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Oxidation Stabilization of the Carbonaceous Mesophase

J. L. WHITE and P. M. SHEAFFER
Materials Sciences Laboratory
Laboratory Operations

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The extent to which oxidation stabilization can be applied to bulk mesophase was studied by oxidizing specimens of well-defined microstructure that were produced by magnetic orientation or by uniaxial deformation. Stabilization depths approaching 50 μm were observed, proceeding from the surface and from cracks that have access to the atmosphere.

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OXIDATION STABILIZATION OF THE CARBONACEOUS MESOPHASE

Prepared

J. L. White

P. M. Sheaffer

Approved

R. A. Meyer, Head
Carbon and Polymers Department

R. W. Fillers, Director
Materials Sciences Laboratory

The information in a Technical Operating Report is developed for a particular program and is therefore not necessarily of broader technical applicability.

FOREWORD

The information in this report was included in an Extended Abstract for the 17th Biennial Conference on Carbon, held in Lexington, Kentucky, 16-21 June 1985.

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FIGURES

TABLE

I. INTRODUCTION

Oxidation stabilization is a key step in the manufacture of mesophase carbon fiber because the mesophase must be immobilized to permit carbonization without loss of the layer alignment imposed by fiber spinning.[1] The objective in the present work is to use micrographic methods to observe the depth of oxidation stabilization in mesophase bodies with dimensions greater than those of fibers. The approach is to prepare oriented mesophase bodies by application of a magnetic field[2] or by uniaxial deformation,[3] oxidize them under conditions that stabilize the microstructure, and carbonize them to observe the depth to which the oriented structure is retained.

The starting materials for these experiments were mesophase pitches prepared by applying the Chwastiak process[4] to Ashland A240 petroleum pitch. Each batch was sparged with nitrogen and stirred continuously while held at temperatures near 400°C for 10 to 20 h to achieve transformation levels of 85% or higher.

II. MAGNETICALLY ORIENTED MESOPHASE

Mesophase plates several millimeters thick were prepared by heating the mesophase pitch to about 320°C in a horizontal magnetic field of about 5000 gauss. By rotating the sample dish, the mesophase layers became preferentially oriented parallel to the plane of the dish, and the resulting mesophase plates were nearly free of disclinations and folds. Figure 1a shows a vertical section of an oriented mesophase plate that had been oxidized in air at 240°C for 34 h; the deep cracks formed on cooling after the magnetic orientation treatment.

Figure 1b illustrates the results of carbonizing this specimen to 600°C at 10°C/min. A well-defined boundary is apparent between stabilized mesophase that retained the preferred orientation and mesophase that softened, lost its preferred orientation, and was often driven from its original position by bubbles of pyrolysis gas. In this case, the stabilization depth was 17 μm; oriented mesophase ribs outline the cracks that provided access to air.

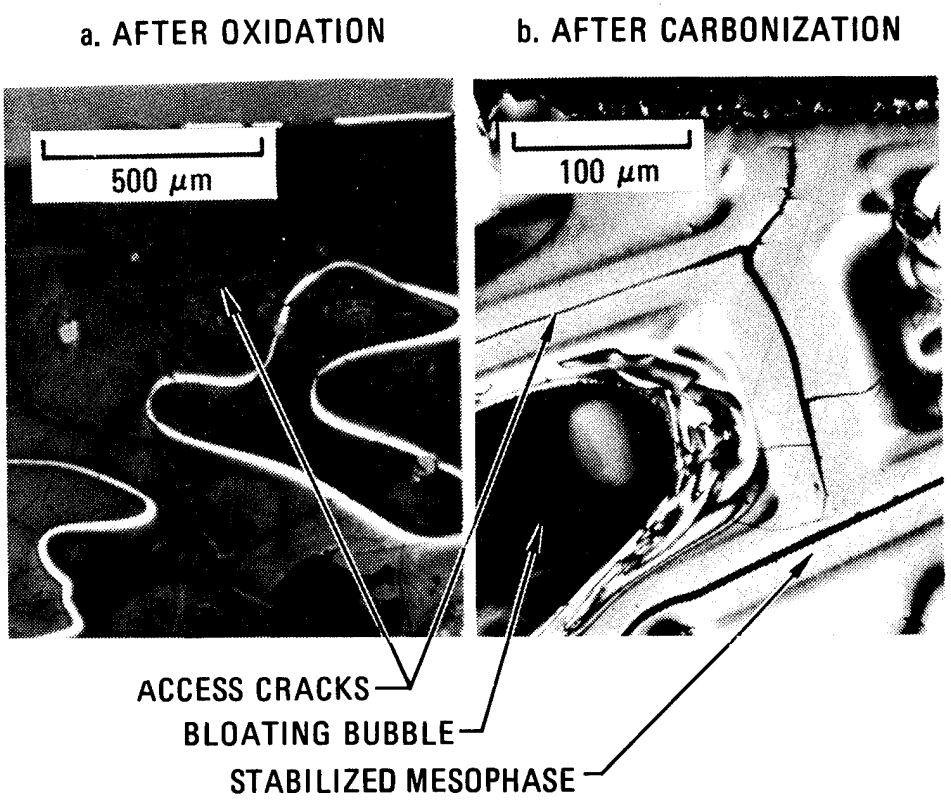

Fig. 1. Magnetically oriented mesophase, observed by crossed polarizers.

III. EXTRUDED AND DRAWN MESOPHASE RODS

Mesophase rods of fine fibrous microstructure were prepared by a method of extrusion and draw similar to that used by Jenkins and Jenkins.[3] The rod illustrated in Fig. 2 was produced from a near-100%-transformed mesophase pitch (400°C for 20 h) with a penetrometric softening point of 309°C. Although pyrolysis bubbles that formed during extrusion tended to disrupt the fibrous microstructure, only a light draw was necessary to restore the preferred orientation. The specimen of Fig. 2 was drawn at a rate of 4 cm/min from a 0.9 mm orifice at 330°C.

The mesophase rods were oxidized under various conditions of atmosphere (air or O_2) and time (8 to 65 h) with temperatures limited to 300°C or less to avoid structural relaxation. Portions of the oxidized rods were carbonized under N_2 to 1000°C at 4°C/min. The results of two experiments are presented in Figs. 3 and 4. The depth of stabilization is delineated by coarsening of the fibrous microstructure. As observed with the magnetically oriented mesophase, oxidation proceeded to equivalent depths from the free surface and from cracks with access to the atmosphere. Mesophase that was insufficiently oxidized was often driven from within the oxidized casing by the pressure of pyrolysis gases.

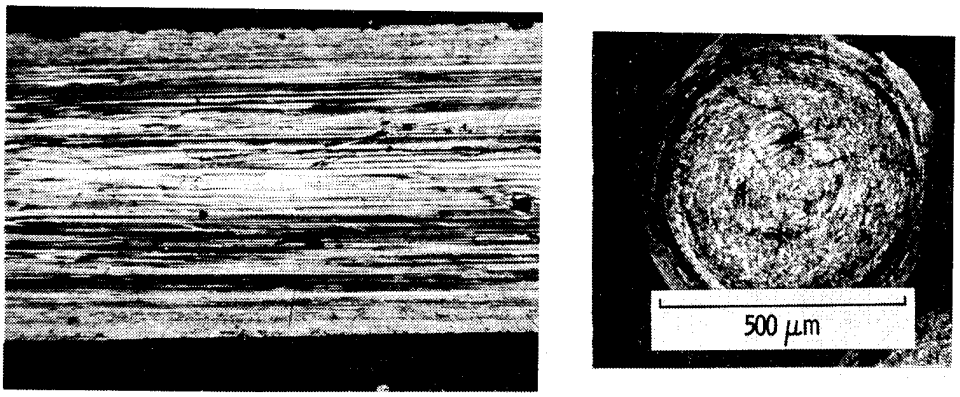

Fig. 2. Longitudinal and transverse views of extruded and drawn mesophase rod.

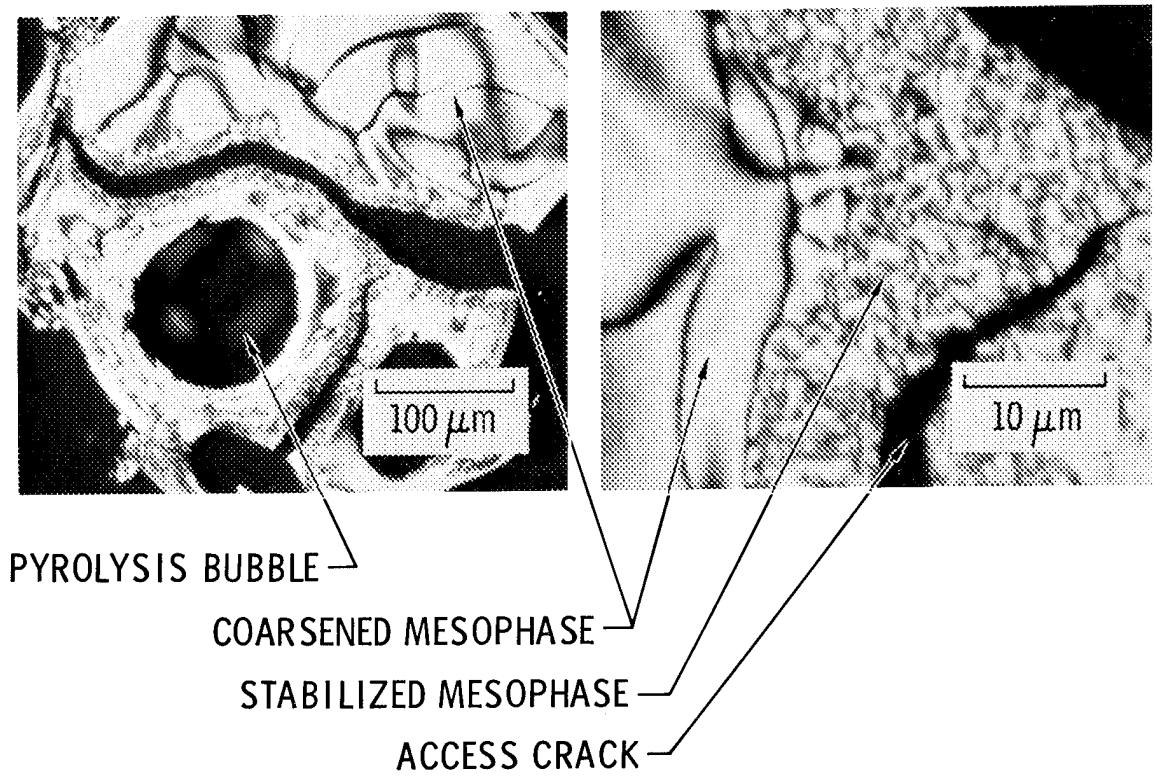

Fig. 3. Transverse microstructure of oxidized mesophase rod (air, 300°C, 8 h) after carbonization to 1000°C. Stabilization depth: 10 μm.

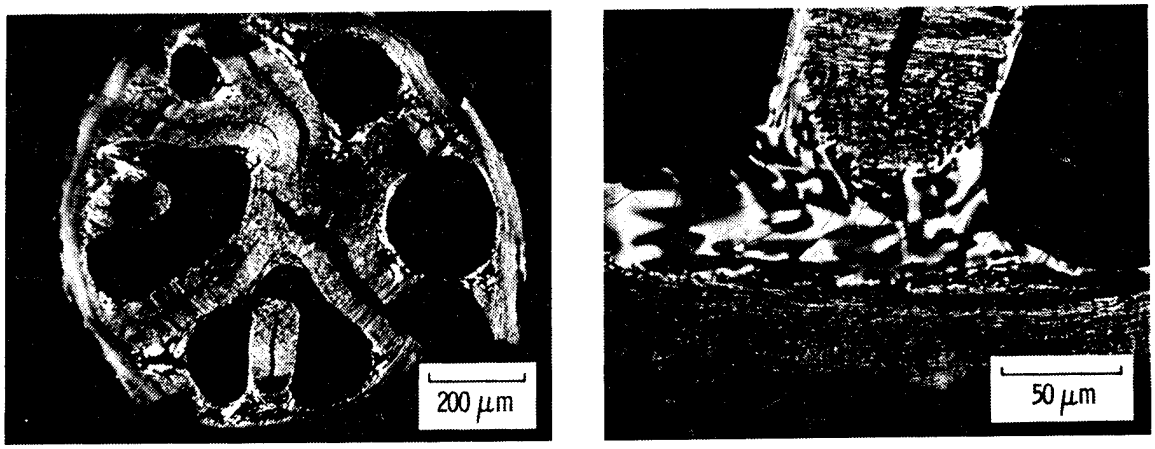

Fig. 4. Transverse microstructure of oxidized mesophase rod (O_2, 265°C, 64 h) after carbonization to 1000°C. Stabilization depth: 36 μm.

IV. MESOPHASE OXIDATION

Observations of weight change in some of the oxidation runs on mesophase rods indicated that substantial quantities of oxygen were absorbed and that both weight-gain and weight-loss reactions were involved. Some thermogravimetric analysis (TGA) results are given in Fig. 5 for the oxidation of sized particles (-325/+400 mesh, 38-45 μm) of the mesophase pitch used to extrude and draw rods. The initial weight gains exceed 10%, but weight-loss reactions subsequently appear; near 300°C, these reactions are sufficiently strong to cause a net weight decrease for long-term stabilization processes.

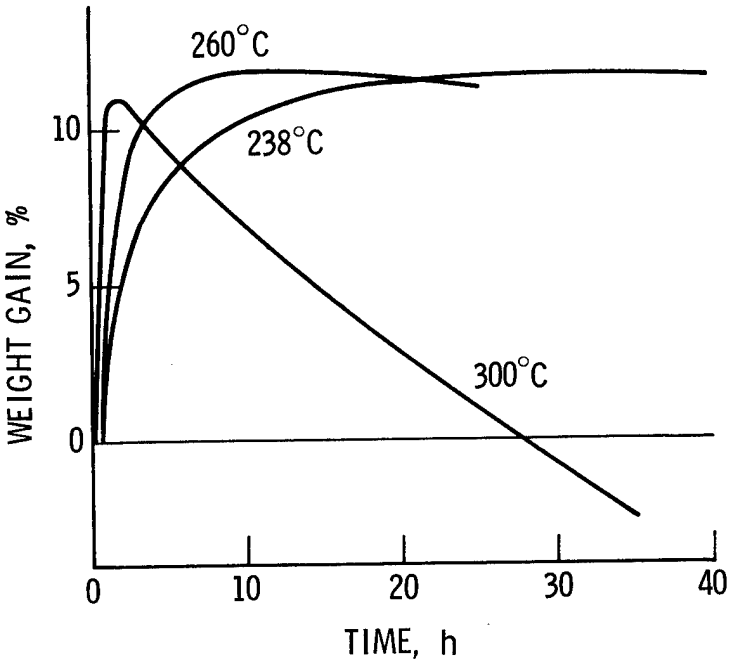

Fig. 5. Oxidation of sized mesophase particles in O_2.

V. DISCUSSION

Observations of the depth of stabilization are summarized in Table 1. Oxidation stabilization appears to be a diffusion-limited process, responding as expected to increased O_2 pressure, temperature, and time. High oxidation levels are attained, at least transiently, at the exposed mesophase surfaces. The oxidation process shows good throwing power in mesophase cracks. A diffusion depth of 50 μm may be adequate to stabilize bulk mesophase, provided that the access porosity is on this scale.

Table 1. Depths of Stabilization by Oxidation

Oxidant	Temperature (°C)	Time (h)	Depth (μm)
Air[a]	240	34	17
Air	300	8	10
Air	300	60	30
Oxygen	300	64	45
Oxygen	265	64	36

[a]Magnetically oriented mesophase.

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4. S. Chwastiak, U.S. Patent 4,209,500 (1980).