

The origin of long-period lattice spacings observed in iron-carbide nanowires encapsulated by multiwall carbon nanotubes

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ABSTRACT

Structures comprising single-crystal, iron-carbon-based nanowires encapsulated by multiwall carbon nanotubes self-organise on inert substrates exposed to the products of ferrocene pyrolysis at high temperature. The most commonly observed encapsulated phases are Fe_3C , $\alpha\text{-Fe}$, and $\gamma\text{-Fe}$. The observation of anomalously long-period lattice spacings in these nanowires has caused confusion since reflections from lattice spacings of ≥ 0.4 nm are kinematically forbidden for Fe_3C , most of the rarely observed, less stable carbides, $\alpha\text{-Fe}$, and $\gamma\text{-Fe}$. Through high-resolution electron microscopy, selective area electron diffraction, and electron energy loss spectroscopy we demonstrate that the observed long-period lattice spacings of 0.49 nm, 0.66 nm and 0.44 nm correspond to reflections from the (100), (010) and (001) planes of orthorhombic Fe_3C (space group Pnma). Observation of these forbidden reflections results from dynamic scattering of the incident beam as first observed in bulk Fe_3C crystals. With small amounts of beam tilt these reflections can have significant intensities for crystals containing glide planes such as Fe_3C with space groups Pnma or Pbmn .

INTRODUCTION

Iron-based ferromagnetic nanowires encapsulated by carbon nanotubes have been studied for over decade owing to the number of potential applications (Sen et al., 1997; Rao et al., 1998, Marco et al., 2002; Prados et al., 2002, Goldberg et al., 2006; Müller et al., 2006; Weissker et al., 2009; Weissker et al., 2010; Lutz et al., 2010) The carbon nanotube serves to chemically passivate the nanowire and prevent its spontaneous oxidation when exposed to air. The subsequent usefulness of the structures arises from the ferromagnetic functionality of the encapsulated nanowires, which display high coercivity due to the shape anisotropy (Grobert et al., 1999). These structures are produced by exposure of an inert substrate to the vapour products of ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$) pyrolysis at high temperature. The detail of the growth mechanism is controversial but the general features are usually expressed within a vapour-liquid-solid framework (Wagner & Ellis, 1964): liquid particles of elemental Fe produced in the vapour deposit on the substrate, small hydrocarbon structures from the vapour then dissolve in this nucleating particle until the solubility limit of carbon in iron is reached, at this point the incoming carbon-containing species effectively form a shell on the exterior of the particle, the particle then serves to catalyse the graphitisation of the shell which results in the growth of a multiwall carbon nanotube (MWCNT) perpendicular to the substrate. The subsequent growth of the MWCNT and the filling of its central capillary by elemental iron or an iron-carbide is driven by supply of species from the vapour either to the base of the structure or to the open tip, or both. This is an entirely self-organised production process. The final reaction product is a closely-packed array of individual MWCNT-encapsulated single-crystal nanowires oriented perpendicular to the substrate. The most commonly observed encapsulated crystals are Fe_3C , $\alpha\text{-Fe}$, and $\gamma\text{-Fe}$ (Sen et al., 1997; Rao et al., 1998, Marco et al., 2002; Prados et al., 2002, Goldberg et al., 2006; Müller et al., 2006; Weissker et al., 2009; Weissker et al., 2010; Lutz et al., 2010).

Previous high-resolution transmission electron microscopy (HRTEM) and selective area electron diffraction (SAED) investigations of the encapsulated phases have revealed the presence lattice spacings significantly longer (≥ 0.4 nm) than those present in the frequently observed iron-carbide Fe_3C [ICSD Ref. Code 16593], and the rarely observed less stable carbides Fe_2C [ICSD Ref. Code 76826], Fe_7C_3 [ICSD Ref. Code 167346], Fe_{20}C_9 [ICSD Ref. Code 740753] and $\text{Fe}_4\text{C}_{0.63}$ [ICSD Ref. Code 9860]. Lattice spacings of 0.57 nm and 0.42 nm are expected for the rare stable carbide Fe_5C_2 [ICSD Ref. Code 76829 and 245334]. Lattice spacings of >0.2 nm are not expected for α -Fe [ICSD Ref. Code 64795] and γ -Fe [ICSD Ref. Code 53803].

Golberg *et al* observed the long-period lattice spacings of 0.43 nm, 0.46 nm and 0.66 nm in nanowires encapsulated by MWCNTs; these non-conventional lattice spacings were assigned, without supporting evidence, to the rarely seen silicon doped octahedral iron carbides (Golberg *et al.*, 2006). Anomalous lattice spacings of 0.51 nm in encapsulated nanowires were also observed by Weissker *et al* (Weissker *et al.*, 2009; Weissker *et al.*, 2010) and Lutz *et al* (Lutz *et al.*, 2010) and identified as Fe_3C with space group Pbnm. Other investigators have assigned the anomalous periodicities 0.64 nm, 0.43 nm, 0.67 nm and 0.69 nm to Fe_3C without explanation (Lee *et al.*, 1975; Bi *et al.*, 1993,; Reibold *et al.*, 2006).

The symmetry of a crystal imposes certain selection rules which allow only certain kinematic reflections to be observed. For orthorhombic Fe_3C with space group Pnma, for which the typical unit cell parameters are labelled $a=0.509$ nm, $b=0.675$ nm and $c=0.452$ nm, the only allowed reflections are (h00) with $h=2n$, (0k0) with $k=2n$, (00l) with $l=2n$, (0kl) with $k+l=2n$ and (hk0) with $h=2n$, where n is an integer [ICSD Ref. Code. 16593]. These selection rules

are also valid for the Pbnm Fe₃C because it differs from Pnma Fe₃C only in the labelling of unit cell parameters [ICSD Ref. Code 43375]. Reflections that cannot be observed are known as “forbidden reflections”. These arguments are generally valid in the kinematic theory of diffraction, where the intensity of the diffracted beam is small compared to that of the incident beam intensity.

If the intensity of the diffracted beam becomes significant, the dynamic scattering of the diffracted beams by atoms in a crystalline specimen should be considered (Hammond, 2009). In electron diffraction, dynamic effects have been commonly observed in many crystalline materials (Takagi & Morimoto, 1963; Smith et al., 1985; Callister, 2007). For a crystal containing glide planes or screw axes, forbidden reflections may appear or disappear owing to the high sensitivity of dynamic scattering to slight changes of the incident beam direction (Cowley & Moodie, 1959; Takagi & Morimoto, 1963; Gjonnes & Moodie, 1965). Observation of significant forbidden reflection intensities in electron diffraction studies of bulk crystals of orthorhombic Fe₃C with space group Pbnm was first reported by Nagakura *et al* in 1982 (Nagakura et al., 1982). It was shown that the 001 forbidden reflection intensity increased with the incident beam angle relative to a principal crystal axis and became significant after 0.5° of tilt owing to the high sensitivity of dynamic scattering to slight changes of the incident beam direction.

We observe anomalous lattice spacings of 0.49 nm, 0.66 nm and 0.44 nm in MWCNT-encapsulated nanowires and demonstrate through high-resolution transmission electron microscopy (HRTEM), selective area electron diffraction (SAED), and electron energy loss spectroscopy (EELS) that these spacings correspond to the (100), (010), and (001) planes of the orthorhombic Fe₃C, with space group Pbnm. The significant intensity of the forbidden

reflections results from the nanowire bending on the TEM grid; that is, the resulting dispersion in the incident beam angle plays the role of tilting in the Nakamura experiment.

MATERIALS AND METHODS

Vertical arrays of close-packed MWCNT-encapsulated nanowires were deposited on flat substrates held within a reactor comprising a horizontal quartz tube within a single-zone electrical furnace at 990 - 1200 °C. Ferrocene vapour was generated in a preheater by sublimation of powder and passed into the reactor tube in an argon flow. The synthesis time was several minutes. For some syntheses C₆₀ was added to the ferrocene mixture in a 1:1 ratio by weight; this was done to create additional carbon-containing species in the vapour and to improve the graphitic quality of the MWCNT walls. The sample was left to cool down at the natural rate of the furnace in an argon flow. The as produced material was dispersed in alcohol and transferred to TEM grids. Ferrocene powder, (Fe(C₅H₅)₂, 98% purity) and C₆₀ (99.5% purity) were purchased from Sigma Aldrich and used as received.

Initial transmission electron microscopy (TEM) investigations were performed using 200 kV Jeol Jem 2010 and 300 kV Jeol 3000F microscopes. HRTEM, SAED, and EELS analyses were performed using a FEI TITAN 80/300 (S)TEM (accelerating voltage of 80 kV) fitted with a GIF Tridiem electron energy-loss spectrometer. The lattice spacings obtained from HRTEM are reported with an accuracy of ±0.01 nm. EELS data were acquired at collection semi-angle of 22 mrad, dispersion 0.2 eV/pixel and acquisition time of 8 s. An Empyrean Panalytical diffractometer and a Siemens D5000 diffractometer (both Cu K_α sources) were used for the X-ray diffraction (XRD) analyses of the material extracted from the reactor.

RESULTS AND DISCUSSION

The long-period lattice spacings were frequently observed in individual nanowires by HRTEM. We observed a single set of crystal planes (a single pattern of spots) in all SAED patterns from individual nanowires, so we conclude that the nanowires are always present as isolated, single-phase, single-crystals with preferred orientation with respect to the MWCNT axis. Typical examples of the HRTEM images of nanowire which exhibit long-period lattice spacings, together with the SAED patterns and fast Fourier transform (FFT) data, are shown in Figs. 1-3. The lattice spacings of 0.49 nm and 0.19 nm, shown in Fig. 1, are close to the (100) and to the (031) planes of orthorhombic Fe₃C with space group Pnma, respectively. The spacings of 0.66 nm and 0.24 nm, shown in Fig. 2, correspond to reflections from the (010) and the (200) planes of Fe₃C, respectively. The lattice spacing of 0.49 nm in Fig. 3 is close to the (100) plane of Fe₃C while the spacing of 0.44 nm could correspond to reflections from the (001) plane of Fe₃C. According to the selection rules discussed in the Introduction, the (100), (010) and (001) planes of Fe₃C are kinematically forbidden (Nakakura et al., 1982).

XRD crystallographic analysis was performed on the material extracted from the reactor to validate the HRTEM and SAD results. The Rietveld refinement method, which uses the least-squares approach to match a theoretical line profile to the diffractogram, was used to identify and estimate the abundances of the encapsulated phases (Hammond, 2009). The main encapsulated phases are: α -Fe, Fe₃C (6.7 wt.% C), and γ -Fe (0.76 wt.% C), where the expected carbon content in brackets is obtained from the literature (Callister, 2007). The presence of Fe₃C was observed through the 211, 102 and 112 Bragg reflections (Fig. 4). The kinematic theory of diffraction is generally valid for almost all the X-ray analyses of thin crystals (Hammond, 2009). If the long-period lattice spacings observed by HRTEM corresponded to the forbidden 100, 010 and 001 reflections of Fe₃C then no peaks should be observed in the range of Bragg angle associated with the long-period crystal planes (low 2θ).

With exception made for diffraction peaks due to the presence of residual crystalline C_{60} which escaped decomposition in the reactor, there are no additional peaks at low 2θ . (Fig.5). If C_{60} is not used in the synthesis, the equivalent diffractograms are featureless in the 2θ range 10-22°. Since electron-sample interaction is stronger with respect to X-ray sample interaction, dynamic scattering could cause the appearance of forbidden reflections if the electron beam direction is not exactly parallel to a principal crystal axis [15, 24]. Consequently, the reflections from the lattice spacing 0.49 nm were provisionally assigned to the (100) planes of Fe_3C and those from the lattice spacing 0.66 nm to the (010) planes of Fe_3C .

The consistency of this interpretation was checked using the Weiss zone law for the "beam direction", [UVW] (Zandbergen et al., 1997; Hammond, 2009). In the case of the (031) and the (100) planes shown in Fig. 1, the beam direction is [01-3] while in the case of the (200) and (010) planes shown in Fig. 2 the direction is [001], and by considering the (100) and the (001) planes shown in Fig. 3 the direction is [010]. The observation of the forbidden 100, 010 and 001 reflections is in agreement with the dynamic extinction rules outlined by Tanaka *et al* (table number five, space group number sixty-two of Tanaka et al., 1983 and referred to the Gjønnes and Moodie lines for space group Pnma (Tanaka et al., 1983). If the long-period lattice spacings observed were due to forbidden reflections, a disappearance had to be observed for beam directions parallel to a principal axis. This was investigated in two different nanotubes in which the nanowires were showing the long-period lattice spacings by tilting the sample around the sample-holder axis. In the first case, the long-period lattice spacings disappeared after a tilt of 4.1°, and in the second case after a tilt 4.5°.

Chemical compositional analyses of the nanowires with long-period lattice spacings was performed by EELS. This technique is commonly used to measure the energy distribution of electrons that have interacted with a specimen and lost energy due to inelastic scattering. The excitation of atomic electrons by a transmitted electron gives rise to Fe-L_{2,3} ionization edges representing excitation of 2p_{3/2} and 2p_{1/2} electrons, respectively. The Fe-L_{2,3} EELS spectra are sensitive to the local environment of Fe in different iron-containing phases so do not include signals from the graphitic MWCNT walls. The ratio of the integrated area under the L₁ and L₂ peaks, Fe-L₃/L₂, was then used to for the identification of the encapsulated phase by comparison with the values found in the literature. This analysis must first consider the continuum contribution to the EELs intensity; following Riedl *et al* (Riedl et al., 2006) we used the method for 3d transition metals of Pearson *et al*, which approximates the Fe-L_{2,3} ionization edges as a sum of two step functions, (Pearson et al., 1993). The following Fe-L₃/L₂ values are expressed with an accuracy of ± 0.1 .

EELS spectra were acquired at multiple points along the axes of nanowires selected from different regions of the TEM grid. The averaging was over four spectra acquired from eleven different nanowires. Two distinct averaged Fe-L₃/L₂ values, 3.1 and 3.4, were extracted from those nanowires that did not exhibit a long-period lattice spacing. The single nanowire that did exhibit a long-period lattice spacing, Fig. 6, yielded an average Fe-L₃/L₂ ratio of 2.7 (averaging over ten spectra from one nanowire; a typical example is given in Fig.7). The observed Fe-L₃/L₂ ratios obtained from previous studies in the literature are 3.0 for α -Fe, 3.5 for γ -Fe, and 2.8 for Fe₃C (Kurata & Tanaka, 1991; Wetscher et al., 2006; Leapman et al., 1982). We conclude that the composition of the long-period lattice spacing nanowires is Fe₃C.

CONCLUSION

We have demonstrated that the chemical composition of the long-period lattice spacing nanowires is Fe_3C . The observed long-period lattice spacings 0.49 nm, 0.66 nm and 0.44 nm correspond to the 100, 010 and 001 reflections of orthorhombic Fe_3C (Pnma), respectively. These reflections are kinematically forbidden. However, with small amounts of beam tilt these reflections can have significant intensities for crystals containing glide planes such as Fe_3C with space groups Pnma or Pbnm.

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FIGURE CAPTIONS

Fig.1 HRTEM image taken at 200 kV of a Fe₃C single-crystal. The inset shows the reciprocal lattice reflections obtained by SAED. The forbidden 100 reflections of Fe₃C depicted between the red lines correspond to the lattice spacing 0.49 nm. The blue circles indicate the allowed 031 reflections of Fe₃C corresponding to the lattice spacing 0.19 nm. The green circles indicate the 002 reflection of graphite (MWCNT walls). The beam direction is [01-3].

Fig.2 HRTEM image taken at 200 kV of a Fe₃C single-crystal. The inset shows the reciprocal lattice reflections obtained by SAED. The forbidden 010 reflections of Fe₃C depicted between the red lines correspond to the lattice spacing 0.66 nm. The blue circles indicate the allowed 200 reflections of Fe₃C corresponding to the lattice spacing 0.24 nm. The beam direction is [001].

Fig.3 HRTEM image taken at 300 kV of a Fe₃C single-crystal nanowire. The inset shows the reciprocal lattice reflections obtained by FFT (of the area within the red square). The forbidden 100 reflections of Fe₃C depicted between the red lines correspond to the lattice spacing of 0.49 nm, while the forbidden 001 reflections depicted between the blue lines correspond to the lattice spacing of 0.44 nm. The beam direction is [010].

Fig.4 XRD diffractogram and Rietveld refinement (green line) from material extracted from the reactor. The abundance of the phases encapsulated by the MWCNT is 12.1% of γ -Fe cubic (Fm-3m), 16.3% of Fe₃C orthorhombic (Pnma) and 21.6% of α -Fe cubic (Im-3m).The

peaks of Fe_2O_3 (R-3CH) were excluded from the analysis since the iron oxide results from spontaneous oxidation of non-encapsulated iron particles when the material is handled in air.

Fig.5 Low-angle XRD diffractogram and Rietveld refinement (green line) of the material extracted from the reactor. There are small diffraction peaks of C_{60} (Fm-3m) that was not completely consumed during the synthesis. The larger peak corresponds to the (012) planes of Fe_2O_3 (R-3CH).

Fig.6 High resolution STEM image taken at 80 kV of the Fe_3C single crystal used for EELS analyses. The inset shows the reciprocal lattice reflections (obtained by FFT of the area within the red square). The forbidden 100 reflections of Fe_3C depicted between the red lines correspond to the lattice spacing of 0.51 nm. The blue circles indicate the allowed 011 reflections corresponding to the lattice spacing 0.39 nm. The beam direction is [0-11].

Fig.7 Typical EELS spectra of the long spacing structure from FIG. 6 before (black spectrum) and after (blue spectrum) the application of the Pearson method. The two step functions are shown in red.