

# Introduction to Carbon Science

Harry Marsh

Butterworths

# Introduction to **Carbon Science**

This page intentionally left blank

# Introduction to Carbon Science

Ian A. S. Edwards  
Harry Marsh  
Rosa Menendez  
Brian Rand  
Sebastian West  
Andrew J. Hosty  
Khim Kuo  
Brian McEnaney  
Timothy Mays  
David J. Johnson  
John W. Patrick  
David E. Clarke  
Jack C. Crelling  
Ralph J. Gray

*Editor* **Professor Harry Marsh**  
University of Newcastle upon Tyne, U.K.

**Butterworths**

London Boston Sydney Toronto Wellington

All rights reserved. No part of this publication may be reproduced in any material form (including photocopying or storing it in any medium by electronic means and whether or not transiently or incidentally to some other use of this publication) without the written permission of the copyright owner except in accordance with the provisions of the Copyright, Designs and Patents Act 1988 or under the terms of a licence issued by the Copyright Licensing Agency Ltd, 33–34 Alfred Place, London, England WC1E 7DP. Applications for the copyright owner's written permission to reproduce any part of this publication should be addressed to the Publishers.

Warning: The doing of an unauthorised act in relation to a copyright work may result in both a civil claim for damages and criminal prosecution.

This book is sold subject to the Standard Conditions of Sale of Net Books and may not be re-sold in the UK below the net price given by the Publishers in their current price list.

First published 1989

© **Butterworth & Co. (Publishers) Ltd, 1989**

**British Library Cataloguing in Publication Data**

Introduction to carbon science

1. Carbon

I. Marsh, Harry

546'.6811

ISBN 0-408-03837-3

**Library of Congress Cataloging-in-Publication Data**

Introduction to carbon science/edited by Harry Marsh.

p. cm.

Includes bibliographies.

ISBN 0-408-03837-3 :

1. Carbon. I. Marsh, Harry.

QD181.C1148 1989

546'.68—dc 19 89-721

# Foreword

---

The international community of carbon scientists, technologists and engineers meet annually and in 1988 the venue was the University of Newcastle upon Tyne, U.K.

Large international meetings usually follow the same format of plenary lectures, short presentations of studies and poster sessions. To those entering the field of carbon science for the first time, either as young people or those who are changing direction of work as part of their career, such a scientific meeting can be somewhat bewildering.

The idea of a Short Course as an introductory series of lectures prior to the main Conference is not new in itself but is new to the carbon community. This book follows the sequence of topics of such a Short Course, each Chapter being built upon the material used by the lecturer in the Short Course of September 1988.

Carbon Science, as a general term, can be very far-reaching, ranging from polymer science to prosthetics, from crystallography to carbonization, spectroscopy to surface science, etc.. Not all aspects could possibly be covered in one week of lectures, *i.e.* nine sessions.

The planning committee considered that the following topics represented the essentials of a foundation course in carbon science:-

1. Structure in carbons and carbon forms.
2. Mechanisms of formation of isotropic and anisotropic carbons.
3. Physical properties of pitch relevant to the fabrication of carbon materials.
4. Kinetics and catalysis of carbon gasification.
5. Porosity in carbons and graphites.
6. Carbon fibres: manufacture, properties, structure and applications.
7. Mechanical properties of cokes and composites.
8. The nature of coal material.
9. Coal to coke transformations.

The intention that the Short Course material should be collected in a permanent and accessible form has been realised.

This book is an introduction to carbon science, it is contemporary and it is anticipated that it will be of interest both to the beginner and to the experienced. For the reader requiring a wider knowledge of specific topics, the text is supplemented with appropriate and extensive references. However, the text alone gives full grounding of the subject.

***Harry Marsh***

# Acknowledgements

---

This book is a collaborative effort, not only in producing Chapters of related topics, but in taking care to prevent overlap and with limited, but necessary, cross-referencing.

Those who have expertise in their subjects have heavy work-loads these days and I am indeed honoured to have had the generous support of the authors of the Chapters who are distinguished in their subject areas and who have taken such care with their manuscripts.

The final texts have been put together by Bridget A. Clow, Marion Poad and Elaine Watson. Assistance with diagrams has been most kindly given by Eduardo Romero Palazon. Brenda Chan supported me in the last stages of compilation. Ed Heintz (University of Buffalo, U.S.A.) was a tremendous help as co-ordinator during the running of the short course.

Finally, the professional assistance of the office of Butterworths, from Jayne Holder in particular, is appreciated.

***Harry Marsh***

This page intentionally left blank

# An Introduction to Authors

## **Professor J.C. Crelling**

Department of Geology, Southern Illinois University  
Carbondale, U.S.A.

Jack C. Crelling graduated in geology from the University of Delaware, U.S.A. After his Ph.D. studies at Penn. State University, he spent five years in the Coal Research Laboratory of Bethlehem Steel Corporation before joining Southern Illinois University where he is presently Professor of Geology and the Head of the Coal Characterisation and Maceral Separation Laboratories. His area of research is coal petrology, including fluorescence spectro-analysis and photo-acoustic microscopy. His most recent work involves the separation of single coal macerals and the determination of their petrology, chemistry and reactivity. He is Chairman of the Coal Division of the Geological Society of America, President of the Society for Organic Petrology and serves on the Editorial Board of Fuel Processing Technology.

## **Dr. D.E. Clarke**

Carbon Research Group  
Loughborough Consultants Ltd.  
Loughborough University of Technology, U.K.

David E. Clarke graduated from the University of Bath in 1978 and entered journalism as an editorial staff member of the Journal FUEL, working under the guidance of the then Editor-in-Chief, Dr. I.C.G. Dryden. In 1982, he joined the Northern Carbon Research Laboratories, University of Newcastle upon Tyne to carry out research under the direction of Professor H. Marsh on the coal-to-coke transformation, briquetting and also the degradation of metallurgical cokes within the blast furnace and was awarded a Ph.D. in 1986. Since 1987, he has been working with Dr. J.W. Patrick at Loughborough on coal liquefaction and continuing studies on metallurgical coke degradation. He is currently a member of the RSC/IOP Joint Carbon Group Committee and Hon. Editor of the CARBON NEWSLETTER.

**Dr. I.A.S. Edwards**

Northern Carbon Research Laboratories  
University of Newcastle upon Tyne, U.K.

Ian A.S. Edwards studied chemistry at King's College, University of Durham, his postgraduate research being in the field of crystallography. The subject of his Ph.D. thesis was 'Crystal Structure Determinations by X-ray Methods'. Following post doctoral research in surface analysis using LEED and AES in the Physical Chemistry Department of the University of Newcastle upon Tyne, he joined the Northern Carbon Research Laboratories in 1980. During the past eight years, he has supervised research in structural and reactivity measurements on a wide range of carbon materials including graphite, coke and pitch. He has presented papers at international conferences on crystallography and carbon science. He is Honorary Secretary of the local section of the Royal Society of Chemistry and Chairman of the local section of the Society of Chemical Industry.

**Mr. R.J. Gray**

Process and Energy Management Corporation  
Pittsburgh, PA, U.S.A.

Ralph J. Gray is a coal scientist with 38 years experience in coal exploration, evaluation and development, his B.S. and M.S. being in geology. In 1957, after joining U.S. Steel, he began to develop a petrographic classification of coals which introduced vitrinite reflectance as V-Types and the first U.S. coke-strength prediction system based on coal petrography. He developed microscopic techniques for analysis of coke carbon forms, non-macerals microstructures and quinoline insolubles from coal-tar and pitches and automatic microscopic systems for monitoring coals and coal blend proportions for coke making. He has written 54 publications and received the Iron and Steel Societies Joseph Barker Award in 1986 for his contributions to coke making. In 1987, he worked with the EEC on the new international classification of coal. He retired from US Steel in 1983 and is currently with the Process and Energy Management Corporation, Pittsburgh, U.S.A.

**Mr. A.J. Hosty and Mr. S.West**

Division of Ceramics, Glasses & Polymers,  
University of Sheffield, U.K.

Mr. Andrew J. Hosty and Mr. Sebastian West are graduate students in The School of Materials at The University of Sheffield. They both graduated with honours in Materials Science in 1987. Mr. Hosty is investigating the fabrication of carbon-carbon composites using carbonaceous mesophase as a matrix precursor and Mr. West is investigating rheological aspects of pitch-coal interactions.

**Dr. D.J. Johnson**

Department of Textile Industries  
University of Leeds, U.K.

David J. Johnson is Reader of Textile Physics at the University of Leeds, and has worked on the structure/property relationships of carbon fibres since 1968. He has published extensively and has contributed plenary lectures at a number of International Carbon Conferences. He collaborated with W. Watt and W. Johnson, the inventors of PAN-based carbon fibres, for many years and continues to carry out project work for industry. His main fields of experience are X-ray diffraction and electron microscopy, particularly lattice-fringe imaging; current research work is concerned with the compressive failure of carbon and other high-performance fibres. Dr. Johnson is Education Secretary of the Royal Microscopical Society.

**Dr. A.K. Kuo**

Northern Carbon Research Laboratories  
University of Newcastle upon Tyne, U.K.

Khim Kuo graduated in chemistry from the University of Newcastle upon Tyne in 1982 and subsequently spent one year teaching and carrying out research in radiation chemistry at the University of Delaware, U.S.A. Following her return to the U.K. and M.Sc. studies in biochemistry, she joined the Northern Carbon Research Laboratories studying under the supervision of Professor H. Marsh. The subject of her Ph.D. studies was "The Concept of Active Surface Area in Carbon/Coke Gasification". At the time of publication, Dr. Kuo is working in the field of aluminium reduction cell lining materials at the Comalco Research Centre, Thomastown, Australia.

## **Professor H. Marsh**

Northern Carbon Research Laboratories  
University of Newcastle upon Tyne, U.K.

Harry Marsh graduated from The University of Durham. He studied under Professor H. L. Riley for a Ph.D. in coal chemistry, subsequently taking a D.Sc. in carbon science at The University of Newcastle upon Tyne. His professional career has centered around carbon and coal science with an emphasis on relating research to industrial requirements. Professor Marsh has published about 300 papers and conference proceedings and trained about 60 research students and 60 postgraduate researchers. He has lectured in all five continents. In 1985 he received the George Skakel Memorial Award from the American Carbon Society and, in 1989, the Henry H. Storch Award from the American Chemical Society for promoting interactions between Academe and industry. In 1989, he established a Coal Research Forum in the U.K. to promote both the interests of coal within the U.K. and the influence on coal markets abroad. Currently, he holds a Chair in Carbon Science and is Head of the Northern Carbon Research Laboratories. He is a Principal Editor of FUEL, on the Editorial Board of CARBON, Chairman of the Industrial Carbon and Graphite Group of the Society of Chemical Industry and is a member of the sub-committee of SERC with interests in coal.

## **Dr. T.J. Mays**

School of Materials Science  
University of Bath U.K.

Tim Mays is a Research Fellow in the School of Materials Science of the University of Bath. He graduated with a first-class honours degree in physics and, after working as a statistician with the CEGB, studied under Dr. B. McEnaney for his Ph.D. on gaseous diffusion and pore structure in graphites. He has recently worked in the Carbon Research Group in the School on the determination of pore structure in carbons using computer-aided quantitative microscopy and is currently researching into the fundamental theory of adsorption in microporous carbons. Dr. Mays is a member of the Committee of the Joint Carbon Group of the Institute of Physics and the Royal Society of Chemistry and recently co-edited, with Dr. McEnaney, the Proceedings of the International Carbon Conference, "Carbon 88".

**Dr. B. McEnaney**

School of Materials Science  
University of Bath, U.K.

Brian McEnaney is a Reader and Head of the Carbon Research Group in the School of Materials Science of the University of Bath. He is presently Chairman of the Committee of the Joint Carbon Group of the Institute of Physics and the Royal Society of Chemistry and a member of the Editorial Board of the Journal CARBON. He has published over 100 papers mainly in the field of carbons and graphites but also on metallic corrosion. Recently, he co-edited with Dr. T.J. Mays the Proceedings of the International Carbon Conference, "Carbon 88". Dr. McEnaney presented Plenary Review Lectures on aspects of porosity in carbons and graphites at the 1985 American Carbon Conference and the 1986 German Carbon Conference.

**Dr. R.M. Menendez**

Instituto Nacional del Carbon,  
Oviedo, Spain.

Rosa Menendez is a graduate of the University of Oviedo where, after her first degree in organic chemistry, she gained a masters degree in pollution control and, in 1986, a Ph.D. in the characterization of coal products. She spent two years (1987 - 1988) working in the Northern Carbon Research Laboratories, University of Newcastle upon Tyne, researching into coal and pitch carbonization. Currently, her work at INCAR is related to industrial applications of petrology, particularly carbonization and combustion. She is a member of the ICCP and the American Chemical Society.

**Dr. J.W. Patrick**

Carbon Research Group  
Loughborough Consultants Ltd.  
Loughborough University of Technology, U.K.

John W. Patrick obtained his B.Sc. in chemistry and his Ph.D. from the University of London for a study of carbon-sulphur complexes. He is currently Director of the Carbon Research Group at Loughborough University of Technology following 24 years service with the British Carbonization Research Association where he held the position of Head of Fundamental Studies. He has over 30 years experience

in studying various aspects of carbon science ranging from the carbonization process to the gasification of carbon and the inter-relation of the strength and structure of cokes and carbons. He has made a special study of the strength of metallurgical cokes and its relation to the coke porous structure and to the nature of the coke carbon, *i.e.*, optical texture. He is a Principal Editor of the Journal FUEL and a former chairman of the Joint Carbon Group of the Royal Society of Chemistry and the Institute of Physics.

### **Dr. B. Rand**

Division of Ceramics, Glasses and Polymers  
University of Sheffield, U.K.

Brian Rand graduated from King's College, University of Durham in chemistry taking his Ph.D. in carbon science under the supervision of Professor H. Marsh. After a period of industrial employment, Dr. Rand is currently Senior Lecturer in the School of Materials, University of Sheffield, U.K. He has published extensively with particular interest in thixotropic changes involved in reheating coal-tar pitches and the general rheological behaviour of pitch precursors used in composites and fibres. Emphasis is given to the significance of glass transition temperature. Other studies include porosity in carbons and surface characteristics of PAN fibres.

# Contents

---

<b>Foreword</b>	v
<b>Acknowledgements</b>	vii
<b>An Introduction to Authors</b>	ix
J.C. Crelling	ix
D.E. Clarke	ix
I.A.S. Edwards	x
R.J. Gray	x
A.J. Hosty and S. West	xi
D.J. Johnson	xi
A.K. Kuo	xi
H. Marsh	xii
T.J. Mays	xii
B. McEnaney	xiii
R.M. Menendez	xiii
J.W. Patrick	xiii
B. Rand	xiv

# Chapter 1

## Structure in Carbons and Carbon Forms

	<b>Summary</b>	1
<b>1</b>	<b>Introduction - Setting the Scene</b>	2
	1.1 The element carbon	2
	1.2 Bonding in carbon materials	3
	1.3 Diamond and graphite - perfect structures	4
<b>2</b>	<b>Order/Disorder</b>	6
	2.1 More-ordered structures	6
	2.2 Less-ordered structures	8
	2.3 Range of order	9
<b>3</b>	<b>Carbon Forms</b>	10
	3.1 Graphitic carbons (Natural and synthetic graphites)	10
	3.2 Non-graphitic carbons and graphitization	11
	3.3 Graphitizable and non-graphitizable carbons	11
	3.4 Pitches	11
	3.5 Cokes	12
	3.6 Coals	13
	3.7 Carbon fibres	14
	3.8 Other carbon materials	15
<b>4</b>	<b>Composites</b>	16
	4.1 Graphitic composites	17
	4.2 Carbon electrodes	17
	4.3 Carbon/carbon composites	18
<b>5</b>	<b>Methods of Studying Carbon Structure</b>	19
	5.1 Optical microscopy	19
	5.2 Electron microscopy (SEM and TEM)	22
	5.3 X-ray diffraction	27
	5.4 Raman spectroscopy	29
	5.5 Surface techniques	29
<b>6</b>	<b>Factors in Carbon Structures</b>	30

<b>7</b>	<b>Conclusions</b>	<b>30</b>
	7.1 The diversity of carbon	31
	References	31

## Chapter 2

### Mechanisms of Formation of Isotropic and Anisotropic Carbons

	<b>Summary</b>	<b>37</b>
<b>1</b>	<b>Introduction</b>	<b>38</b>
<b>2</b>	<b>Isotropic Carbon</b>	<b>39</b>
<b>3</b>	<b>Graphitizable Carbon - The problem</b>	<b>46</b>
	3.1 Background	46
	3.2 Mesophase: Early recognition	47
	3.3 Nematic liquid crystals	48
	3.4 Structure in liquid crystals	48
	3.5 Nucleation of mesophase	50
	3.6 Structure within mesophase	51
<b>4</b>	<b>Chemistry and Viscosity of Pyrolysis Systems</b>	<b>55</b>
	4.1 Growth and properties of mesophase: Summary	59
	4.2 Aspects of mesophase chemistry	59
	4.3 Mesophase growth and coalescence	60
	4.4 Carbons/cokes from mesophase from pitch	61
<b>5</b>	<b>Mesophase from Coal</b>	<b>65</b>
	5.1 Metallurgical coke	65
	5.2 Coal chemistry	65
	5.3 Mesophase formation during coal pyrolysis	66
	References	70