Alloy nanowires: Invar inside carbon nanotubes

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Invar ($Fe_{65}Ni_{35}$), a 'zero' thermal expansion alloy consisting of Fe and Ni, has been successfully introduced into carbon nanotubes by pyrolysing, at 800 °C, aerosols of $NiCp_2$/$FeCp_2$ mixtures dissolved in C_6H_6; scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) studies reveal the presence of flake-like structures (*ca.* 1–2 mm²) consisting of filled/aligned carbon nanotubes (⩽200 μm in length and ⩽80 nm in diameter) in a carpet pile-like configuration; analysis of the filling material (⩽500 nm in length and ⩽40 nm in diameter) by X-ray powder diffraction and high-resolution electron energy loss spectroscopy (HREELS) line scans, confirmed that Invar was formed; this appears, to the best of our knowledge, to be the first report of mixed metal alloy nanowires forming inside carbon nanotubes.

Invar ($Fe_{65}Ni_{35}$) alloy, discovered by Guillaume in 1897,[1] exhibits an extremely low thermal expansion coefficient, *ca.* one tenth of that of steel.[2] Furthermore, Fe/Ni alloys are interesting not only for their low thermal expansion, but also for their remarkable magnetic properties. These alloys have various uses in, for instance, the fabrication of electronic devices, aircraft controls, laser systems, bimetallic thermostats, *etc*.[2–4]

To date, various techniques for encapsulating metals, metal oxides and chlorides in multi-walled (MWNT) or single-walled carbon nanotubes (SWNT) have been developed.[5,6] However, the encapsulation of alloys has so far been unsuccessful although the formation of segregated phases of Sn and Pb has been observed in carbon-coated nanowires.[7] High temperature routes involving the arc-discharge of graphite and metal mixtures, such as Fe:Co, Fe:Ni or Ni:Y, results in the formation of SWNTs rather than alloy-filled MWNTs. Here we report, for the first time, the encapsulation of Invar in MWNTs by pyrolysing aerosols consisting of $NiCp_2$/$FeCp_2$/C_6H_6 mixtures in an Ar atmosphere at 800 °C.

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 in length) placed in a furnace (30 cm in length) 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. A detailed description of the aerosol generator is given elsewhere.[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) similar to those reported previously (Fig. 1).[9] 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, 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 widths ⩽40 nm and were mainly found within highly crystalline carbon walls (Fig. 2). This result is in agreement with that reported by Itoh and Sinclair, who described the graphitisation of amorphous carbon layers in the presence of Ni.[10] It has also been observed that metal-filled carbon nanotubes, generated by pyrolysis, generally tend to exhibit a higher degree of graphitisation than unfilled nanotubes.[9–12]

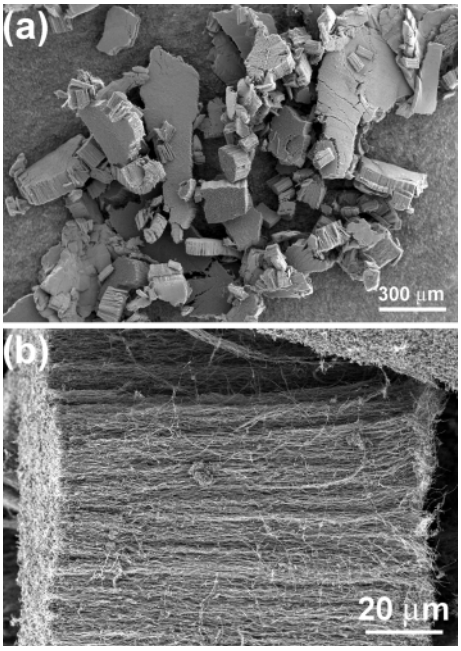

Fig. 1 (a) SEM images of aligned nanotube films (flakes) grown on the walls of the pyrolysis tube; other carbonaceous material is notably absent. (b) Higher magnification of an individual 'flake' showing the degree of alignment and that the nanotubes possess uniform diameters (< 80 nm) and lengths (< 200 μm).

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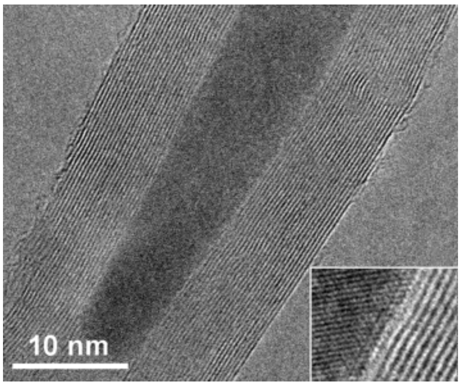

Fig. 2 HRTEM image of an Invar-filled nanotube with an inset showing the crystallinity of the filling (carbon interlayer spacing 0.34 nm).

X-Ray powder diffraction measurements (XRD, Siemens Diffraktometer D5000; Cu-Kα radiation) were carried out on the samples as well as on a commercially available Invar foil (Fe65 : Ni35, Goodfellow) for comparison. The diffraction patterns of the sample exhibit graphite peaks with a small shift of the (00l) reflections due to curvature of the concentric graphene sheets constituting the carbon nanotubes (*d*-spacing 0.34 nm). Distinct peaks for 2θ are observed at *ca.* 43.5, 50.7, 74.7 and 90.7, in agreement with those resulting from the Invar foil. They correspond to the (111), (200), (220) and (311) reflections of γ-FeNi alloys (fcc structure containing 30 atom% Ni and above) respectively. It is noteworthy that individual peaks for Fe or Ni were not observed, confirming the absence of segregated Fe or Ni domains [Fig. 3(a)]. The variation of Ni content in the fcc structure of γ-FeNi alloys induces a linear change in the lattice parameter (Vegard's Law).[13,14] Determinations of this parameter for the fcc structure of the γ-FeNi alloy present in the samples indicate an overall Ni content of *ca.* 45 ± 2 at%.

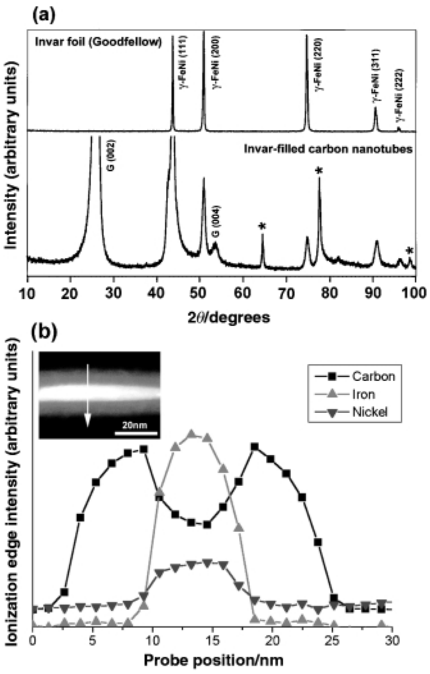

Fig. 3 (a) X-Ray powder diffraction pattern showing distinct peaks for 2θ at *ca.* 43.5, 50.7, 74.7 and 90.7, in agreement with peaks resulting from the Invar foil and corresponding to the (111), (200), (220) and (311) reflections of γ-FeNi alloys (fcc structure containing ⩾30 at% Ni) respectively. (* signals belong to the XRD holder). (b) High-spatial-resolution EELS spectra profile of an Invar-filled nanotube axis (*ca.* 23 nm across) showing the relative concentrations of C, Fe and Ni. Ni and Fe are homogeneously distributed within the inner core of the carbon tube. The inset shows the high angular dark field (HADF) image of the nanowire contained within the carbon nanotube as well as the line-scan recorded during the measurement. The EELS spectra reveal that the wires contain Ni and Fe with a *ca.* 0.55±0.03 Ni/Fe ratio including the Invar composition ($Fe_{65}Ni_{35}$, Ni/Fe = 0.54).

Elemental mapping (Zeiss EM 912 Omega, operated at 120 kV) using EELS revealed that Ni and Fe are uniformly distributed within the wires. HREELS line scans along and across the fillings (carried out using a dedicated STEM VG- HB 501UX equipped with a Gatan Digi-PEELS 766) also confirmed that Ni and Fe concentrations correlate, which is consistent with alloy formation. The C and Ni–Fe concentration profiles anti-correlate, indicating that the metal is located in the nanotube core [Fig. 3(b)]. The presence of sharp features corresponding to the π* and σ* excitations on the energy loss near-edge structure (ELNES) of the carbon K edge at 284.5 eV indicates that the material is highly 'graphitic'. The edges at 708 and 854 eV are characteristic of Fe-L and Ni-L respectively. Quantification of representative EEL spectra reveal that the wires consist of Ni and Fe with a *ca.* 0.55 ± 0.03 Ni/Fe ratio, commensurate with the Invar composition ($Fe_{65}Ni_{35}$, Ni/Fe = 0.54).

We have demonstrated that pyrolysis of aerosols obtained from $C_6H_6/NiCp_2/FeCp_2$ mixtures generates aligned Invar-filled carbon nanotubes 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 level. The magnetic and mechanical properties of these novel structures may find applications in the fabrication of magnetic storage devices and nanoscale thermostats.

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