Enhanced magnetic coercivities in Fe nanowires

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We describe a way of generating films ($<2\ \mathrm{mm}^2$; $<40\ \mu$m thick) of aligned Fe-filled carbon nanotubes. These Fe nanowires are usually composed of single Fe crystals, and have dimensions from 5–40 nm outer diameter and $<10\ \mu$m in length. The carbon tubes, which coat the wires, have external diameters of $\sim 20-70$ nm and are $<40\ \mu$m in length. High-resolution electron energy loss spectroscopy, x-ray powder diffraction, and elemental mapping of the tubular structures reveal only characteristic metallic signals and the effective absence of oxygen (or any other nonmetallic element) within the wires. The material exhibits coercivities in the 430–1070 Oe range, i.e., greater than those reported for Ni and Co nanowires. © *1999 American Institute of Physics.* [S0003-6951(99)00247-8]

Two-dimensional arrays of ferromagnetic nanowires (reminiscent of a carpet pile), which can be magnetized, have significant potential as data storage devices due to their size and anisotropic magnetic response. Such film structures, based on single-domain elements, exhibit the best available storage densities (e.g., 65 Gb/in.^{2}).[1] Here we describe a way of generating films ($<2\ \mathrm{mm}^2$; $<40\ \mu$m thick) of aligned Fe-filled carbon nanotubes, their nanoscale structure and composition, as well as their magnetic properties. The results suggest that the material may have novel magnetic properties and applications.

The generation of very small Fe nanowires has proved difficult due to the facile oxidation tendency displayed by finely divided metals such as Fe. The idea of encapsulating Fe nanowires within carbon nanotubes, whereby the protective carbon coating ensures that the metal is retained in a reduced state,[2] is shown here to be feasible. Ferromagnetic material has been produced in which the nanoscale crystalline iron domains are prevented from developing antiferromagnetic oxide layers.[3] In this context, various attempts have been made to encapsulate ferromagnetic metals within nanotubes, using graphite plasma arc techniques, but with little success. To date, only ferromagnetic nanocrystals have been encapsulated within ''graphitic'' polyhedral cages.[2–4] It has also been reported that very low concentrations of S ($\sim$0.25% by weight), present as an impurity in the graphite rods, are responsible for the continuous filling of long tubes with metal sulphide phases.[5,6] Furthermore, chemical/wetting approaches,[7,8] aimed at determining the conditions necessary to fill nanotubes by capillarity, demonstrated that high surface tension metals (e.g., Fe) will not spontaneously fill nanotubes in the liquid state.

Thermolysis of feedstocks, such as hydrocarbons and triazines, over metal nanocluster catalysts (Ni, Co, and Fe) provides a route to nanotube arrays[9–11] which can, under certain conditions as described here, also lead to the formation of

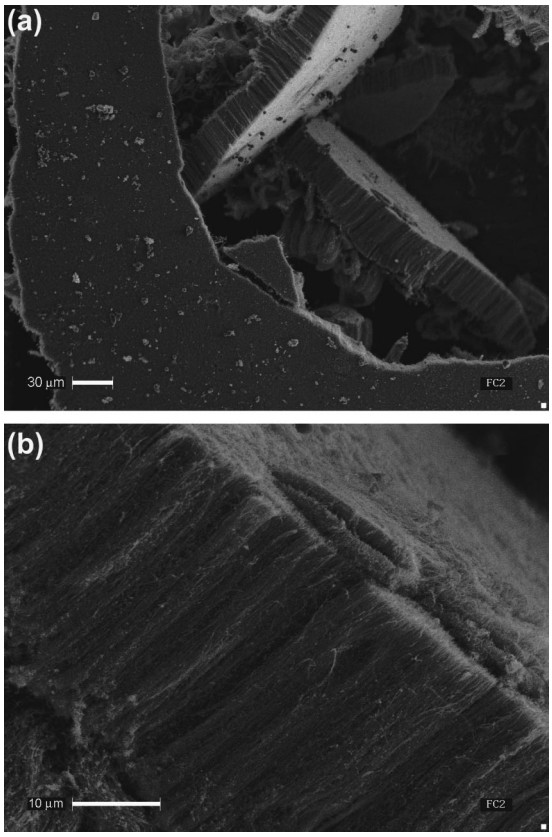

FIG. 1. SEM images of flake-like particles (films) consisting of aligned Fe-filled nanotubes at lower (a) and higher (b) magnification. The material was grown by pyrolyzing ferrocene/C_{60} mixtures (e.g., 1:1) at 900–1050 °C in an argon flow using a conventional two-stage furnace.[9,12]

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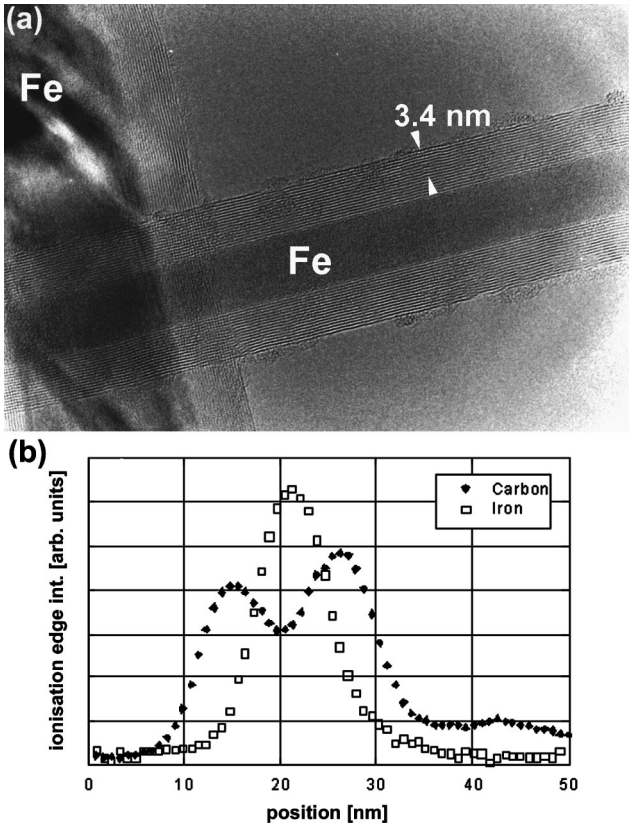

FIG. 2. (a) HRTEM image of two crossed Fe-filled nanotubes exhibiting different diameters and high degrees of graphitization (interlayer spacing ~0.34 nm); (b) Concentration profiles of C and Fe across the diameter of an Fe-filled tube derived from EELS line scans (see white arrow). These display the chemical profile perpendicular to the tube axis and indicate the presence of C on the periphery and Fe within the inner core of the structures. The central dip in the carbon profile is commensurate with an internal core, filled with metallic Fe.

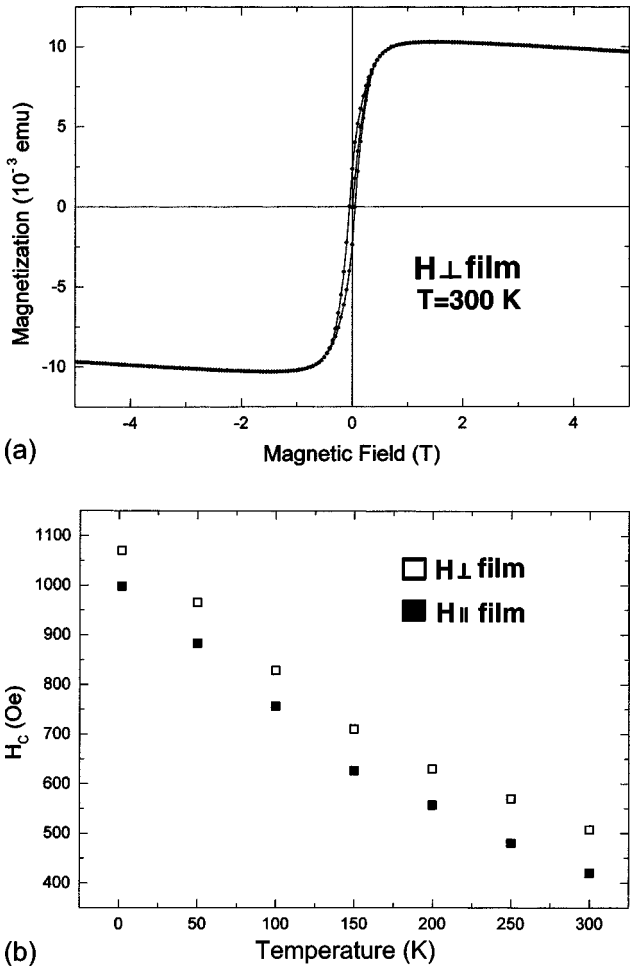

FIG. 3. (a) Magnetization vs applied field curves, measured parallel and perpendicular to the applied field on individual carpets, exhibiting saturation fields of ~14 000 Oe. By increasing the applied field, the hysteresis curve also undergoes a decrease in magnetization; (b) The coercive fields at different temperatures, which decrease in a linear fashion with increasing temperature and reveal traces of anisotropy due to the geometric orientation of the tubes. When the field is applied parallel and perpendicular to the nanowires' axis, the demagnetization factor is zero and close to 2π, respectively.

metal-filled tubes, provided an excess of catalyst is used. It has been reported recently that the thermolysis of ferrocene, under vacuum, results in the formation of carbon-coated Fe nanowires.[12] However, the nanoscale composition and magnetic properties of these nanowires do not appear to have been reported. In addition, their degree of ''graphitization'' seems to be low and the carbon coating tends to be very thick.[12] Here, we show that thermolysis of C_{60} (pure carbon source) at 900–1050 °C under an Ar flow at atmospheric pressure, in the presence of ferrocene, generates arrays of aligned, Fe-filled, carbon nanotubes of uniform dimensions and high crystallinity. The material was grown by pyrolyzing (1:1 by weight) mixtures of powdered ferrocene (dicyclopentadienyliron, Aldrich 98%, ~20–100 mg) and C_{60} (Hoechst, gold grade), at 900–1050 °C in an argon flow (20–40 ml/min) using a conventional two-stage furnace.[9,12]

Scanning electron microscopy (SEM) images of the products, indicate that the material consists mainly of carpet-like flakes or films (2 mm^2 and $<40\,\mu$m thick) where the ''pile'' is composed of aligned, carbon-coated tubules (Fig. 1). X-ray powder diffraction studies of the bulk sample reveal the presence of graphite together with body-centered-cubic iron. Transmission electron microscopy, high-resolution transmission electron microscopy (HRTEM), nanoscale elemental mapping, and high-resolution electron energy loss spectroscopy (HREELS) studies of the material show that ~40%–60% of these tubes are filled with Fe (see Fig. 2). We also note that the degree of graphitization exhibited by the nanotube walls is extremely high[13] and is comparable to that observed in high temperature nanotube generation processes, such as arc discharge techniques. In addition, the average number of concentric carbon coated layers (<25) is lower (40–50 layers) than reported previously[10] [Fig. 2(a)]. The near edge electron energy loss spectroscopy (EELS) fine structure of the carbon K shell (~284 eV) confirms that the material is highly graphitic, the L edge (~708 eV) being characteristic of metallic Fe. HREELS line scans across individual tubes reveal that the C and Fe concentration profiles anticorrelate, indicating that pure Fe is indeed encapsulated within the C layers [Fig. 2(b)]. These measurements also confirm that nonmetallic elements, such as oxygen and sulphur, are absent.

Plots of the magnetization versus applied field (measured parallel and perpendicular to the field for an individual ''carpet''), Fig. 3(a), exhibit saturation at fields of ~14000 Oe. At high fields, the hysteresis loop also exhibits a decrease in magnetization [Fig. 3(a)]. This observation may be due to a diamagnetic influence caused by graphitic

material coating the Fe wires. The plots of the coercive field versus temperature [Fig. 3(b)], indicate that the field decreases linearly with increasing temperature, revealing the presence of anisotropy, possibly due to tube geometry and orientation.

In practice we have observed higher coercivities (e.g., hundreds of oersteds) for the Fe-filled nanotubes as compared with pure bulk Fe (e.g., tenths of oersteds) or even Ni and Co nanowire arrays.[14] Therefore, the small size, anisotropy, and the single (isolated) domain nature of the encapsulated Fe crystals, appear to be responsible for this enhanced coercivity. Finally, it is important to note that measurements were performed over several months, and that no variation in the values here reported was detectable. This result clearly confirms that Fe nanostructures do not degrade and that they are almost certainly hermetically sealed within the graphitic tubes.

Although these experiments produce material $\sim 2\ \mathrm{mm}^2$, the method indicates that it should be possible to develop a continuous flow approach in order to generate larger strips and areas (i.e., centimeter wide) of this new material. Nanowire arrangements of this novel kind should find applications in the fabrication of high density magnetic recording devices, as well as fine particle magnets in magnetic inks and toners in xerography.

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