STABILIZATION OF MESOPHASE-MATRIX COMPOSITES AT OXIDATION TEMPERATURES BELOW 270°C

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Introduction

Several reports [1-4] have cited potential advantages in the use of relatively low oxidation temperatures for the stabilization step in fabricating mesophase-based carbon materials. We present here quantitative evidence in terms of stabilization threshold, carbonization yield, and exposure time that recommends oxidation temperatures near 170°C for the fabrication of mesophase-matrix composites.

Experimental

The mesophase-matrix composites studied were disks, 35 mm in height by 70 mm in diameter, prepared by injecting mesophase through CVD-rigidized preforms [5,6]. The mesophase pitch was ARA24R (Mitsubishi Gas Chemical), a naphthalene-based 100%-mesophase pitch with a softening point of 296.7°C and a density of 1.30 g/ml. Optical micrography confirmed that the composites were well-filled with 21 (±1) mass-% mesophase; the as-injected densities were 1.69 (±0.01) g/ml.

Each injected disk was cut to six nearly identical 60°-wedges that were exposed together in flowing oxygen at one of the selected temperatures: 171, 222, or 271 (all ±4) °C. The 60°-wedges were removed at intervals from 2.5 to 200 h.

Carbonization tests (to 1150°C) were then applied to 30°-slices cut by a diamond saw to expose planar surfaces intersecting the effective centers of the oxidized wedges. Specimens that were insufficiently stabilized were clearly observed, as illustrated in Fig. 1. Carbonization yields (to 1150°C) were calculated from the mass losses; in cases of mesophase exudation, two yields were obtained, the total coke yield within each container crucible, and the coke yield after cleaning the specimen to remove exudate.

Results

Oxidation mass gains, relative to the mesophase contents, of the 60°-wedges are plotted as a function of the square root of exposure time in Fig. 2. The open (unfilled) symbols represent specimens that exuded mesophase upon carbonizing; the well-stabilized specimens are indicated by filled symbols. The curves are sketched with the benefit of experience with other mesophase-injected composites [3]. Although the initial rate of mass gain increases with

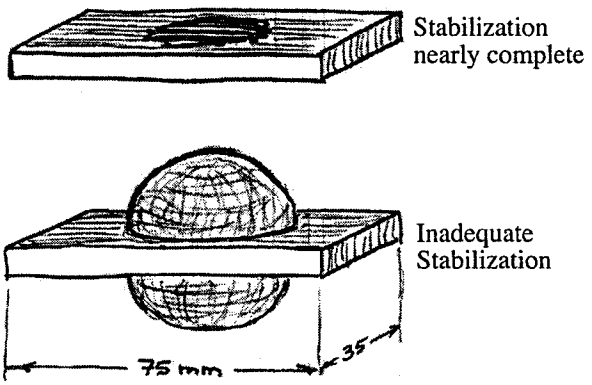

Fig. 1. Mesophase exuded during the carbonization of inadequately stabilized composites.

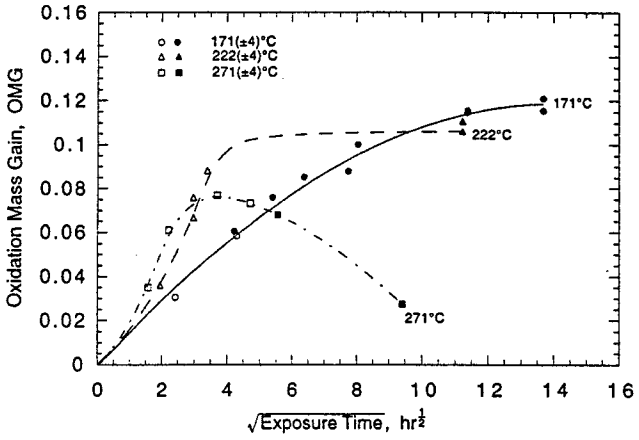

Fig. 2. Oxidation mass gains, relative to mesophase contents of 60°-wedges cut from injected preforms

oxidation temperature, the stabilization threshold appears to be reached first at the lower of the three temperatures, i.e., 171°C.

The carbonization yields to 1150°C are plotted in Fig. 3, again as a function of the square root of the exposure

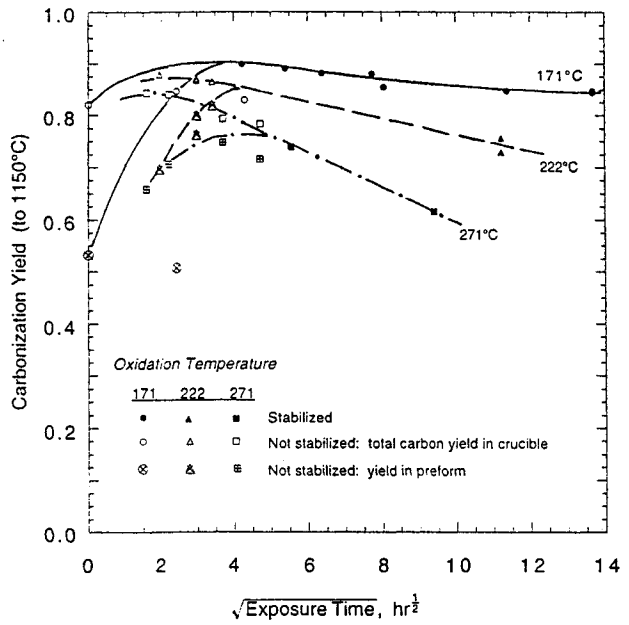

Fig. 3. Carbonization yields to 1150°C, relative to original mesophase contents, for the oxidized preforms depicted in Fig. 2.

time. In the region of incomplete stabilization, two curves are sketched: the total yield of mesophase coke, and the yield of coke within the preform. The results provide evidence that oxidation stabilization can be practiced at relatively low temperatures to obtain substantial benefit in carbon yield and with some improvement in exposure time. However we note a significant caveat, that for such a diffusion-controlled process, we must expect the oxidation threshold for stabilization in depth to increase with the size of the specimen.

Discussion

The present results confirm that oxygen can "dissolve," or somehow be absorbed [4], in mesophase near 170°C to an extent sufficient to assure stabilization [1,2]. Further, oxygen mobility within a mesophase matrix subject to shrinkage cracking is much higher than in mesophase free of shrinkage cracks, such as as-spun mesophase fiber. Studies of pitch-oxygen reactions, e.g., by differential scanning calorimetry [1,2,7], show that many reactions can proceed above 160°C, and apparently some, perhaps many, of these reactions can immobilize diffusing oxygen and thus limit the penetration depth for stabilization.

Thus an oxygen-processing window appears to exist, in the neighborhood of 170°C but quite possibly dependent on mesophase chemistry, in which oxygen can dissolve in sufficient concentration to effect stabilization in the early stages of subsequent carbonization. The effective utilization of this window to reduce oxygen gradients and to extend oxidation stabilization to larger-scale artifacts may depend on the patterns of microstrains resulting from the difference in thermal expansivities of the mesophase and intimately associated components such as the fibers of a carbon-carbon composite [3].

References

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