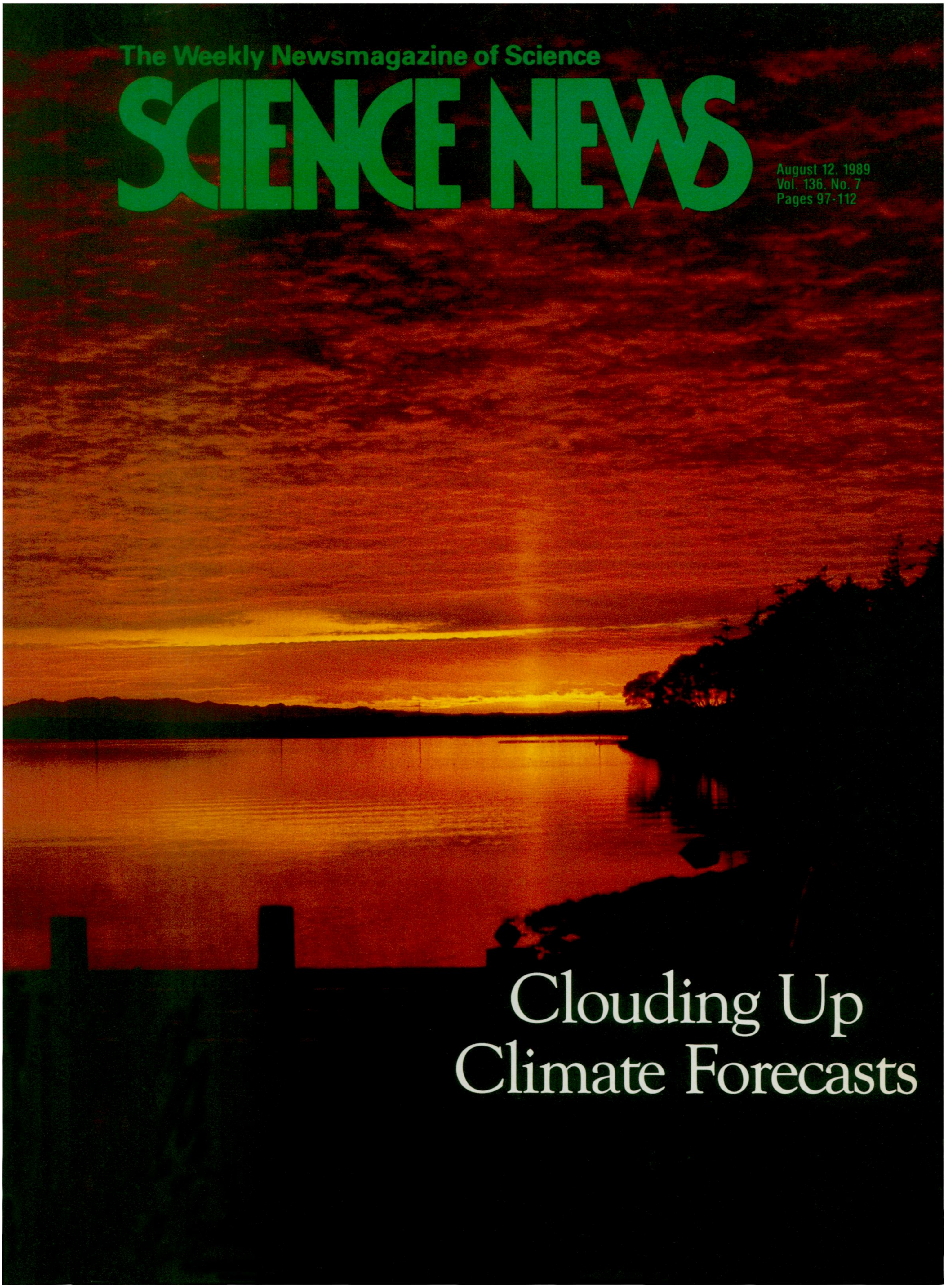

The Weekly Newsmagazine of Science

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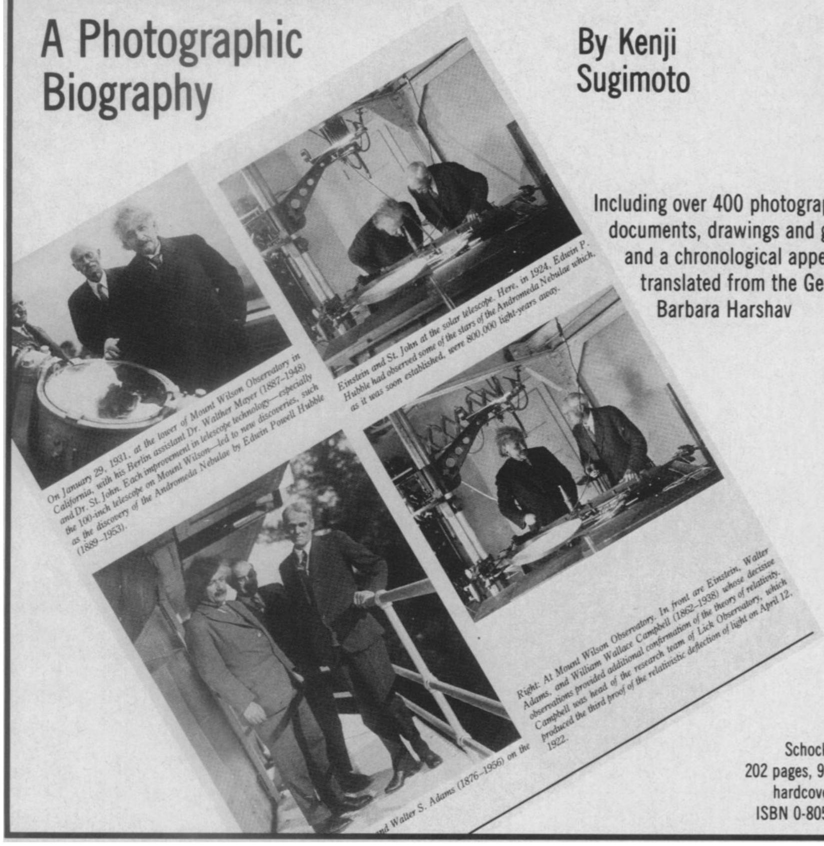
By Kenji Sugimoto



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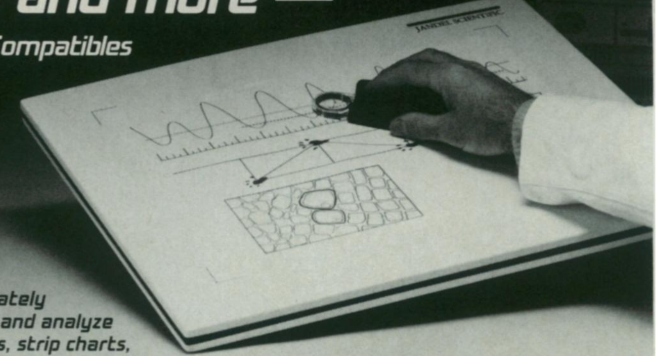

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The Carbon Gradient

Hollow carbon filaments catalytically produced by submicron-size iron particles can be the template for larger carbon fibers used in composite structural materials. A scientist at the General Motors Research Laboratories has identified how these filaments grow and why they take their characteristic form.

Carbon Fiber Growth

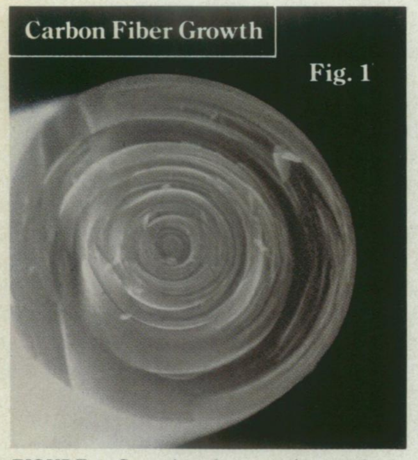
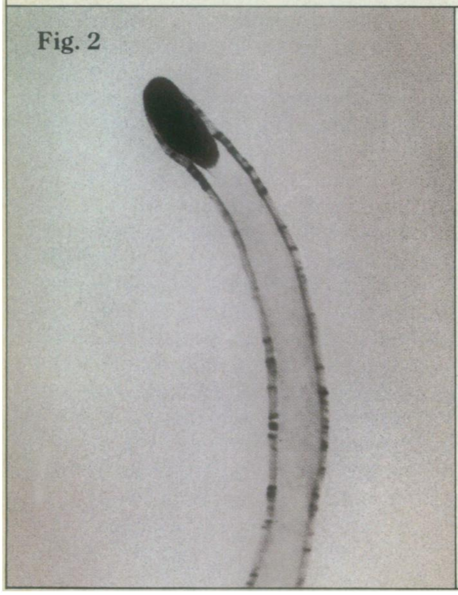
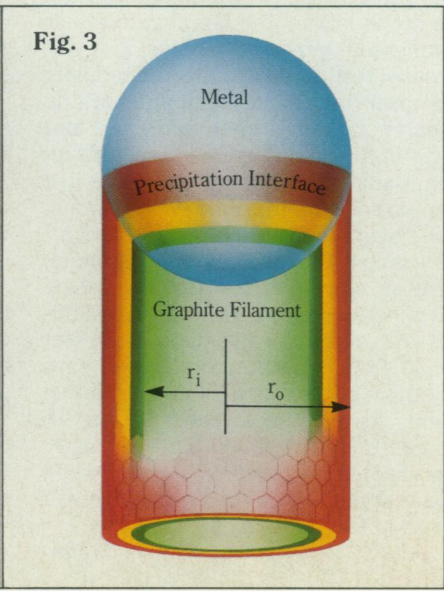


FIGURE 1: Scanning electron micrograph of a cross section of a vapor-grown carbon fiber.

FIGURE 2: Typical carbon filament grown from natural gas by an iron catalyst particle.

FIGURE 3: Schematic model showing inner and outer radii, the precipitation interface, and the nested basal planes of the outer surface.





Dr. Gary Tibbetts was measuring the diffusion rate of carbon in iron when his carefully planned experiment took an unexpected turn. Dr. Tibbetts, a physicist at the General Motors Research Laboratories, had been introducing carbon to the inside surface of a hot stainless steel tube while extracting carbon from the outer surface.

At the end of one particular trial, he found the inside surface covered with a mass of black "whiskers." His initial investigations verified that the fibers were made of carbon and that they had characteristics typical of the crystal structure of graphite. But the question of how they formed was not so easily answered. The search for an answer would change the course of his investigation and dominate his research for the next ten years.

The fibers that surprised Dr. Tibbetts were made up of concentric layers primarily composed of basal (0001) plane graphite, resembling in cross section the annular rings of a tree (Figure 1). Research showed that they were formed by vapor deposition of carbon on a hollow central filament. The central filament itself was grown by catalytic action on a small metal particle (Figure 2).

These long, slender, uniform filaments had been widely observed since the availability of the electron microscope. Still, no valid explanation had been advanced to account for their hollow structure. Many scientists thought that surface diffusion of carbon-containing molecules around the catalytic particle caused the hollow core.

Instead, Gary Tibbetts proposed a model in which carbon atoms from decomposing hydrocarbons diffuse through the bulk of the catalytic particle and precipitate as graphite in the growing filament. The diffusion process is driven by the carbon gradient–the difference between carbon concentrations at the adsorbing surface of the particle and at its opposite, precipitating surface (Figure 3).

The exterior surfaces of these carbon cylinders expose the basal plane of graphite because the (0001) plane has a surface free energy at 970°C of about 77 erg cm^{-2}, while a typical surface perpendicular to the basal plane has a surface energy in excess of 4000 erg cm^{-2}. The free energy required for filament growth, therefore, will be a minimum when the exterior surface is made up of basal planes–as observed in these filaments.

The entire filament, then, should consist of nested, rolled-up basal planes of graphite. Bending these planes into cylinders, however, requires that extra elastic energy be provided during the precipitation process. The core is left hollow because too much energy would be required to bend the planes near the axis into very small diameter tubes.

In describing the total energy necessary for filament formation, Dr. Tibbett's model takes into account the chemical potential change ($\Delta\mu_o$)when a carbon atom precipitates from the dissolved phase, as well as the energy required to form the surface, plus the energy needed to bend the basal planes into nested cylinders.

The change in chemical potential ($\Delta\mu$) driving the precipitation can be expressed as follows:

$$\Delta\mu = \Delta\mu_o - \frac{2\,\sigma\,\Omega}{r_o - r_i} - \frac{E\,a^2\,\Omega}{12(r_o^2 - r_i^2)}\ln(r_o/r_i)$$

where σ is the energy required to form a unit area of (0001) graphite; Ω is the volume of a carbon atom in graphite; r_o and r_i are the outside and inside radii of the filament, respectively; E is the filament modulus; and a is the interplanar spacing.

A filament catalyzed by a particle of radius r_o will adjust its r_i to give the largest $\Delta\mu$–in fact, r_i may be directly calculated by maximizing $\Delta\mu$. Doing so yields results that compare nicely with experimental values.

Understanding the growth of the hollow core of the filaments was one key to producing them in abundance. "From there," says Gary Tibbetts, "it is a simple step to thicken the filament into a macroscopic fiber by vapor deposition of carbon on the exterior surface. The deposited carbon has a high degree of orientation parallel to the tube axis, giving the fiber exceptional stiffness.

"Fibers of this type should be excellent for making chopped-fiber composites using plastic, ceramic, metal, or cement matrices. GM's Delco Products Division is already building a pilot plant to develop a low-cost production process that would permit the use of vapor-grown fibers in high-volume applications."

General Motors

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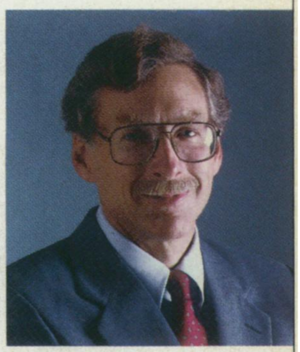

THE MAN BEHIND THE WORK

Dr. Gary G. Tibbetts is a Senior Staff Research Scientist in the Physics Department of the General Motors Research Laboratories.

Gary received his undergraduate degree in physics from the California Institute of Technology. He holds both an M. S. and a Ph. D. in the same discipline from the University of Illinois.

Dr. Tibbetts joined General Motors after two years of postdoctoral work as Guest Scientist at the Technical University of Munich. Since coming to the Labs in 1969, Gary has pursued interests ranging from carbon filaments, to surface physics, to chemical vapor deposition. He has published almost forty papers on the results of his research.

Gary is a member of the American Physical Society, the American Carbon Society, and the Materials Research Society. In 1988, he was a GM Campbell Award Winner. Gary lives in Birmingham, Michigan, with his wife and their three daughters.