

Metal and Alloy Nanowires: Iron and Invar Inside Carbon Nanotubes

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Abstract. Pyrolysis of hydrocarbons over metal catalysts has proved to be a very efficient and versatile technique for generating metal-filled carbon nanotubes. At reduced pressures Fe-filled nanotubes are formed efficiently from ferrocene and C₆₀. Recently, alloys such as invar (Fe₆₅Ni₃₅) were successfully introduced in carbon nanotubes by pyrolysing aerosols of nickelocene/ferrocene (Cp₂Ni/Cp₂Fe) mixtures dissolved in benzene. 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 results also confirm that the use of C₆₀ or Ni/Fe also enhances the growth and crystallinity of the products. The products 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 NANOTUBES AND THE EFFECT OF C₆₀

Arrays of aligned Fe-filled carbon nanotubes were prepared by pyrolysis of Cp₂Fe intercalated C₆₀ (C₆₀:2Cp₂Fe) [1] and mixtures of C₆₀ (Hoechst, gold grade) and Cp₂Fe (dicyclopenta-dienyliron, Aldrich 98%) powders under reduced pressures (*e.g.* 100 torr) with an Ar flow rate of *ca.* 20 sccm at 1050°C. The role of C₆₀ was investigated by comparing the outcome with pyrolysis of other ferrocene-hydrocarbon [*e.g.* C₁₆H₁₀ (pyrene), C₃₆H₁₈ (decacyclene) or C₁₀H₈ (naphthalene)] mixtures of different ratios (1:4, 1:2, 1:1, 2:1, 4:1 by molecular weight) [2].

Scanning electron microscopy (SEM) observations revealed that the pyrolysis products reveal marked differences among samples, ascribed to the hydrocarbon source in the starting material. In general, C₆₀ appears to be responsible for the formation of faceted flakes exhibiting almost crystalline appearance [2]. 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

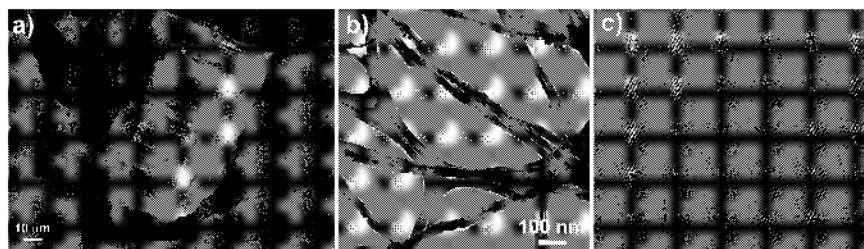


FIGURE 1. a) SEM image showing pyrolytically grown aligned carbon nanotubes comprising a single flake. Carbonaceous particles are notably absent (using ferrocene/ C_{60} mixtures); b) Low resolution TEM images revealing six well-filled carbon nanotubes; c) HRTEM image of an individual Fe-filled nanotube with a high degree of graphitisation (interlayer spacing 0.34 nm).

in the formation of closed graphene shells, whereas the presence of hydrogen is responsible for open C structures, such as fish-bone type filaments [3,4]. In this study we observed the best results for ferrocene in conjunction with C_{60} . The use of intercalated C_{60} with Cp_2Fe did not lead to much better products, thus no further investigation was carried out, especially in view of the time and effort needed to prepare $C_{60} \cdot 2Cp_2Fe$.

Transmission electron microscopy and EEL analysis revealed that the carbon nanotubes exhibited pure Fe-fillings [5]. It is noteworthy that other elements such as oxygen or sulfur, which was reported to be responsible for higher filling yields [6], are absent.

INVAR-FILLED CARBON NANOTUBES

A benzene solution containing $FeCp_2$ (Aldrich, 99%) and $NiCp_2$ (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 [7,8].

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 μm in length, < 80 nm in diameter). 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 $FeCp_2$ only. In this context, small amounts of encapsulated and carbonaceous particles and other by-products were observed.

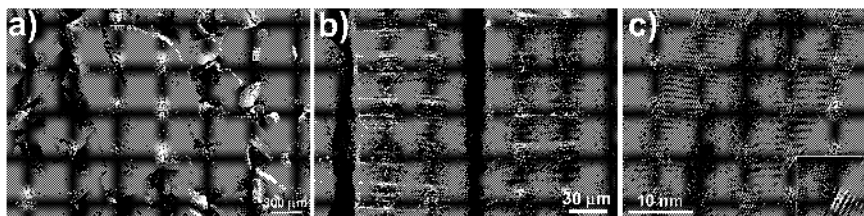


FIGURE 2. SEM images of the as produced material; a) showing a large flake of aligned nanotubes surrounded by various smaller ones; b) close-up of an individual flake (side view); c) HRTEM image depicting an Invar-filled carbon nanotube. The degree of crystallinity of the filling can be seen in the inset (carbon interlayer spacing 0.34 nm).

HRTEM (JEM3000F FEG-TEM operating at 300 kV and JEOL-JEM4000 EX operating at 400 kV) observations 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 diameters < 40 nm and were mainly found within highly crystalline carbon walls. 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 [9]. It is also been observed that metal-filled carbon nanotubes, generated by pyrolysis, generally tend to exhibit a higher degree of graphitisation when compared to unfilled nanotubes [5,9,10].

High-spatial-resolution EELS spectra profile (carried out using a dedicated STEM VG- HB 501UX equipped with a Gatan Digi-PEELS 766) of an Invar-filled nanotube axis (*ca.* 23 nm across) revealed the relative concentrations of C, Fe and Ni. Ni and Fe are homogeneously distributed within the inner core of the carbon tube. The wires contain Ni and Fe with a *ca.* 0.55±0.03 Ni/Fe ratio including the Invar composition (Fe₆₅Ni₃₅, Ni/Fe = 0.54), the X-ray powder diffraction pattern (XRD, Siemens Diffraktometer D5000; Cu-Kα radiation) exhibits distinct peaks for 2θ at *ca.* 43.5, 50.7, 74.7 and 90.7, in agreement with peaks resulting from bulk Invar and corresponding to the (111), (200), (220) and (311) reflections of γ-FeNi alloys (fcc structure containing = 30 at% Ni) respectively. It is important to note that individual peaks for Fe or Ni were not observed, confirming the absence of segregated Fe or Ni domains.

CONCLUSIONS

Pyrolysis has shown to be an efficient route to metal-filled carbon nanotubes, however the presence 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. 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 $C_6H_6/NiCp_2/FeCp_2$ mixtures generates aligned Invar-filled carbon nanotubes samples of high purity. It is important to note that the pyrolysis of $NiCp_2/FeCp_2$ 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. The magnetic and mechanical properties of these novel structures may find applications in the fabrication of nanothermostats.

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REFERENCES

1. Crane, J.D., Hitchcock, P.B., Kroto, H.W., Taylor, R., Walton, D.R.M., *Chem. Commun.* **24**, 1764-1765 (1992)
2. Grobert, N., Ph.D.Thesis *Novel Carbon Nanostructures*, University of Sussex (2000)
3. Nolan, P.E., Schabel, M.J., Lynch, D.C., Cutler, A.H., *Carbon* **33**, 79-85 (1995)
4. Nolan, P.E., Lynch, D.C., Cutler, A.H., *Carbon* **32**, 477-483 (1994)
5. Grobert, N., Hsu, W.K., Zhu, Y.Q., Hare, J.P., Kroto, H.W., Walton, D.R.M., Terrones, M., Terrones, H., Redlich, P., Rühle, M., Escudero, R., Morales, F., *Appl. Phys. Lett.*, **75**, 3363-3365 (1999)
6. Demoncy, N., Stephan, O., Brun, N., Colliex, C., Loiseau, A., Pascard, H., *Synthetic Metals* **103**, 2380-2383 (1999)
7. Grobert, N., Mayne, M., Terrones, M., Sloan, J., Dunin-Borkowski R.E., Kamalakaran R., Seeger T., Terrones, H., Rühle, M., Walton, D.R.M., Kroto, H.W., Hutchison, J.L., *Chem. Commun.* **5**, 471-472 (2001)
8. Mayne, M., Grobert, N., Terrones, M., Kamalakaran, K., Rühle, M., Kroto H.W., Walton, D.R.M., *Chem. Phys. Lett.* **338**, 101-107 (2001)
9. Grobert, N., Terrones, M., Osborne, A.J., Terrones, H., Hsu, W.K., Trasobares, S., Zhu, Y.Q., Hare, J.P., Kroto, H.W., Walton, D.R.M., *Appl. Phys. A* **67**, 595-598 (1998)
10. Terrones, M., Grobert, N., Zhang, J.P., Terrones, H., Olivares, J., Hsu, W.K., Hare, J.P., Cheetham, A.K., Kroto, H.W., Walton, D.R.M., *Chem. Phys. Lett.* **285**, 299-305 (1998)