

EVOLUTION OF MICROSTRUCTURE IN PITCH-BASED CARBON FIBERS DURING HEAT TREATMENT

*A. A. Ogale**
Chemical Engineering
Clemson University
Clemson, SC 29634

D. P. Anderson
Univ. Dayton
Research Institute

K. M. Kearns
Materials and
Manufacturing Directorate
AF Research Labs

Abstract

The evolution of structure at various heat treatment temperatures (HTT) ranging from 300°C to 3000°C was investigated for pitch-based carbon fibers. Dimensional changes of individual AR- and SCF-mesophase fibers were measured. Starting from an oxidized state, the length of the fibers shrinks about 8% at a HTT of 900°C, and about 6% at 3000°C. The change in diameter was measured to be about 22%, with the most significant change observed at 900°C. Graphitic crystalline parameters of these fibers were also measured; the fibers heat-treated to 2875°C displayed about 80% crystallinity.

Experimental

Two grades of mesophase pitch-based fibers were investigated: AR-mesophase (Mitsubishi, Japan) and mesophase fraction separated by supercritical fluid extraction (SCF provided by the courtesy of Prof. Thies). The AR-fibers were stabilized by air-oxidation at 200°C for 3 days. The SCF fibers were stabilized in two steps: 12 hrs at 180°C followed by a 10°C/min heating to 280°C, a holding time of approximately 17 hours, and a cooldown at 10°C/min. The stabilized fibers were heated to a final temperature (Tmax) ranging from 300°C to 3000°C in increments of 300°C (10 sets) at a nominal heating rate of 3°C/min. Heat treatment temperatures up to 900°C were attained in a Mellen furnace (Webster, New Hampshire), whereas those above 900°C were attained in a graphitizing furnace (Materials Research Furnace Inc., NH).

Results and Discussion

Although the microstructure and properties of pitch-based fibers have been investigated by a number of researchers [Ref. 1, for example],

only a limited number of studies have dealt with dimensional changes [2]. The unique aspect of the present study was the measurement of dimensional changes of individual fibers in terms of their length and diameter and simultaneous characterization of the microstructure.

The dimensional measurements for AR fibers, Fig. 1, indicate very clearly that starting from an oxidized state, the length of the fibers shrinks about 8% at a HTT of 900°C. Above 900°C, the length does not reduce any further, instead it appears to increase slightly. The final shrinkage of the length (relative to the oxidized state) is about 6%. The slight increase can be explained by the alignment of the graphene layer planes along the fiber axis that result in the shrinkage of fibers in the transverse direction (diameter) but an expansion along the longitudinal direction.

Considerably larger changes are observed in the diameter of the fibers, as illustrated in Fig. 2. Starting from the oxidized state, a significant drop of 15% is observed till 900°C HTT. From 900°C till 1500°C, there appears to be a slight increase in the diameter. Beyond 1500°C, there is again a significant reduction of the diameter with the ultimate shrinkage being about 20% at HTT approaching 3000°C.

The fiber microstructure was characterized by scanning electron microscopy (SEM). Consistent with the dimensional measurements, the SEM micrograph of Fig. 3A reveals that the first major change is observed at 900°C, where a radial texture is observed. At higher HTT, the development of radial texture is more pronounced and by 2400°C the graphene-layer planes are seen very clearly in Fig. 3B.

Wide-angle x-ray scattering (WAXS) measurements indicate that at the higher HTT, the fibers have a d_{002} spacing as small as 0.3371 nm indicating that the material is over 80% graphitic.

Conclusions

The present study establishes that in AR mesophase pitches, the first significant change in dimensions and microstructure occurs at about 900°C. Whereas microstructure and properties continue to evolve over higher heat treatment temperatures, the next significant change is observed above 2400°C. These results should help in the establishment of optimum processing conditions for carbon fiber/carbon matrix composites.

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References

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2. V. Liedtke and K. J. Huttinger, "Mesophase Pitches as Matrix Precursor of Carbon Fiber Reinforced Carbon: III. Mechanical Properties of Composites," Carbon, 34 (9), 1081-86, 1996.

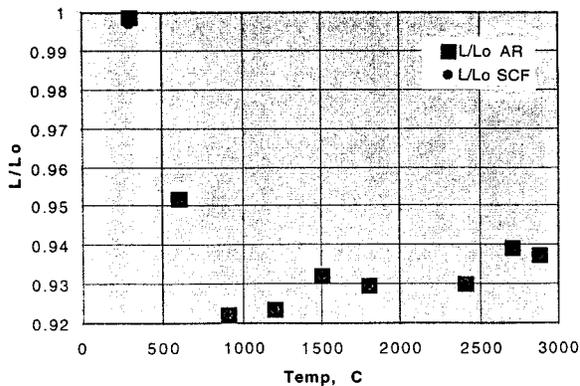


Fig. 1: Length ratio as a function of heat treatment temperatures.

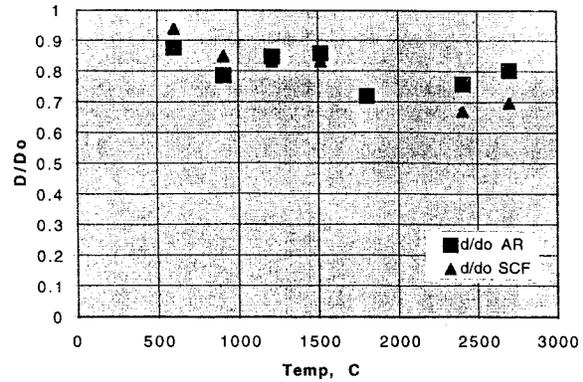


Fig. 2: Diameter ratio as a function of heat treatment temperatures.

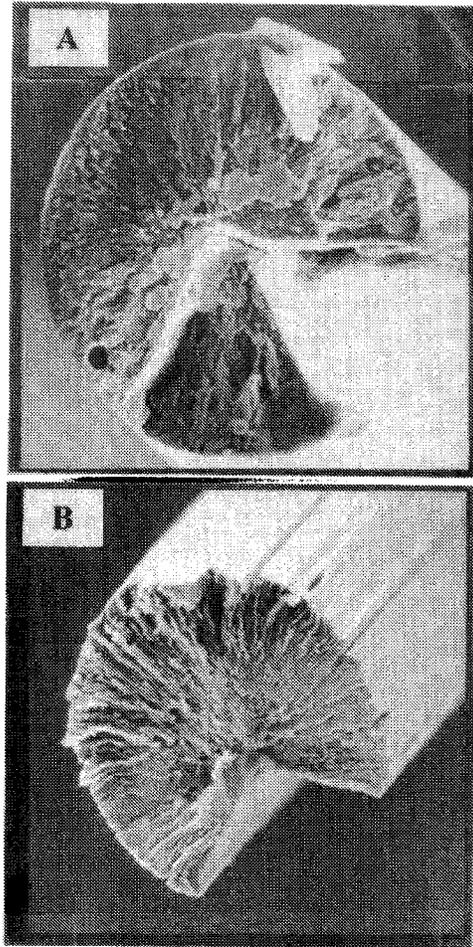


Fig. 3: SEM micrographs of fiber cross-sections. A: heat treated to 900°C; B: heat treated to 2400°C.