Length Distributions of Carbon Fibers Grown from Natural Gas

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Introduction

Carbon fibers produced by pyrolysis of natural gas require submicron-sized metallic particles which act as catalytic nuclei for fiber growth (1). In the present work we have investigated the lengths of fibers grown by particles from five different types of iron-containing dopants.

When one examines a mass of vapor grown carbon fibers on a substrate, it is apparent that a broad distribution of lengths is present (1). Our quantitative evaluations of fiber growth have dealt with this problem by utilizing quantities such as "mean fiber length" (1). However, until now no statistical study of the length distribution of carbon fibers grown from the vapor phase has been attempted.

Experiments

Alumina substrates of 96% purity and 0.64 mm thickness were doped with thin lines of five different dopants. Lines of dopant thinner than 1 mm were doposited by masking most of the substrate with tape and painting liquid phase suspensions of dopant over the tape. The dopants were selected for their diversity of size and chemistry; they are listed in Table I. The average particle diameters in these dopants ranged from 12 to 71 nm. In both the magnetite and ferrofluid samples the iron is in oxide form. Likewise, the $Fe(NO_3)_3$ dopant decomposes to a mixture of oxides before use (2). However, x-ray diffraction shows that the iron of the "smoke" suspensions is not oxidized. The average size of particles shown in Table I was obtained by direct measurement from transmission electron micrographs.

Fibers were grown on these substrates at 1054°C using an isothermal two step process which was somewhat more simple than the one previously described (1). Filaments were lengthened at 1054°C by exposure to a 6.25% natural gas mixture in H_2 for 30 minutes. The filaments were thickened in 100% natural gas. The natural gas was a mixture of 2.1% C_2H_6 and 1.0% N_2, with the remainder being 99.99% CH_4. After the fibers were removed from the growth reactor they were photographed in a scanning electron microscope. Because the lengthening step natural gas concentration of 6.25% selected for these experiments was considerably below the optimum for growth of long fibers, it was possible to frame the overwhelming majority of the fibers in photographs at 30X magnification. This allowed fiber length to be directly measured from the photographs.

Results and Discussion

Table I shows the results from the substrate doped with five types of particles. Fibers shorter than 0.3 mm were omitted because it was not always possible to count them or discern their lengths with sufficient accuracy. The average lengths are quite similar, particularly among the last four data sets for which more than 40 fibers each were counted. Since the mean lengths of fibers grown from the five separate dopants are quite similar, we consider first the collective distribution of lengths of all fibers grown in this experiment. A histogram of the fiber length distribution for the 271 fibers comprising this data set is plotted in Fig. 1. These data may be fitted to an exponential function of fiber length ℓ, $N \exp(-c\ell)$ by using the Simplex technique (3). The optimal fit with $c = 2.18\ mm^{-1}$ is plotted as

Table I. Dopant Size and Resultant Fiber Length

Dopant	Source	Average Size of Particle (nm)	Average Fiber Length (mm)
Fe-Ni alloy smoke (metallic)	ULVAC, Japan	28	.66
$Fe(NO_3)_3$	Fisher (99.9%)	31	.812
Ferrofluid	Ferrofluidics Corp., USA	12	.830
Fe smoke (metallic)	ULVAC, Japan	34	.746
Magnetite	W. E. Yetter, GMR	71	.878

the solid line. Figure 1 also includes estimated error bars obtained by augmenting the merely sta-tistical error in counting n fibers, $\sqrt{n}$,* to $\sqrt{n+1}$ to account for systematic errors (4). Now we must answer the question: Do the data sets for the five different dopants fit the same functional form of length distribution? Each of the five data sets was therefore plotted and fitted to the functional form $N\ e^{-2.18\cdot\ell}$; the results are shown in Fig. 2. As in Fig. 1, it may be seen that most of the data points fit this relation to within experimental error. A χ^2 test of this data shows that the probability is high that these data sets have statistically indistinguishable length distributions.

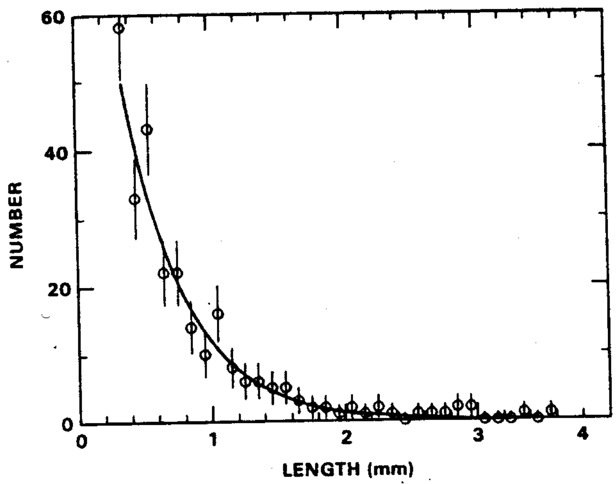

Figure 1. Fiber length distribution histogram for all of the fibers which could be measured on the substrate. Solid line is the least mean squares fit to the data points, $n = 91.3\ \exp(-2.18\ \ell)$ where ℓ is measured in mm.

Thus, under the lengthening conditions selected for this experiment, the distribution of fiber lengths obtained for each dopant were statistically indistinguishable. Moreover, a detailed analysis of the aggregate data set of all fibers longer than 0.3 mm showed that the distribution of fiber lengths is an exponential function in which the number of fibers n having a given length ℓ is proportional to $\exp(-c\ell)$.

This form of length distribution may be obtained by assuming that the fibers lengthen linearly with time (1) until they cease growing, with a constant probability of growth cessation at any time. Such picture is consistent with poisoning of the catalytic particles from the gas phase.

References

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2. J. R. Bradley and G. G. Tibbetts, Carbon (to be published).

3. J. A. Nelder and R. Mead, Comp. J. 7, 308 (1965).

4. P. R. Bevington, Data Reduction and Error Analysis for the Physical Sciences, (McGraw-Hill, New York, 1969).

*Otherwise the error associated with measuring 0 fibers in a 0.1 mm interval is 0, which violates our intuition and introduces a pole in the Simplex fitting routine.

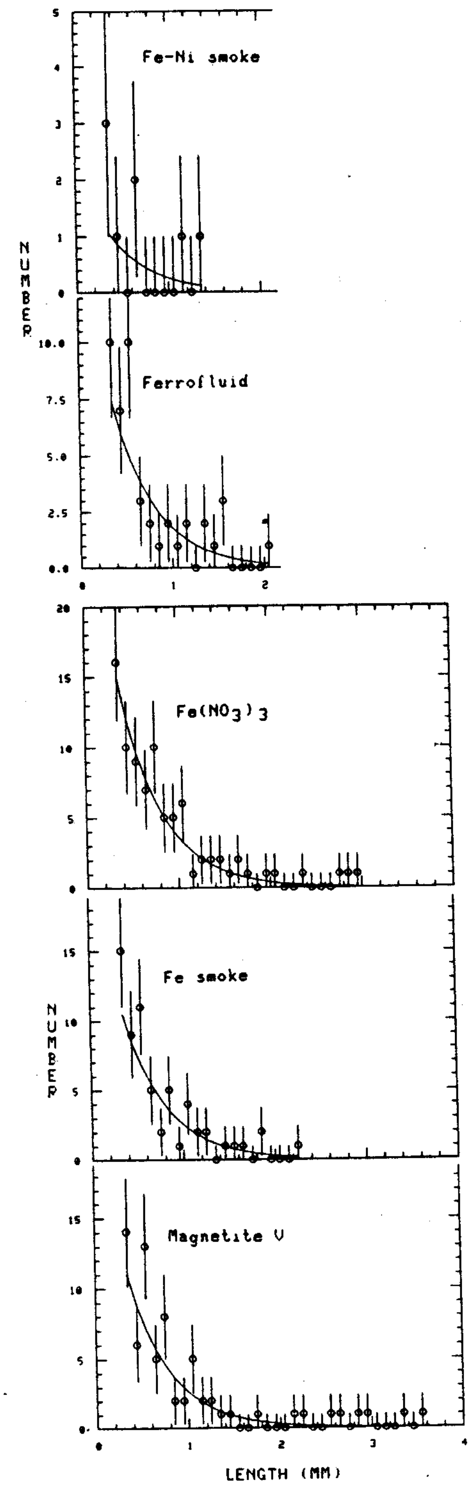

Figure 2. Length distribution histograms for fibers grown from each of the five separate dopants. Solid line is a fit to the data points using, as in Fig. 1, $n = N\ \exp(-2.18\ \ell)$ where ℓ is measured in mm.