GROWING CARBON FIBERS NEAR THE IRON-GRAPHITE EUTECTIC

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INTRODUCTION

Filamentous carbon is produced at high temperature by transition metal catalyst particles in an atmosphere of decomposing hydrocarbons or CO. Growth rates as high as several mm/minute have been recorded; these rates correspond to converting virtually all of the reactive carbon molecules incident on the catalyst particle to lengthening filamentous carbon [1].

Because of the high probability of molecular adsorption and decomposition after impinging on a liquid surface, Wagner and Ellis's VLS (Vapor Liquid Solid) growth process [2], originally conceived to explain the growth of Si whiskers, offers the requisite high efficiency for forming filamentous carbon. But carbon filament growth differs from VLS in one very significant way: VLS growth of Si whiskers may be catalyzed by liquid metal catalyst droplets of any diameter; whereas carbon filaments of above 1 μm have not been reported. This observation seems to be consistent with a rate limitation imposed by carbon atom diffusion through a solid catalyst particle.

In the particular case of iron-particle-catalyzed filament growth, the iron graphite eutectic at 1154°C might be expected to be the temperature boundary between profuse and unsuccessful filament growth. In fact, the growth of long filaments has been found to be most efficient far below this temperature, and to be almost negligible above 1154°C [3]. The resolution of these facts was provided by the work of Benissad *et al* [4], who recognized that small catalyst particles could melt far below the eutectic, even below 900°C, and maintained that liquid particles were responsible for efficient carbon fiber growth.

The results reported below are the first to show a convincing onset of filament growth at a well defined particle melting temperature.

EXPERIMENT

The growth apparatus utilized an electrical furnace with SiC heating elements to heat a 14.5 mm ID mullite tube. Although the total furnace length was 91 cm, the uniformly heated portion of the tube was about 65 cm long. In most experiments, a flow rate of 2600 cm^3/min of 99.99% pure methane gas was used. In experiments which we labeled "Fe", the methane was mixed with a flow of 102 cm^3/min of 99.999% pure He bubbled through $Fe(CO)_5$ maintained at 22°C. In experiments labeled "Fe+S", a flow of 4.5 cm^3/min of H_2S was added to the two gases listed above. For each type of experiment performed at 1150°C, the gas residence time in the heated portion of the tube was about 0.55 second. At the end of the 2 minute growth period, the feedstock manifold was valved off while any fibers remaining in the system were purged out by a rapid flow of high pressure nitrogen.

RESULTS

Figure 1 displays both the yield and the apparent density (mass/unconstrained volume of fluffy material obtained from the reactor) during these experiments. Material produced without sulfur addition always had a apparent density over 0.04 g/cm^3 and thus must be classified as soot.

Scanning electron micrographs verify the inferences based on yield and apparent fiber densities. Well formed, relatively soot free fibers were grown above 1183°C with the "Fe+S" mixture. Without hydrogen sulfide addition only a few fibers formed, while each fiber was covered with small soot particles. Material formed using the "Fe+S" mixture far below the eutectic temperature formed a compact soot mass without a hint of fibrous character.

Figure 2 shows a histogram of catalyst particle diameters obtained from a mixture of iron carbonyl, hydrogen sulfide, and He at 1161°C.

DISCUSSION

The yield data clearly show that, at least in the regime we have chosen, fiber growth is more efficient above the iron-graphite eutectic than below (Figure 1,

bottom panel). This is consistent with the concept discussed in the introduction that only molten particles are effective in catalyzing fiber growth. Although fiber growth is observed in Figure 1 as far as 30°C below the eutectic, this may be attributed to fibers grown from particles small enough to melt far below the eutectic.

By using Benisaad *et al's* expression [4] for the melting point $T(r)$ (in °C)as a function of Fe particle diameter r (in nm),

$$T(r) = 1153 - 400 / r \qquad (1)$$

it is possible to calculate the fraction of our particles which are molten as a function of temperature and compare this with the observed yield. If melting as a function of particle diameter is the sole determinant of fiber yield, our results should resemble the measured yield curve. We shall assume a constant yield Y_0 of 17% above the eutectic to normalize this model to the experimental results. The initial decline in yield corresponding to the freezing of the largest particles in the histogram occurs at 1144°C and decreases the yield by the fraction of particles in that bar. In general, if r_i is the value of fiber radius at the center of the ith element of the histogram of Figure 9, and $T(r_i)$ is the melting point of a particle of this radius from Equation 1, the yield Y_i may be determined by using

$$Y_i(T) = Y_0\left(1 - \frac{\sum_{k=0}^{i} f_i(r)}{\sum_{k=0}^{9} f_i(r)}\right) \qquad (2)$$

The Y_i values are plotted vs. the $T(r_i)$ values as a dashed line in Figure 1 and may be qualitatively compared with the observed yield for the "Fe+S" curve. The drop in yield below the eutectic to 1140°C is in good agreement with the experimental curve. Below 1140°C the experimental results do not fall as sharply as the model's calculation, but this may be attributed to the fluctuations of the temperature along the growth tube, which we estimate to be 5°C. Overall, however, the model is fairly consistent with the hypothesis that yield is controlled by the melting of catalyst particles, and it encourages us to believe that only molten catalyst particles can grow fibers.

REFERENCES

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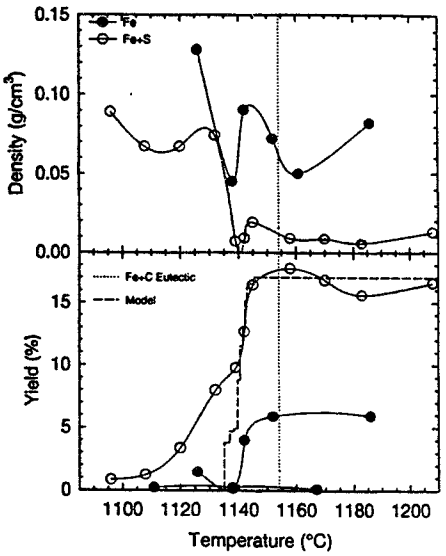

Figure 1. Apparent density (product mass/unconstrained volume) and carbon yield (product mass/mass of carbon atoms in feedstock) as a function of temperature.

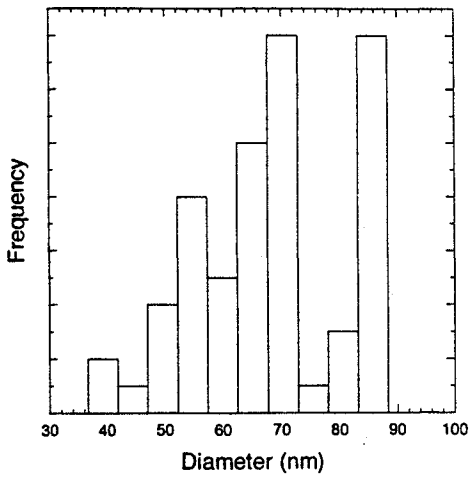

Figure 3. Histogram of catalyst particles.