METAL AND ALLOY NANOWIRES: IRON AND INVAR INSIDE CARBON NANOTUBES


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Introduction

Pyrolysis of hydrocarbons over metal catalysts has proved to be a very efficient and versatile technique for generating carbon nanotubes and related materials. For example, the employment of ferrocene (C2F5) as a precursor and catalyst in conjunction with solid hydrocarbons or C60 has revealed that the carbon/hydrogen ratio in the reactants plays a crucial role in nanotube formation. The presence of C60 in particular enhances nanotube crystallinity. At reduced pressures Fe-filled nanotubes are formed efficiently from Cp2Fe and C60. Recently, alloys such as invar (Fe65Ni35) were successfully introduced into carbon nanotubes by pyrolysing aerosols of nickelocene/ferrocene mixtures dissolved in benzene at 800°C. With the introduction of invar in carbon nanotubes it is now possible to study the physico chemical properties of these wires. Furthermore, the alloy formation notably reduces the formation of unwanted by-products such as amorphous carbon, or metal encapsulated particles. The filling of the tubes is carried out in-situ during the formation of the aligned nanotubes. The results confirm that the use of Ni/Fe also enhances the growth and crystallinity of the products. The materials have been characterised by SEM, HRTEM, EELS, XRD and SQUID. The magnetic properties of metal- and alloy-filled nanotubes may be applied to the fabrication of high density magnetic storage devices, magnetic inks, etc.

Iron-filled carbon nanotubes

Arrays of aligned carbon nanotubes were prepared via pyrolysis of mixtures of C60 (Hoechst, gold grade) with Cp2Fe (dicyclopenta-dienyliron, Aldrich 98%) powders.

The role of C60 was investigated by comparing these products with ferrocene-hydrocarbon [e.g. C16H10 (pyrene), C26H18 (decacyclene) or C10H8 (naphthalene)] mixtures of different ratios (1:4, 1:2, 1:1, 2:1, 4:1 by molecular weight). The respective solid precursors were inserted at one end of a silica tube (60 cm long; 0.5 cm ID), which was placed inside a two stage furnace fitted with temperature controllers, so that the precursor remained outside the first furnace (Fig.1). Ar (5-20 ml/min; at atmospheric pressure) was passed through the silica tube and over the precursor, towards the furnaces, in order to remove oxygen from the system. Both furnaces were heated to 1050°C. Subsequently, the precursor inside the silica tube was shifted towards and located in the first furnace region, where it vaporised at 1050°C. The resulting gases then pass through the second furnace, in which the reaction occurs at a temperature of 1050°C. After 10 min, the furnaces were switched off and the resulting soot, upon cooling of the furnaces to roughly 500°C, was collected from the silica tube walls.

Fig. 1: Pyrolysis apparatus.
SEM images of the pyrolysis products reveal marked differences among samples, ascribed to the hydrocarbon source in the starting material. Series of samples were observed by SEM, and the ‘cleanest’ samples were analysed further. In general, C₆₀ appears to be responsible for the formation of faceted flakes exhibiting almost crystalline appearance. C₆₀ has a high melting point (ca. 1180°C) in comparison to other hydrocarbons [1]. Furthermore, C₆₀ is a source of pure carbon. In this context, H appears to have a significant effect on the morphology of C nanostructures as it serves to satisfy valences at the edges within graphene planes. It was suggested by Nolan et al. that the absence of hydrogen results in the formation of closed graphene shells, whereas the presence of hydrogen is responsible for open C structures, such as fish-bone type filaments [2,3].

In this study we observed the best results for FC2 (1:2; ferrocene : C₆₀), FC3 (1:1) and FC4 (2:1) (Fig. 2). In the case of FC1 (1:4), an excess of C₆₀ crystals was observed within the products, suggesting that little catalyst was present during the reaction. FC5 (4:1) yielded similar material to that obtained for the ferrocene pyrolysis which resulted in samples containing large amounts of amorphous C and other carbon particles.

The EELS fine structure of the C K shell (ca. 284 eV) confirms that the material is highly ‘graphitic’ and that the L-edge (ca. 708 eV) is characteristic of metallic Fe (Fig. 3). HRTEM 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. These measurements also confirm that non-metallic elements, such as oxygen and sulphur, are absent [4].

X-ray powder diffraction patterns (Fig. 4) reveal that the pyrolysis of only ferrocene [4] (at atmospheric pressure under an Ar atmosphere at 1050 °C) generates less crystalline carbon nanotubes. The graphite reflections appear to be broad, due to a decreased size within the ‘graphitic’ domains. In addition, the (002) peak appears to be slightly non-symmetric (due to various ranges of interlayer spacings e.g. 3.35, 3.4, etc. and possibly due to graphite in encapsulated particles), however it is centred at ca. 0.34 nm (interlayer spacing close to that of graphite). Reflections characteristic of Fe (bcc) and Fe₃C are also present (the Fe signal being dominant when compared to Fe₃C). It is interesting to note that the Fe (211) and Fe (220) peaks exhibit shoulders on the higher angle sides. This is possibly due to lattice distortions and size effects within the Fe nanocrystals [1].

The XRD pattern of a FC4 sample (pyrolysing ferrocene + C₆₀ at atmospheric pressure under an Ar atmosphere at 1050°C) exhibits different features from those mentioned above. In this sample the (002) graphite peak is centred at ca. 0.34 nm as above but the Fe (221) and the Fe(220) peaks do not show any splittings or shoulders. In addition, the pattern shows peaks indicating the presence of C₆₀ (marked arrows), which remain after the experiment. According to the intensities of the G(002) and the Fe(220) peaks, the amount of Fe is less than in the case of pure ferrocene pyrolysis. The sample also contains Fe₃C crystals and traces of possible phases of Fe₂O₃ and Fe₃O₄. The presence of Fe₃C, Fe₂O₃, Fe₃O₄ appears to contradict...
the EELS result, showing the absence of O₂ or FeC₃ nanocrystals. However, X-ray powder diffraction studies were carried out on bulk samples; thus the presence of encapsulated particles (not studied by HREELS) is likely to be responsible for the Fe₂C, Fe₂O₃, Fe₃O₄ reflections [1].

Fig. 4: XRD patterns of three different pyrolysis samples.

The third sample was again prepared by pyrolysis of ferrocene + C₆₀ (FC4) but this time at reduced pressure (100 Torr Ar) and 1050 °C. XRD studies revealed enhanced reflections of Fe₂O₃ (and possibly Fe₃O₄) when compared to the above cases. The C₆₀ reflections are also present in this sample, implying that C₆₀ is not totally consumed during pyrolysis. The bcc Fe peaks are relatively broad, therefore the average crystalline size of the Fe nanocrystals appears to be smaller than in the previous samples. The Fe (211) and the Fe (220) peak do not show well-defined shoulders as in the case of ferrocene; however clear reflections appear for Fe₃C [1].

Invar-filled carbon nanotubes

A benzene solution containing Cp₂Fe (Aldrich, 99%) and Cp₂Ni (dicyclopenta-dienynickel, Aldrich, 98%) mixtures (atomic ratios 65:35 Fe:Ni; 5% by weight), was prepared ultrasonically during 3-5 min. The solution was transferred to the reservoir of an aerosol generator (sprayer), then nebulized by a high Ar flow rate (ca. 2000 sccm), and dispersed through the sprayer (nozzle diameter ca. 0.45 mm). The aerosol was passed through a quartz tube (2 cm i.d. and 50 cm long) placed in a furnace (30 cm long) fitted with a temperature-controller. The sprayer was operated for 5 min while the furnace was maintained at 800°C. Subsequently, spraying was discontinued and the Ar flow rate reduced to 300-500 sccm in order to avoid oxidation of the products upon cooling. The product, a black powder, was scraped from the inner walls of the hot zone of the quartz tube [5].

SEM studies (JEOL-JSM 6300F operating at 2-5 kV) revealed the presence of flake-like material (ca. 1-2 mm²) consisting of arrays of aligned nanotubes (< 200 nm in length, < 80 nm in diameter, Fig. 5). The material resembles a carpet of exceptionally uniform length (or height), and the purity of the material is strikingly high when compared to experiments carried out with FeCp₂ only. In this context, only small amounts of particles and other by-products were observed.

HRTEM (JEM3000F FEG-TEM operating at 300 kV and JEOL-JEM4000 EX operating at 400 kV) images showed the presence of partly-filled nanotubes, the walls of which are relatively disordered in places where there was no metal filling. The nanowires exhibit lengths < 500 nm and width < 40 nm and were mainly found within highly crystalline carbon walls (Fig. 6). This result is in agreement with that reported by Sinclair et al., who described the graphitisation of amorphous carbon layers in the presence of Ni [6,7,8]. It is also been observed that metal-filled carbon nanotubes, generated by pyrolysis, generally tend to exhibit a higher degree of graphitisation than unfilled nanotubes [6].

Fig. 5: (a) SEM images of aligned nanotube films (flakes) grown on the walls of the pyrolysis tube; other carbonaceous material is notably absent; (b) Higher magnification of an individual ‘flake’ showing the degree of alignment and that the nanotubes possess uniform diameters (< 80 nm) and lengths (< 200 µm).
X-ray powder diffraction pattern (XRD, Siemens Diffraktometer D5000; Cu-Kα radiation) showing distinct peaks for 2θ at ca. 43.5, 50.7, 74.7 and 90.7 (Fig. 7), in agreement with peaks resulting from the Invar foil and corresponding to the (111), (200), (220) and (311) reflections of γ-FeNi alloys (fcc structure containing 30 at% Ni) respectively (Fig. 10). It is noteworthy that individual peaks for Fe or Ni were not observed, confirming the absence of segregated Fe or Ni domains [9].

Conclusions

Pyrolysis has shown to be an efficient route to metal-filled carbon nanotubes, however pyrolysis of hydrocarbons or other organic precursors over catalysts (e.g. Ni, Fe, Co) rarely leads to ‘well-graphitised’ nanostructures. This is possibly due to the presence of hetero-atoms (e.g. H, N, etc.) during the creation of C networks from the hydrocarbons, compared with the experiments where the source is pure C. The results suggest that C₆₀ holds considerable promise as a precursor for pure carbon nanostructures, particularly when metal catalysis is involved. This also holds true for the formation of aligned Fe-filled carbon nanotubes produced by pyrolysing C₆₀ - ferrocene mixtures. Although these experiments produce aligned nanotube films of ca. 2 mm² and ≤ 40 µm in thickness it should be possible to develop a continuous flow approach in order to generate larger strips and areas (i.e. cm-wide) of this exciting 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 or even magnetic force microscopy tips. We also have demonstrated that pyrolysis of aerosols obtained from C₆₀/H₄/NiCp₂/FeCp₂ mixtures generates aligned Invar-filled carbon nanotubes samples of high
purity. It is important to note that the pyrolysis of NiCp₂/FeCp₂ powder mixtures or of hydrocarbons over metal powder mixtures at higher temperatures does not result in the formation of alloy nanowires because the metals tend to segregate. The generation of Invar nanowires opens up new avenues for further exploration at the nanoscale level. The magnetic and mechanical properties of these novel structures may find applications in the fabrication of nanoscale thermostats.

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