



Short residence time graphitization of mesophase pitch-based carbon fibers

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Abstract

The effects of graphitization time and temperature on the properties of three mesophase pitch-based carbon fibers have been characterized. Graphitization temperatures studied were 2400, 2700, and 3000 °C and residence times ranged from 0.7 to 3600 s. Helium pycnometry, measurements of fiber tow resistance, and X-ray diffraction were employed to study fiber properties. As anticipated, substantial variations in fiber properties were noted for the range of graphitization conditions studied and among the three fiber types. Significant structural evolution and property development occurred even at the shortest furnace residence times. For example, for one of the fibers, a furnace residence time of 0.7 s at 3000 °C resulted in a degree of graphitization value of ~50%, a density of 1.98 g/cm³, and an electrical resistivity of 6.3 μΩ m (corresponding thermal conductivity ~200 W m⁻¹ K⁻¹). A simple energy consumption analysis suggests that short residence time graphitization at high temperature may result in both lower costs and substantially higher production rates for fibers prepared from mesophase pitch. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Carbon fibers are finding increasing use in a wide variety of applications because of their superior strength and stiffness, low weight, and high thermal conductivity. Applications range from sporting goods to aircraft structures and missile nose cones. The fibers are manufactured from two main sources: polyacrylonitrile (PAN) and petroleum pitch (mesophase pitch) [1]. Carbon fibers prepared from pitch precursors typically utilize an extraction step to obtain the mesophase, followed by melt spinning, and a thermal processing paradigm that includes stabilization (thermosetting; ~300 °C), carbonization (<1800 °C) [1,2], and graphitization (up to 3000 °C), which promotes the development of the three-dimensional graphitic structure. A detailed review of the process has been presented by Edie [3].

Two general approaches may be used to enhance the graphitization behavior of pitch-based precursors. First, the structural characteristics of the fiber precursor may be controlled to promote more rapid structural development of graphite-like fibers. Precursor structure may be controlled by the shape of the spinnerette die, drawdown ratio, temperature, viscosity, flow conditions, and shear rate as reported by Hamada [4], Matsumoto [5], and Edie [6]. The second approach to optimize fiber properties involves control of graphitization time and temperature. Because of the high thermal input required for the development of graphitic structure, optimization of properties through this method may also allow for a reduction in manufacturing costs, since graphitization represents a significant portion of the total production cost for graphite-like carbon fibers prepared from mesophase pitch.

In this study, the effects of graphitization time (from ≤1 s to 1 h) on the properties of mesophase pitch-based carbon fibers have been characterized; results are reported for the degree of graphitization, electrical resistivity, and fiber density. The purpose of these investigations was to evaluate the rate at which graphitization occurred, and properties

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such as thermal conductivity were developed for three different carbonized pitch precursors. Although the specific nature of these precursors was not revealed by the supplier (BP Amoco), we believe these results are of interest because there are few reports on the development of carbon fiber properties at short graphitization times. Previously, Richardson and Zehms [7] reported on heat treatment of pyrolytic carbon at temperatures between 2600 and 3000 °C for times ranging from 15 s to 10 min. Time-dependent changes in gross dimensions and interlayer spacing were reported, although further analysis was limited. Pandic [8] studied graphitization of a petroleum coke and measured the interlayer spacing, stack height, and coherence length for fibers processed at furnace residence times of 20 and 40 s, and 1, 3, and 4 min. The results suggested that carbon passed through a rhombohedral form during graphitization since the measured interlayer spacing was greater than the hexagonal form. Fischbach [9] performed heat treatments on petroleum and coal tar pitch cokes (similar to pitch mesophase) to study the kinetics of graphitization for time periods lasting from 2 to 1000 min at temperatures of 2200 to 2900 °C. Effective reaction rates increased by a factor of $\sim 10^5$ over this temperature range and the variation in the unit cell parameter was reported.

These earlier results indicate that graphitizable carbons (such as mesophase) should transform rapidly at high temperature. The results of the present study confirm that significant graphitization may be attained within very short times. We also show that fibers with comparatively high thermal conductivities may be produced using graphitization times of <1 s. An energy analysis of the manufacturing costs associated with the preparation of carbon fibers under these conditions is presented, and we suggest that fiber production under these conditions appears economically favorable.

2. Experimental

2.1. Precursor fibers

The three pitch-based precursor fibers supplied by BP Amoco (Alpharetta, GA, USA) were simply designated A, B, and C. The only information provided was that the fibers were carbonized, but not graphitized, implying that they had been heat treated to temperatures less than 1800 °C. Fibers A and C were difficult to handle and would break if manipulated too harshly. Fiber B, in contrast, was quite easy to handle without difficulty. Fiber diameter, shape, and microstructure were not characterized.

2.2. Fiber heat treatment in batch and continuous modes

A water-cooled resistance furnace (Bethlehem Advanced Materials, Knoxville, TN, USA) was used for fiber heat treatment. The exterior dimensions of the furnace

measure 18 inches long \times 9 inches wide \times 8.75 inches in height. The heating element of the furnace and all internal parts are graphite and the hot zone length was estimated at 3.5 inches. The temperature inside the hot zone was measured with an Ircon Mirage dual wavelength pyrometer [10,11]. Argon was used as the purge gas.

Graphitization of the fibers was achieved by one of two methods: continuous or batch processing. Continuous processing was used to obtain hot zone residence times from 0.7 to 58.5 s, while batch processing was used to heat the fibers for residence times ranging from 900 to 3600 s. Graphitization temperatures of 2400, 2700 and 3000 °C were evaluated.

For continuous mode operation, the fiber tow was threaded through the furnace from a supply reel at one end to a take-up winder at the opposite end using two pulleys at the entrance and exit of the furnace. Only sufficient tension was applied to the tows to eliminate any slack; it is estimated that the pulling force was less than 50 g. Six residence times: 0.7, 2.0, 5.4, 12.5, 33.1, and 58.5 s were studied. These times were determined by measuring the time required for the fiber to travel through the hot zone and carrying out a rudimentary heat transfer calculation. This analysis was performed using approximate heat transfer equations, assumptions regarding the thermal conductivities of the fibers, modeling the fiber tow as a uniform infinite cylinder, and calculating the centerline temperature. It was determined that the fiber tows attained the hot zone temperature nearly instantaneously [10]. The cooling rate of the fibers heated by the continuous method was also very rapid; i.e., the fibers were essentially 'quenched' from elevated temperature. Although the effects of cooling rate on fiber properties were not characterized, the rapid cooling rate employed may also influence the structural properties of the fibers.

Batch mode processing was carried out by loosely wrapping approximately 8 m of the fiber tow around a small piece of carbon felt which was then placed in the hot zone. All batch-mode samples were heated at a rate of ~ 20 °C/min with an intermediate hold at 500 °C. The cooling rate of the furnace following the graphitization hold was also estimated to be 20 °C/min. Heating and cooling rates were obtained by using the manual control mode of the furnace. Due to the high thermal activation energy of the graphitization process [9,12], time at temperatures below the final heat treatment temperature was neglected in the heat treatment analysis and was not included in the isothermal residence times reported.

2.3. Fiber characterization

The densities of the precursor and heat treated fibers were measured by He pycnometry using a Micromeritics AccuPyc 1330. To increase precision, the sample cell was purged 10 times prior to each measurement and each sample was run 25 times. The calculated standard devia-

tions typically ranged from 0.002 to 0.005 g/cm³, although a few samples showed lower (0.0015 g/cm³) and higher (up to 0.008 g/cm³) standard deviations. Density values were used both as an indication of the degree of graphene plane alignment and for calculation of resistivity.

The resistivities of the fiber tows were determined with a micro-ohm meter. To improve the reproducibility of the measurement, tows were twisted approximately 50 times prior to measurement to contain any loose or broken filaments within the tow. The apparatus employed was constructed in-house and allowed for the characterization of multiple 0.25 m segments of 1 m long fiber tows. To minimize instrumental resistance effects, large diameter copper wire was used for connection to the micro-ohm meter and polished copper rods were employed to make contact to the fiber tows. Resistivity, r ($\mu\Omega$ m), was calculated using

$$r = (R*Y)/(\rho_f^*l_s) \quad (1)$$

where R is the measured resistance in Ω , Y is the yield of the fiber tow (g/m), ρ_f is the fiber density (Mg/m³), and l_s is the segment length (m). Each fiber segment was measured between eight and 10 times to obtain a reliable average of the resistance. Resistivity values ranged from 2 to 14 $\mu\Omega$ m and standard deviations were between 0.015 and 0.066 $\mu\Omega$ m.

The thermal conductivities of the fibers were estimated from the measured resistivity values using the Lavin equation [13], a form of which is shown below:

$$\kappa = 4400/(r + 2.58) - 295 \quad (2)$$

where κ is the thermal conductivity (W m⁻¹ K⁻¹) and r is the electrical resistivity ($\mu\Omega$ m) as determined by Eq. (1).

Structural characterization of the fibers was achieved with X-ray diffraction. Short lengths of tow were dipped into melted paraffin wax, and after solidifying, a 2.54 cm length of this composite was cut and affixed to an aluminum ring. This was then set on top of a sapphire disc in the sample cup of a Scintag XDS 2000 diffractometer (Cu K α radiation) and the diffraction pattern between 20 and 90° 2θ was obtained at a scan rate of 0.50° per minute. The scans were analyzed for any anomalous shifts in peak position (due to imperfect calibration of the diffractometer) using the known peak positions of sapphire. Following

determination of d_{002} , the degree of graphitization was calculated according to

$$g = \frac{3.44 - d_{002}}{3.44 - 3.354} \times 100 \quad (3)$$

In this equation, 3.44 represents the interlayer spacing of turbostratic graphite (in Å) and 3.354 is the interlayer spacing for single crystal graphite (in Å).

3. Results and discussion

3.1. Precursor fiber properties

The density, electrical resistivity, and interlayer spacing of the precursor fibers were measured with the techniques described above and are reported in Table 1. All of the results suggest that Fiber B is the most turbostratic; i.e., structurally, this fiber bears the least resemblance to graphite-like carbon. This fiber has a substantially lower density and a much greater resistivity. The d_{002} spacings, peak intensities, and peak widths of the three precursors also suggest that Fiber B is more turbostratic in nature. In contrast, Fibers A and C are much more similar, with Fiber A demonstrating a structure that is more graphite-like.

3.2. Fiber A

The effects of graphitization time and temperature on density are shown in Fig. 1a. Although Fiber A has the highest initial density, 1.8550 g/cm³, significant additional densification occurs, even for short residence times. For a 0.7 s residence time, fiber density increased to 1.9045, 1.9653, and 1.9823 g/cm³ for graphitization at 2400, 2700, and 3000 °C, respectively. From a structural perspective (Eq. (3)), the transition from a turbostratic to a graphitic structure can only account for a density increase of ~2.5%. Therefore, void, or pore, elimination within the fiber must also contribute to densification.

For longer residence times, densification continues for all heat treatment temperatures. For example, after 58.5 s, density values ranged from 1.9512 (2400 °C) to 2.0049 g/cm³ (2700 °C). While these values are lower than those of graphite (2.1–2.3 g/cm³), they indicate that substantial densification occurs under these heat treatment conditions.

Table 1
Densities, resistivities, calculated thermal conductivities, and crystallographic properties of precursor fibers

Fiber type (as-received)	Density (g cm ⁻³)	Resistivity ($\mu\Omega$ m)	Thermal conductivity (W m ⁻¹ K ⁻¹)	$d_{(002)}$ Peak position (Å); intensity (A.U.); and FWHM ^a (° 2θ)
A	1.8550	8.36	107	3.432/38,000/0.6
B	1.6793	14.19	Undetermined	3.454/100/3.4
C	1.8212	8.55	100	3.447/30,700/1.0

^a FWHM: peak full width at half maximum.

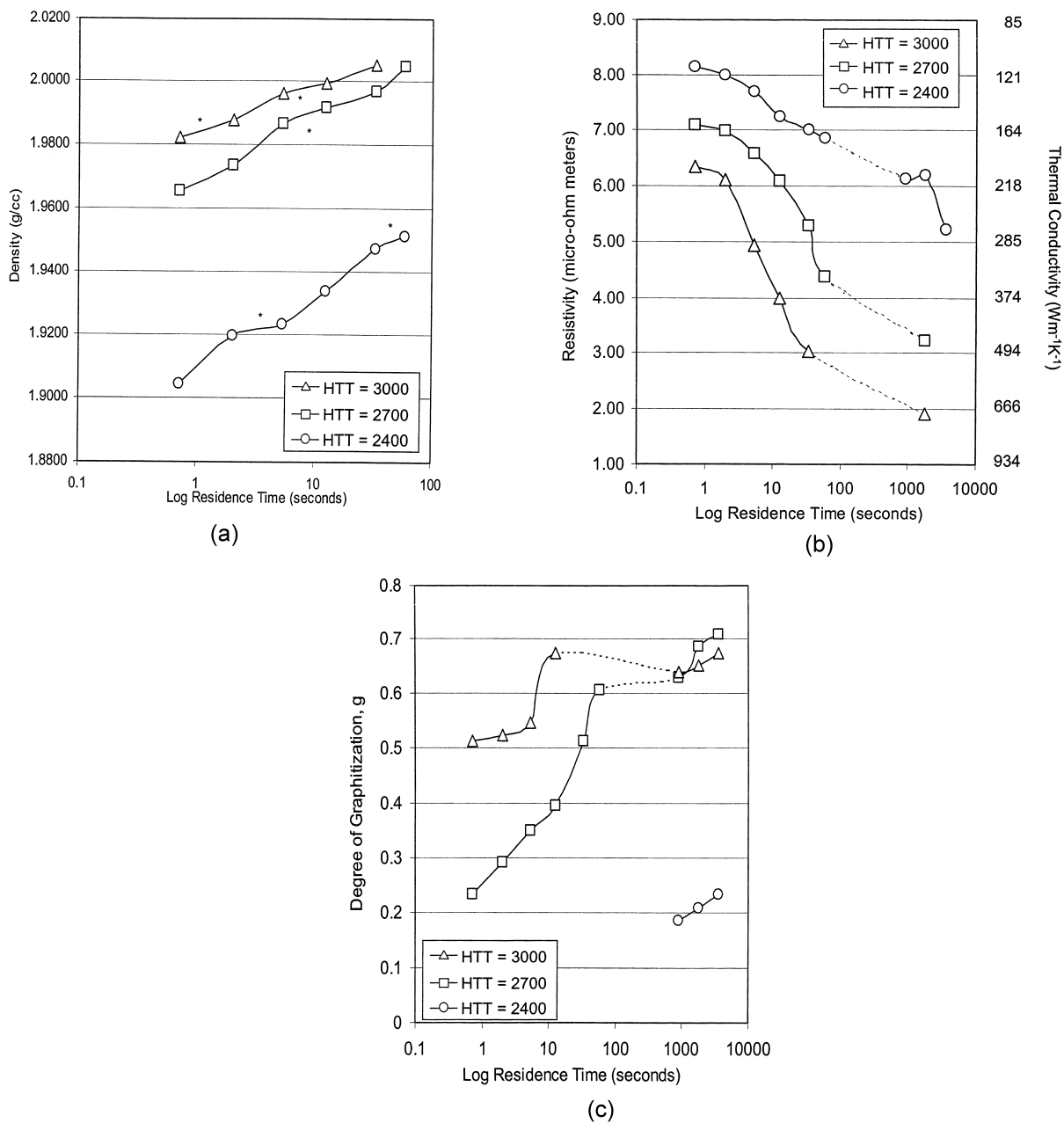


Fig. 1. (a) Density, (b) resistivity/thermal conductivity, and (c) calculated degree of graphitization of Fiber A as a function of residence time at graphitization temperatures of 2400, 2700, and 3000 °C. Asterisks (*) indicate heat treatment times during which densification proceeds at a slower rate.

Fig. 1a also suggests that the rate of densification is not logarithmically dependent on the graphitization time (nor is it linearly dependent on time). Because the error associated with the measured density values is approximately two to three times the symbol size, it appears that a simple straight line fit does not adequately describe the densification behavior. This implies that the rate of densification is

not constant, as discussed previously [12]. Time periods at which the densification rate lags are indicated by asterisks, but at this time, the reasons for the decreased densification rates at these times are not clear.

Fig. 1b illustrates the effects of graphitization time and temperature on the electrical resistivity of the fiber. The variation in resistivity as a function of time is greatest at

3000 °C, but a significant decrease in resistivity is noted for all temperatures. At 2700 °C, the resistivity of the carbonized precursor is reduced by 20% after heat treatment for 5.4 s, by more than 45% for a residence time of approximately 1 min, and by more than 60% for a 30 min heat treatment. Since the electrical resistivity of these materials is dependent on structural perfection, these results indicate that significant order develops within Fiber A within the first minute or two of graphitization, both at 2700 and 3000 °C. As for density, the resistivity behavior of the fiber heated at 2400 °C was different than the fibers heated at 2700 and 3000 °C. Also, as observed for densification, the change in electrical resistivity as a function of heat treatment time is non-uniform; for longer heat treatment times at 2700 and 3000 °C, the rate of change of the resistivity becomes smaller.

The structural analysis (Eq. (3)) of the fibers graphitized under different conditions is presented in Fig. 1c. Again, there is a large difference in the degree of graphitization between the fibers heat treated at 2400 °C and those at 2700 and 3000 °C, in agreement with expectations from density and electrical resistivity. Even for the longest heat treatment times, at 2400 °C, the graphitization of the fibers is below 25%. This suggests that significant densification, as well as enhancements in electrical and thermal conductivity, can be obtained without the extensive formation of graphitic structure in this pitch-based fiber.

In contrast to the results observed at 2400 °C, significant development of graphitic structure occurs at 2700 and 3000 °C, even for short heat treatment times. For a residence time of 0.7 s, at 2700 °C, a *g* value of 23% was obtained, while at 3000 °C, a degree of graphitization of 51% was determined. This indicates that graphene plane alignment can occur rapidly in these materials at the elevated temperatures employed for graphitization and confirms expectations from earlier studies on cokes [9]. The results for degree of graphitization are well correlated with the relatively high densities that were observed for these heat treatment conditions. Fig. 1c also confirms the suggestion of the density and resistivity results that the rate of graphitization of this fiber is non-uniform in time and that the behavior at 2700 and 3000 °C is more similar than at 2400 °C. The curves at 2700 and 3000 °C show an apparent step in the transformation process beyond which the rate of graphitization significantly decreases. While a contributing factor to this behavior may be the two different graphitization methods used (continuous and batch), analogous steps have previously been seen in X-ray diffraction and diamagnetic susceptibility studies performed by Pacault and coworkers [12].

The graphitization results for the samples prepared in the batch mode at long residence are not as consistent as those prepared by continuous processing. A significant increase in graphite content is observed when the heat treatment temperature is raised from 2400 to 2700 °C, but the results obtained at 2700 and 3000 °C are very similar,

with the 2700 °C heat treatment actually yielding an apparently higher degree of graphitization. While some degradation in the structure at 3000 °C might give rise to this effect, it seems equally likely that there is a slight error in the measurement of the d_{002} spacing which results in an error in the degree of graphitization calculated by Eq. (3). This equation is sensitive to small changes in *d*-spacing and a relatively minor measurement error of 0.001 Å in d_{002} can give an error in the calculated percent graphite of more than 1%.

Finally, we consider the calculated thermal conductivity of Fiber A as a function of graphitization time and temperature. These results, shown in Fig. 1b, were obtained by the method of Lavin [13] for the conversion of electrical resistivity. Although the identity of this fiber is not known, the initial thermal conductivity of $107 \text{ W m}^{-1} \text{ K}^{-1}$ (Table 1) indicates it is the best thermally conducting precursor of the three evaluated. A thermal conductivity scale, obtained using Eq. (2), is marked on the right side of the figure. At 3000 °C, even for a residence time as short as 0.7 s, the thermal conductivity increases to $\sim 200 \text{ W m}^{-1} \text{ K}^{-1}$; for heat treatments as short as 12.5 s, a thermal conductivity of $374 \text{ W m}^{-1} \text{ K}^{-1}$ is obtained. These values compare favorably with those of commercially available P-75 and P-100 [13] and approach the thermal conductivity of copper. With longer heat treatment times (1800 s), a thermal conductivity of nearly $700 \text{ W m}^{-1} \text{ K}^{-1}$ was obtained.

3.3. Fiber B

As-received Fiber B had a significantly lower density (1.6793 g/cm^3) and higher resistivity ($14.19 \mu\Omega \text{ m}$) than Fiber A. On this basis, we speculate that the fiber has a lower mesophase content than Fiber A, or that it possesses less structural order. The measured density of Fiber B as a function of graphitization time and temperature is shown in Fig. 2a. While the general relationships between density and graphitization time and temperature are similar to those of Fiber A, there are notable differences. For Fiber B, graphitization at 2400 and 2700 °C yielded relatively minor differences in fiber density, with substantially more densification occurring at 3000 °C. Another difference between these fibers is the final densities that were obtained, irrespective of heat treatment time. Comparing the results for the continuously processed fibers, the final density (1.8536 g/cm^3) of Fiber B subjected to the most severe graphitization conditions (3000 °C, 58.5 s) was still less than the initial density of Fiber A. However, the relative increase in density as a function of residence time was greater for B than A. As with Fiber A, Fiber B also exhibited certain temperature regimes where the rate of densification decreased. We also note that the densification behavior of Fiber B is, in general, somewhat less dependent on graphitization time and temperature than Fiber A.

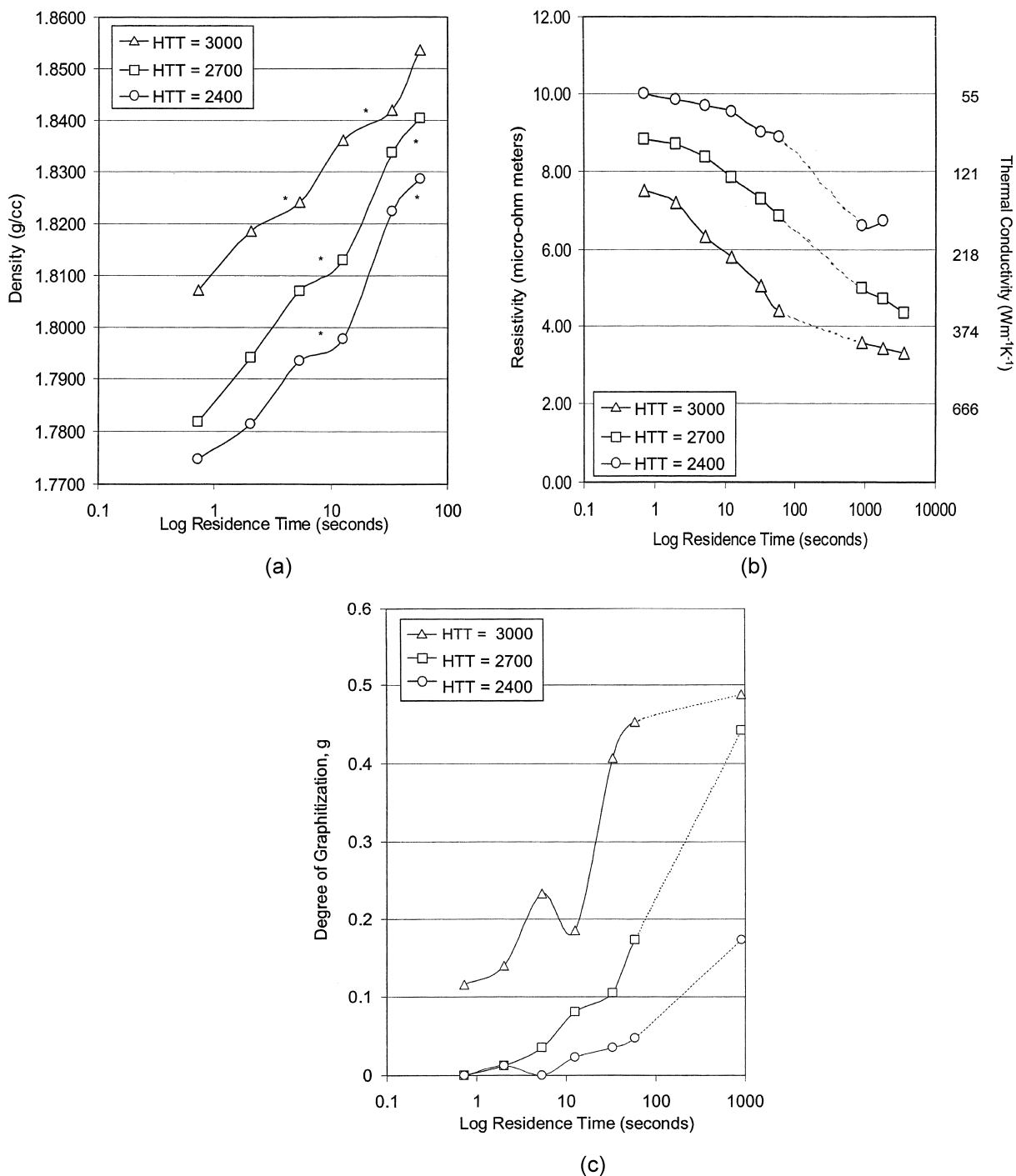


Fig. 2. (a) Density, (b) resistivity/thermal conductivity, and (c) calculated degree of graphitization of Fiber B as a function of residence time at graphitization temperatures of 2400, 2700, and 3000 °C. Asterisks (*) indicate heat treatment times during which densification proceeds at a slower rate.

Fig. 2b shows the electrical resistivity of Fiber B as a function of graphitization conditions. Fiber B (as-received) had the highest electrical resistivity of the three precursors,

14.19 $\mu\Omega$ m, and the broadest d_{002} diffraction peak, suggesting a low degree of structural order in this fiber. With graphitization, the resistivity decreased significantly,

but remained much higher than Fiber A for analogous heat treatment conditions.

The estimated thermal conductivity values of Fiber B graphitized under different time and temperature conditions are indicated by the scale on the right side of Fig. 2b and ranged from $55 \text{ W m}^{-1} \text{ K}^{-1}$ (0.7 s, 2400 °C) to $\sim 450 \text{ W m}^{-1} \text{ K}^{-1}$ (3600 s, 3000 °C). Values between 90 and $330 \text{ W m}^{-1} \text{ K}^{-1}$ may be obtained for a residence time under 1 min depending upon graphitization temperature.

The g values for Fiber B calculated from Eq. (3) are presented in Fig. 2c and, as expected, were much lower than for Fiber A, for equivalent heat treatment conditions. However, the general trends of increased degree of graphitization with longer residence time, or higher heat treatment temperature, were again observed. At 3000 °C, graphitization appears to reach a plateau, yielding a g value < 0.50 after going through a rapid increase for times between 12.5 and 33.1 s.

Finally, comparing the graphitization results (Figs. 1c and 2c) with the resistivity values (Figs. 1b and 2b), it appears that a measurable degree of graphitization of the fiber (approximately 10% or greater) is required to attain a resistivity below $8 \mu\Omega \text{ m}$ and a thermal conductivity above $120 \text{ W m}^{-1} \text{ K}^{-1}$. For example, Fiber A heat treated at 2700 °C for 0.7 s displays a resistivity of $7.08 \mu\Omega \text{ m}$ with a corresponding graphitization degree of 23.3%. Fiber B heat treated at 2700 °C for 33.1 s demonstrates an electrical resistivity of $7.29 \mu\Omega \text{ cm}$ and a degree of graphitization of 10.5%. In contrast, all fibers heat treated under conditions that yielded resistivity values greater than $8.0 \mu\Omega \text{ m}$ had g values of a few percent or less. The relationship between electrical resistivity and graphitization is discussed further below. In general, it is observed that there is a strong correlation between properties such as density and electrical resistivity and the degree of graphitization of the fiber; however, residual effects of precursor type on this relationship persist after heat treatment.

3.4. Fiber C

The density and electrical resistivity behaviors of Fiber C as a function of graphitization are similar to Fiber A, as shown in Fig. 3. The density of this precursor fiber, 1.8212 g/cm^3 , was intermediate to Fibers A and B, as were the densities obtained for analogous graphitization conditions.

The resistivity of as-received Fiber C, $8.55 \mu\Omega \text{ m}$, was also intermediate between Fibers A and B. Fig. 3b shows that the general characteristics of the resistivity vs. heat treatment response are very similar to Fiber A, and that the thermal conductivities of these fibers ranged from ~ 100 (0.7 s , 2400 °C) to $\sim 650 \text{ W m}^{-1} \text{ K}^{-1}$ (1800 s , 3000 °C).

The degree of graphitization for Fiber C samples processed continuously at 2400 and 2700 °C was measured and the results are presented in Fig. 3c. It is difficult to directly compare these results with those of Fiber A, due to

the smaller data set for this fiber, and the fact that the continuously processed Fiber A samples treated at 2400 °C were not studied by XRD. However, it appears there are significant differences in the extent of graphitization of the two fibers when heated at 2700 °C. For analogous heat treatment times at 2700 °C, Fiber C demonstrates a much lower g value than Fiber A, while at the same time, the Fiber C samples display similar electrical resistivities. This implies that the degree of graphitization is not the sole factor in defining the observed electrical (and, hence, thermal) properties of these materials, as expected. Other factors, such as defect content, layer orientation, coherence length, etc., also play a role.

3.5. Correlation of graphitization behavior to physical properties

The densification and electrical resistivity responses as a function of degree of graphitization are shown in Figs. 4 and 5, respectively. All three fibers show a trend of increasing density with an increase in graphite content; however, the responses are non-linear and appear to show steps, similar to those noted for densification vs. graphitization time. The results for Fiber B are confined to comparatively low degrees of graphitization and low density values. In contrast, Fibers A and C show that a wide range of g values can contribute to comparatively small changes in fiber density. This is to be expected since the structural changes (variations in the d_{002} spacing) that occur with graphitization between the purely turbostratic and graphitic structures can only account for a density increase of $\sim 2.5\%$. Because the overall increase in density resulting from graphitization ranges from 8.1 to 10.4%, other processes, such as void collapse and an increase in layer orientation, neither of which affects g , must also play a major role in densification. Thus, the apparent correlation between density and graphitization is largely fortuitous because these other densification processes proceed simultaneously with graphitization.

The relationships between the electrical resistivities and degrees of graphitization of the three fibers (Fig. 5) are also informative. For Fibers B and C, the relationship between these two properties is nearly linear, and several of the data points overlap. Fiber A also shows a strong correlation, as would be expected due to the importance of structure on resistivity. However, this fiber demonstrates a lower dependence of resistivity on degree of graphitization. A more in-depth understanding of these relationships requires further characterization of additional fiber structural properties such as layer orientation and coherence length. Unfortunately, the characterization of these properties has not yet been completed. The results do indicate, though, that expected relationships between fiber properties and degree of graphitization exist, and that these relationships are dependent on precursor type.

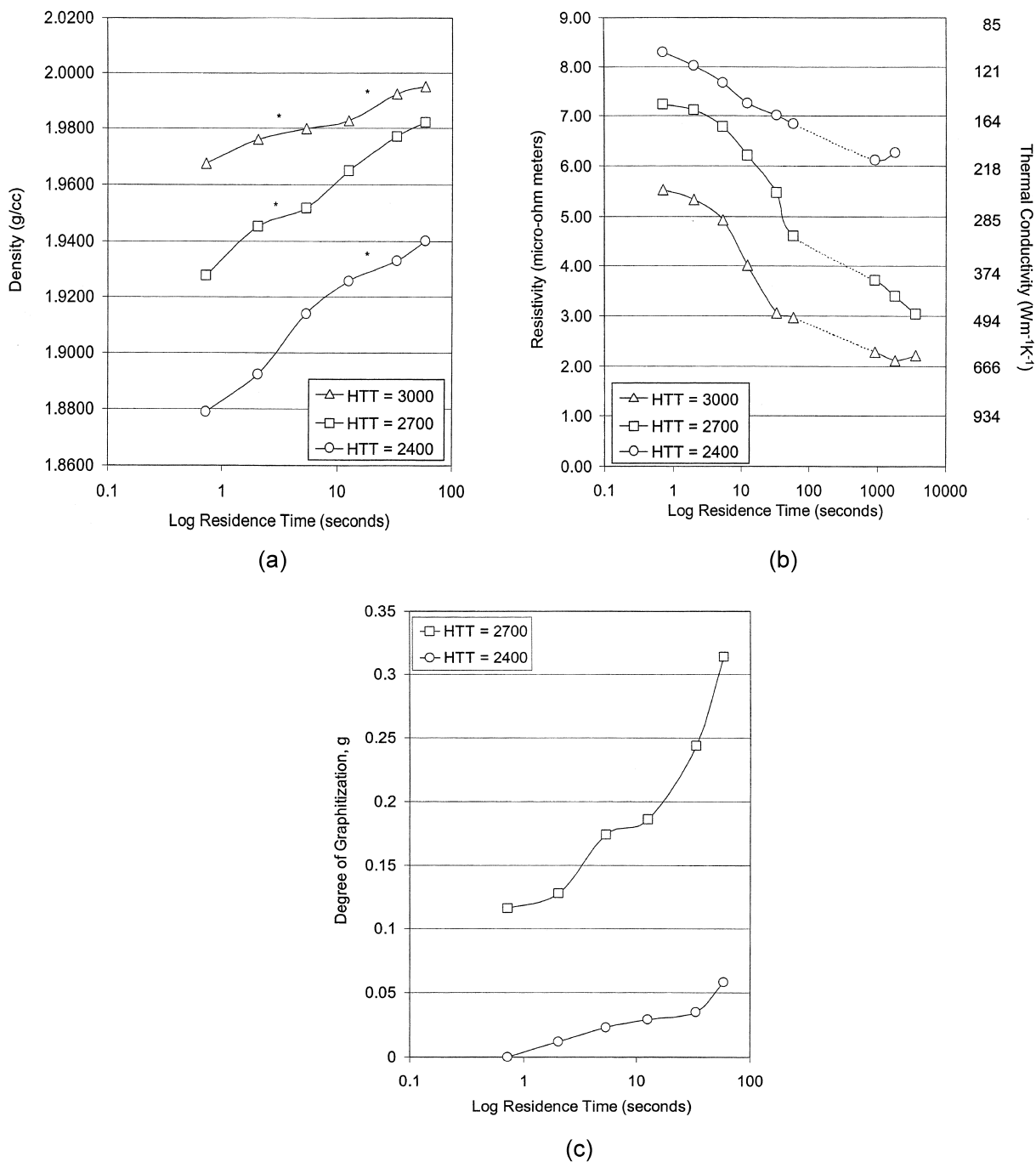


Fig. 3. (a) Density, (b) resistivity/thermal conductivity, and (c) calculated degree of graphitization of Fiber C as a function of residence time at graphitization temperatures of 2400, 2700, and 3000 °C. Asterisks (*) indicate heat treatment times during which densification proceeds at a slower rate.

3.6. Energy analysis of fiber production

To evaluate the graphitization conditions that were most energy efficient for the production of carbon fibers, time

and temperature conditions that resulted in fibers with similar electrical resistivities/thermal conductivities were first identified. Then, utility costs in kWh to produce the fibers under these different conditions were calculated

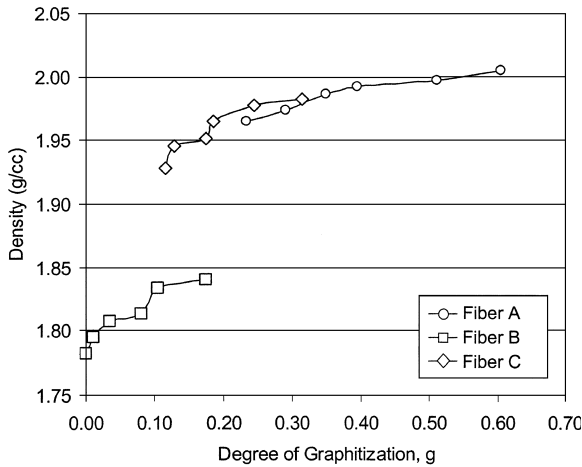


Fig. 4. Carbon fiber density as a function of the degree of graphitization for fibers heat treated at 2700 °C.

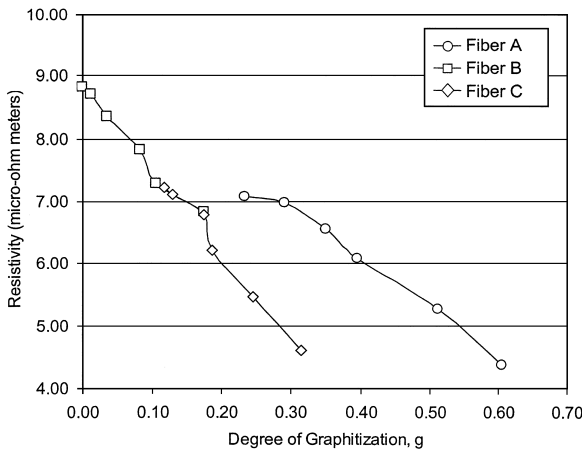


Fig. 5. Electrical resistivity as a function of the degree of graphitization for fibers heat treated at 2700 °C.

from the furnace volt and amp requirements. Since fibers with identical thermal conductivities were not available, fibers with similar conductivities (that ranged from 266 to 290 $\text{W m}^{-1} \text{K}^{-1}$) were used. The residence times and temperatures required to produce carbon fibers with these properties (from precursor A) are shown in Table 2. The

different residence times reported imply that different production rates can be expected for the manufacture of carbon fibers with similar properties. For example, by graphitizing this precursor fiber at 3000 °C for 5.4 s ($\kappa = 290 \text{ W m}^{-1} \text{K}^{-1}$), fiber production can be increased by a factor of approximately six compared to graphitization at 2700 °C ($\kappa = 266 \text{ W m}^{-1} \text{K}^{-1}$), and by a factor of 670 times compared to graphitization at 2400 °C ($\kappa = 270 \text{ W m}^{-1} \text{K}^{-1}$).

The relative energy costs to produce (graphitize) an arbitrary unit length of fiber under these different conditions can be estimated from the experimental data given in Table 2. The product of the furnace voltage and current and the furnace residence time, $V \times I \times t \times 10^{-3} / 3600$ s/h, is the electrical energy consumption (in kWh) required to process a 3.5 inch (~ 0.09 m; the furnace hot zone) length of fiber in this laboratory furnace. The calculations for 2400, 2700, and 3000 °C may be used to estimate the relative energy costs for fiber production, ignoring other operating costs, such as cooling water and furnace maintenance. This simple analysis suggests, perhaps contrary to expectations, that the best approach to reduce production costs does not lie in furnace operation at lower temperature, but furnace operation at higher temperature with greatly reduced residence times and higher throughput rates.

4. Conclusions

We have investigated the effects of graphitization time and temperature on the properties of carbon fibers prepared from different mesophase pitch precursors. By using a continuous mode processing paradigm, it was possible to investigate the effects of very short (≤ 1 s) residence times at elevated temperatures on the properties of the carbon fibers. Significant variations in density, electrical resistivity, and degree of graphitization were all observed, as were residual effects of precursor type on each of these properties. The rapid development of desirable material properties was consistent with the known thermal activation energy associated with graphitization [9]. Irrespective of precursor type, significant densification and decreases in electrical resistivity were observed for all fibers at a residence time of only 0.7 s. Corresponding thermal

Table 2

Analysis of energy requirements for the manufacture of carbon fibers from precursor fiber A with thermal conductivities between 266 and 290 $\text{W m}^{-1} \text{K}^{-1}$

Heat treatment temp. (°C)	Furnace power current/voltage (A/V)	Residence time (s)	Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	Energy requirements for production of 0.09 m of fiber (kWh)
2400	1650/7.5	3600	270	12.38
2700	1900/9.5	33.1	266	0.17
3000	2150/11.1	5.3	290	0.04

conductivities for these fibers were as high as $\sim 250 \text{ W m}^{-1} \text{ K}^{-1}$. These results indicate that fibers with desirable performance characteristics can be produced with very short graphitization treatments and, thus, at high throughput rates.

A simple analysis was carried out to estimate the energy requirements of graphitization for the production of carbon fibers with similar thermal conductivities. Contrary to expectations, the manufacture of these fibers at high temperature for very short times appeared significantly less energy intensive (~ 350 times less) than graphitization at lower temperatures.

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