag Berlin Heidelberg New York
ISBN 0-387-18938-6 Springer-Verlag New York Berlin Heidelberg

Library of Congress Cataloging-in-Publication Data. Dresselhaus, M.S. Graphite fibers and filaments. (Springer series in materials science ; v. 5). Bibliography: p. Includes index. 1. Graphite fibers. I. Title. II. Series. TA455.G7D74 1988 620.1'93 88-4593

Printed in Germany

Printing: Druckhaus Beltz, 6944 Hemsbach/Bergstr.
Binding: J. Schäffer GmbH & Co. KG, 6718 Grünstadt
2153/3150-543210

Preface

This book was begun after three of the present authors gave a series of invited talks on the subject of the structure and properties of carbon filaments. This was at a conference on the subject of optical obscuration, for which submicrometer diameter filaments with high length-to-diameter ratios have potential applications. The audience response to these talks illustrated the need of just one scientific community for a broader knowledge of the structure and properties of these interesting materials.

Following the conference it was decided to expand the material presented in the conference proceedings. The aim was to include in a single volume a description of the physical properties of carbon fibers and filaments. The research papers on this topic are spread widely in the literature and are found in a broad assortment of physics, chemistry, materials science and engineering and polymer science journals and conference proceedings (some of which are obscure). Accordingly, our goal was to produce a book on the subject which would enable students and other researchers working in the field to gain an overview of the subject up to about 1987.

Most of the present commercial production consists of fibers manufactured from polyacrylonitrile (PAN). These fibers have high strength and relatively low extensional moduli, making them particularly suited for applications in structural composites. For specialized applications, a smaller production of fibers from mesophase pitch precursors is also important. These ex-polymer PAN and pitch fibers have extraordinary potential as high strength-to-weight components for aerospace applications.

In the last few years a newer form of non-continuous filament, prepared by a catalytic chemical vapor deposition (CCVD) process has been studied extensively. These filaments have a more ordered structure than their polymer-based counterparts, and are more suited for research applications. In addition, there may be increased commercial use of the CCVD fibers in applications where short lengths can be used. This is particularly important since their cost may be considerably lower than present commercial carbon fibers. Accordingly, applications of the CCVD filaments may go well beyond the aerospace industry.

This book contains information on both ex-polymer and CCVD fibers, thereby distinguishing it from previous reviews, which have not included the

newer CCVD fibers. This volume specifically considers the preparation, microstructure and defects, electronic structure, lattice, thermal, mechanical, magnetic, electrical and high temperature properties of carbon fibers, together with modifications induced by intercalation and ion implantation, and finishes with a brief discussion of applications. Over 500 references are included, which are chosen as much as possible from the recent literature.

This book is aimed at an audience of practitioners using carbon fibers in their many applications, and wanting information about their properties. Another audience is the researchers in the field of carbon science generally, who need to make contact with other carbon-based materials. The book will be of particular interest to students entering the field of carbon science and carbon fiber technology, since much of the material in the book is tutorial. Some of the results are new, having been developed to answer specific questions which arose as the book was being written.

It is the hope of the authors that this book has brought together a large body of material in a coherent fashion, and that it will stimulate further advances in the fascinating field of carbon fibers by presenting both the fundamental concepts and the engineering applications.

The MIT authors wish to acknowledge AFOSR (# F49620-85-C-0147) for support of this work and Ms. Phyllis Cormier for the long hours she worked in preparing the manuscript. The MIT authors wish to thank Professor M. Endo for his advice and encouragement throughout the preparation of this manuscript and for his inspiration which has been largely responsible for the interest of many physicists in this field. Ian Spain wishes to acknowledge B.J. Wicks, R.A. Coyle, D.J. Johnson, J.W. Johnson, and A. Oberlin for donation of figures, Mr. Charles Bowers who helped prepare figures, and W.N. Reynolds who supplied unpublished data. Ian Spain also thanks the Centre d'Etudes Nucléaires Grenoble for hospitality, and AFOSR for a grant (# F49620-86-C-0083) for support in writing this review. Thanks are due to Dr. I.L. Kalnin for introducing Harris Goldberg to the field of carbon fibers and for many years of collaborative research. In addition, the help and support of numerous colleagues and collaborators at the R.L. Mitchell Technical Center are gratefully acknowledged by Harris Goldberg.

Cambridge, MA, January 1988 *The Authors*

Contents

1. Introductory Material on Graphite Fibers and Filaments

The purpose of this book is to review the physical properties of carbon filaments and fibers. These materials have been developed in the last 25 years, and new types are still being discovered and tested. It is hoped that in this book we will demonstrate that scientifically interesting and technologically important physical research has been, and can be carried out on these novel materials.

Carbon fibers are of technological importance today because fiber/resin composites have strength-to-weight properties superior to those of any other materials. This is bringing about a revolution in aircraft design, so that modern civilian and military aircraft are increasingly using carbon fiber composites in all but their main structural components. Several designs which employ essentially 100% carbon fiber composites for the airframe [B.W. Anderson 1987] are in the stage of certification for civilian use. Of course, experimental aircraft of this type have been flying for some time, and one of them, the "Voyager", completed a non-stop around-the-world flight in 1986 without refueling.

While their use in airframes has pushed carbon fiber development, other applications are current, and envisioned. For instance, carbon fibers in bulk carbon composites are used in rocket engines, while automobile manufacturers are possibly about to follow the aviation industry in using fiber/resin composites to reduce the weight of vehicles and reduce the time and expense required to change styles and designs. The critical factor for this latter application is the cost. Accordingly, research is being carried out on new ways of producing strong and tough carbon fibers with costs as low as 10% of current values.

Research has been of the utmost importance in bringing about this technological revolution. Although many of the details of processing conditions (which are absolutely essential for superior mechanical properties) have not been released by manufacturers, it is fortunate that a large body of literature has appeared concerning the relationship between structure and physical properties. Even so, much research carried out by companies has not been published. We acknowledge the fact that some of the material on ex-polymer fibers appearing in this review may be out-of-date when viewed from the perspective of leading carbon fiber manufacturers. It is hoped, however, that this

review illuminates the major principles governing the physical properties of these and related materials.

There are many different types of carbon fibers and filaments. It has been known since the last century that cellulose-based threads can be carbonized in inert atmospheres to form carbon filaments. Edison used ex-cotton and ex-bamboo carbon threads as lamp filaments until tungsten was found to be superior. These ex-cotton carbon filaments do not possess high enough mechanical strength to make them technologically interesting. The factor which is of crucial importance to the fiber strength is the alignment of the carbon hexagons along the fiber axis, with structurally coherent fibrils extending over long distances. Ex-cotton filaments are essentially isotropic, so that the high in-plane bond strength of graphite is not the controlling factor in their strength, but rather the relatively weak inter-planar bond.

Carbon fibers with well-aligned carbon hexagons became commercially available in the early 1960s after extensive research in Great Britain, Japan, and the USA. These filaments are in most cases derived from organic precursors by extrusion into polymeric fibers, followed by heat treatment (stabilization) and subsequent carbonization (heat treatment above ~1000°C) and then further heat treatment up to ~3000°C in an inert atmosphere. We refer to these fibers as "ex-polymer fibers". Correspondingly, "ex-rayon" fibers are carbon fibers prepared from rayon precursors, etc. Ex-rayon fibers were produced in quantity first [Bacon et al. 1966]. It was soon demonstrated by Shindo [1961a, 1961b, 1964] that polyacrylonitrile (PAN) was a better starting material. This PAN precursor became of increased importance when English workers [Watt et al. 1966; Standage and Prescott 1966] showed that high strength fibers could be obtained by oxidizing the PAN precursor while under strain without the need for a hot-stretching stage after carbonization. More recently, a new type of fiber has appeared, based on pitch [Hawthorne et al. 1970; Otani et al. 1970]. These mesophase pitch-based carbon fibers attain their alignment through a liquid-crystal-like state (mesophase). The resulting spun fibers have high elastic moduli (~500–800 GPa) after carbonization and heat treatment. However, the major commercial use for carbon fibers is for relatively low modulus (~200 to 300 GPa), high strength (>3 GPa) applications where ex-PAN fibers have superior properties. An isotropic pitch-based carbon fiber can be spun at lower cost; these fibers are finding application in high bulk, low performance applications, such as reinforced cement.

An important milestone in the understanding of the potential of these commercial, ex-polymer fibers was the study of a highly organized form of carbon filament (called a carbon whisker) obtained from carbon arcs [R. Bacon 1960]. Extremely high breaking strengths were obtained, which have only been fractionally realized in commercial filaments. A comparison of the mechanical properties of steel and carbon fibers and whiskers is given in Table 1.1. This table provides an indication of the potential improvements which can still be made in commercial materials.

Table 1.1. Comparison of densities and strengths of typical steel and carbon fibers[a]

Material	Density [kg/m^3]	Tensile strength [GPa]	Normalized strength[b]
Steel	7870	1.5	1.0
High modulus carbon fiber[c]	1800	2.4-2.6	7.0-7.6
High strength carbon fiber[c]	1800	3.1-4.6	9.0-13.5
Carbon whiskers[d]	2240	up to 20	up to 47

[a] See [Riggs 1985].
[b] Normalized strength compares Tensile strength/Density relative to steel.
[c] See Table 2.2.
[d] [R. Bacon 1960].

Another kind of filament has been developed recently [Endo 1988b], produced by decomposing a hydrocarbon on a heated substrate in the presence of transition metal catalysts [catalytic chemical vapor deposition (CCVD) carbon filaments]. These filaments are not continuous like ex-polymer fibers, but their lengths can reach several hundred millimeters. It is possible that their production costs will be substantially lower than those of ex-polymer fibers, making them of interest for chopped or milled fiber applications, with aspect ratios (length/diameter) of over 100. CCVD filaments have been the subject of intense research in the last few years, and will be systematically reviewed here for the first time.

In addition to the pristine (unmodified) fibers and filaments, it is possible to modify their properties in two major ways. Firstly, they can be coated with carbon, metals, insulators, superconductors, etc. (Chap. 12). Secondly, they can be intercalated with many elements and molecules, thereby changing their properties. (Intercalation is the process of inserting chemical species between the layer planes – see Chap. 10). Potential applications of modified fibers and filaments include high strength electrical conductors and superconductors, magnetic materials with favorable shape factors for magnetic shielding, etc.

This review is perhaps somewhat unusual for a book on this subject as it spans the interdisciplinary area between physics, materials science, and, to a lesser extent, chemistry. The underlying physical phenomena will be stressed, and it will be seen that many physical models have been applied to these materials in unique ways. In some instances new theories have been applied.

In reviewing the literature we have been overwhelmed by the number of publications, and have been forced to make decisions on omitting material which might appear arbitrary to some readers. To some extent, this is a personal record, which inevitably stresses some of the areas that have been investigated by our own research groups. Wherever possible, we have used previous research reviews, and summarized them, rather than repeating material in detail. As a result, the properties of the newer CCVD filaments are

emphasized at the expense of the older ex-polymer fibers. We apologize to those whose work has not been fairly emphasized as a result of this process.

The review is organized in a way that begins with synthesis (Chap. 2), structural aspects (Chap. 3), then passes to physical phenomena such as lattice properties (Chap. 4), thermal properties (Chap. 5), mechanical properties (Chap. 6), electronic structure (Chap. 7), electronic transport properties (Chap. 8), and high temperature properties (Chap. 9), thence to modified filaments by intercalation (Chap. 10) and by ion implantation (Chap. 11), and ends with a brief discussion of applications (Chap. 12). However, before proceeding to the main body of the review, a brief description of the overall structure of the different kinds of filaments will be given. This will enable some essential concepts and terminology to be introduced. In this book we will attempt to conform to the recently adopted standardized terminology [Donnet et al. 1982, 1983, 1985, 1986, 1987a, 1987b].

1.1 Introductory Discussion of Structure of Carbon Filaments

As mentioned above, there are several types of carbon filaments, and this preliminary discussion will consider their structure.

1.1.1 Ex-polymer Fibers

Ex-polymer fibers are manufactured by extruding a polymer through a nozzle into a continuous filament, after stabilization treatment at about 200°–350°C in air, then heat treatment of the filaments to temperatures (T_{HT}) on the order of 1000°C in order to carbonize the filaments by the removal of H, O, N, ... etc. Further heat treatment to temperatures typically between 1300° and 3000°C modifies their mechanical properties. Heat treatment above

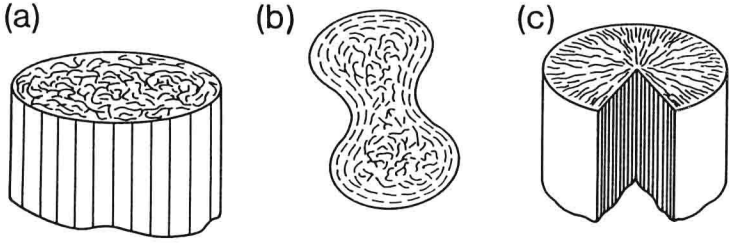

Fig. 1.1a-c. Illustration of observed ex-polymer fiber cross-sectional macroscopic morphology: (a) circular section, showing a disordered arrangement of ribbons, (b) dog-bone section observed in partially graphitic ex-PAN fibers, with a circumferential arrangement of ribbons in the sheath region, and random in the core, (c) ex-pitch (mesophase pitch), "PAC-man" section showing a radial arrangement of the ribbons

Fig. 1.2. Sketch of a typical graphene plane in a carbon fiber showing vacancy-cluster defects [Fourdeux et al. 1971]

~2200°C is referred to as a "graphitization" step. These fibers are manufactured commercially, and are produced from several starting polymers. The most important today are ex-polyacrylonitrile (ex-PAN) and ex-pitch fibers, while ex-rayon fibers were of importance until very recently.

The most obvious feature of carbon fibers is their small diameters, which are typically about 7 μm. This compares with diameters of human hairs of ~70 μm. Carbon fibers can barely be seen by eye, and appear as featureless black filaments under optical magnification. Under closer examination afforded by scanning electron microscopes, the cross sections are often found to be circular (Fig. 1.1a). Sometimes, particularly in the case of ex-PAN fibers, the cross section is double-lobed or "dog-bone" shaped (Fig. 1.1b). Ex-pitch fibers sometimes have a roughly circular cross section, in which a segment has been removed, sometimes called a "PAC-man" section (Fig. 1.1c).

Under even closer scrutiny using x-ray diffraction and transmission-electron microscopy, it is found that the basic structural unit of carbon fibers is a planar network of connected benzene rings, illustrated in Fig. 1.2. This is similar to the planar structure occurring in graphite, in which the carbon atoms lie in hexagonal honeycomb arrays. Note that the planar structure of the carbon fiber is not perfect. We sometimes refer to these two-dimensional planar arrays of carbon atoms as "graphene" planes. Though the planar structures are imperfect, the planar arrays nevertheless lie roughly aligned along the direction of the fiber, and are responsible for the strength of these materials. Coulson (1952), for example, has pointed out that the C–C bond in graphite is the strongest bond occurring in nature.

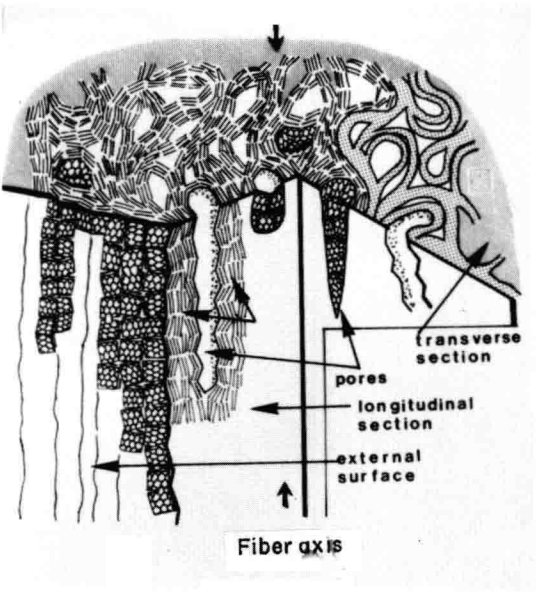

Fig. 1.3. Artist's conception of the structure of a high strength ex-polymer fiber [adapted from Guigon et al. 1984b]

In the carbon fiber, these graphene planes stack on top of each other similar to pages in a newspaper. They are ribbon-like, having typical widths of several tenths of micrometers. Figure 1.3 illustrates the typical arrangement of these planes in an ex-PAN fiber. If a cross section were being viewed along the fiber axis, the ribbons (stacks of graphene planes) would be seen to undulate, and separate, but most would be roughly aligned along the fiber axis (Fig. 1.4). For example, the mean angle made by these ribbons to the fiber axis would be about 20° in typical high strength fibers used in aircraft. Note in Fig. 1.3 the presence of voids, which are typically needle-shaped. These voids reduce the density below the value ($2.26\,\mathrm{g/cm^3}$) expected for an ideal planar hexagonal array of carbon atoms. Also indicated in Fig. 1.4 are the "crystallite" dimensions L_a and L_c, representing the extent of relatively straight portions of the lattice planes along their length, and the stacking height of the graphene planes in the ribbons, respectively.

Increasing the heat-treatment temperature (T_{HT}) allows the graphene planes to grow. (The heat treatment temperature is sometimes denoted by HTT in the literature.) Figure 1.5 illustrates a high resolution electron micrograph of the surface layers of an ex-PAN fiber [D.J. Johnson 1980]. When carbonized at 1000°C, (Fig. 1.5a), the graphene planes are apparently less than 10 nm in length. They are roughly aligned along the fiber axis. At 1500°C (Fig. 1.5b), the graphene planes are more extensive, better aligned and in sharper contrast. Further improvements in the alignment occur on heat treatment at 2500°C (Fig. 1.5c). In this case it can be seen that the ribbons are much more extensive both along and perpendicular to the fiber axis.

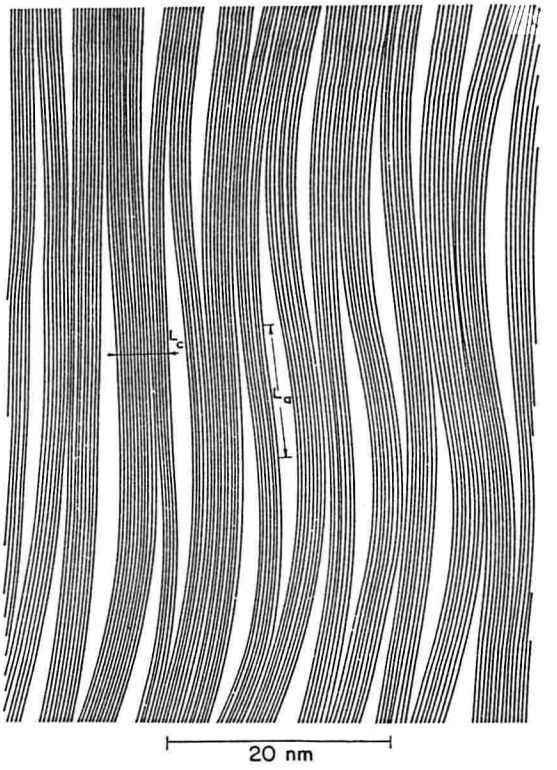

Fig. 1.4. Sketch of the cross section of an ex-PAN fiber along the axis direction [Fourdeux et al. 1971]. Here the in-plane and c-axis structural coherence lengths L_a and L_c are indicated

Even after high temperature heat treatment some crystallites remain badly misaligned (see Chap. 3).

A cross section across the fiber axis, as shown also in Fig. 1.3, indicates a much higher state of disorder than in the longitudinal section (Fig. 1.4). The cross section shows that the planes are twisted over short distances compared to the ribbon widths, and there is a random orientation of planes over the diameter of the fiber. The arrangement of planes over this section varies with fiber type and processing conditions. For instance, some ex-mesophase pitch fibers are found in which the planes are roughly arranged in a radial fashion (see Fig. 1.1c), while a circumferentially preferred arrangement can be found in ex-PAN fibers, as indicated for the outer regions in Fig. 1.1b.

These twists in the planar arrays prevent them from stacking in a regular fashion, as in hexagonal graphite. The stacking of the planar arrays is typically random, although inter-layer correlations are developed by heating the fibers to high temperature T_{HT}. It is also necessary to consider time-at-temperature (or the residence time), since the graphitization processes are kinetic in nature. Most heat-treatment processes for fibers are carried out over a time period on the order of 10 minutes or more, and this will be assumed unless otherwise stated.

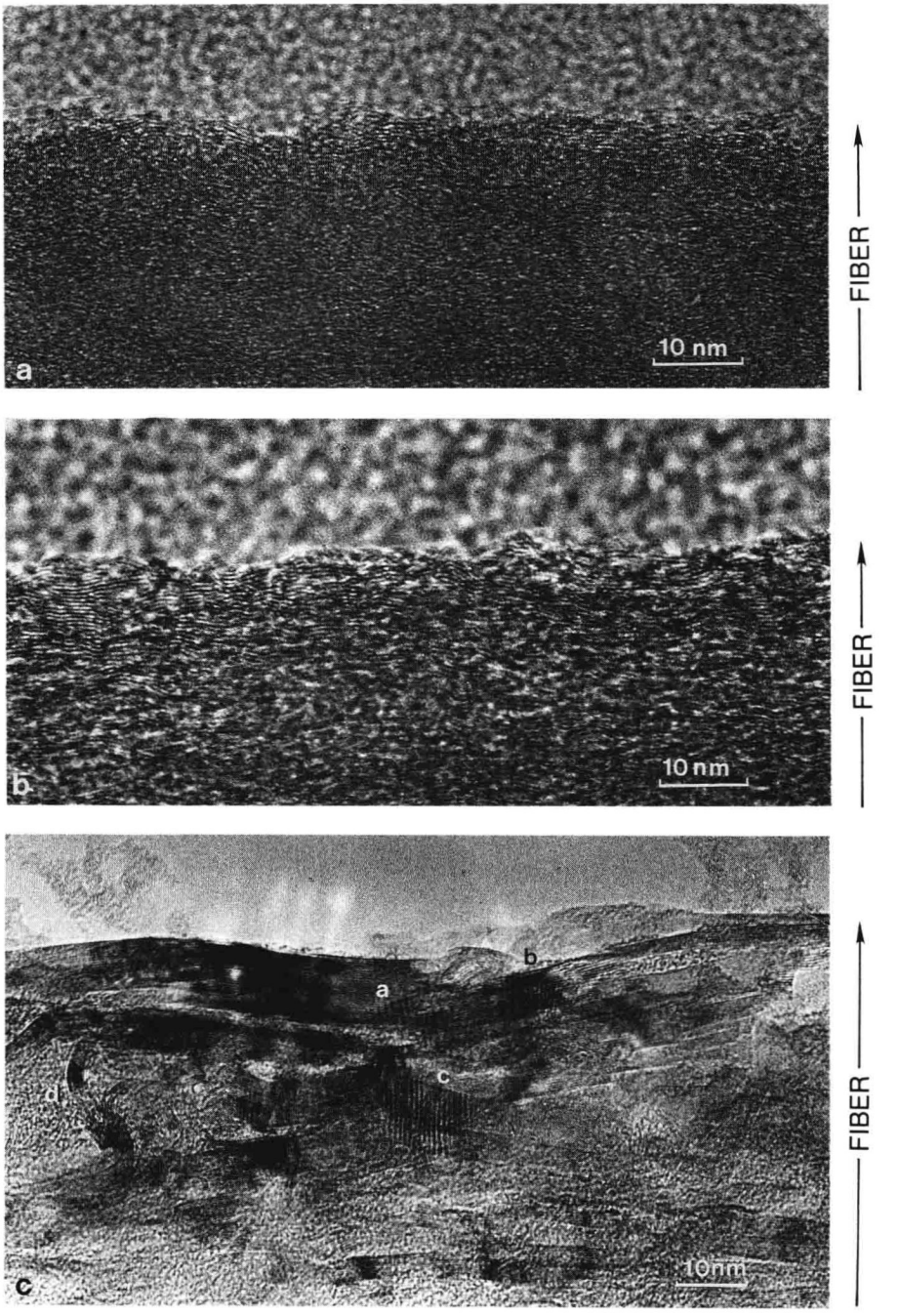

Fig. 1.5 Figure caption see opposite page