

Encapsulation of quaternary 1D pentlandite-type alloy crystals within conical multi-layer carbon nanotubes

Pedro M. F. J. Costa,^a Jeremy Sloan,^{*ab} John L. Hutchison^b and Malcolm L. H. Green^{*b}

^a Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR.

E-mail: jeremy.sloan@chem.ox.ac.uk malcolm.green@chem.ox.ac.uk; Fax: +44-1865-272690;

Tel: +44-1865-272649

^b Department of Materials, University of Oxford, Parks Road, Oxford, UK OX1 3PH

Received (in Cambridge, UK) 10th June 2003, Accepted 29th July 2003

First published as an Advance Article on the web 12th August 2003

Ordered 1D crystals of a complex pentlandite-type alloy with the general composition $(\text{Fe,Ni,Co})_9\text{S}_8$ have been synthesised inside conical Multi Walled Carbon Nanotubes (MWNTs); the crystals are observed as a by-product of an arc-evaporation synthesis of Double Walled Carbon Nanotubes (DWNTs).

Cubic pentlandite is a Fe–Co–Ni–S mixed phase with the general composition of $(\text{Fe,Co,Ni})_9\text{S}_8$. Because the M:S ratio does not always equal 9 : 8 the Greek letter π is used to designate alloy phases containing this ratio.¹ Pentlandite is an important ore of nickel and iron that has been long known to mineralogists. In its natural state it does not produce well-formed crystals and is generally only found in impure form. Knop and Ibrahim² studied in detail the π -phases of pentlandites prepared synthetically by heating mixtures of Fe–Co–Ni–S at 700 °C in a vacuum-sealed quartz ampoule. They determined a ternary phase diagram establishing the boundaries for this phase of the Fe–Co–Ni–S system. They observed that Fe : Co : Ni ratios vary within wide limits while the lattice constant ($a_0 = ca. 0.1$ nm) kept relatively constant. Small nanocrystals of $(\text{Fe,Ni})_9\text{S}_8$ pentlandite have also been identified in matrix olivines of the Allende meteorite.³

In 1973, Rajamani and Prewitt⁴ demonstrated the relationship between the pentlandite alloys and the Co_9S_8 structural archetype. With the space group $Fm\bar{3}m$ (225), the unit cell of cubic cobalt pentlandite contains four M_9S_8 units. In this space group, the 36 metal atoms are distributed over 4 octahedral sites, 4(b), and 32 tetrahedral sites, 32(f). The 32 sulfur atoms are distributed over 8(c) and 24(e) equipoints in four- and five-fold coordination by metal atoms, respectively. Previously, it has been shown that binary Invar-type alloy crystals can be formed within MWNTs.⁵ In this communication, we describe the first observation of complex quaternary π -phase cobalt pentlandite crystals formed within mainly conical MWNTs.

The synthesis of DWNTs followed the method described by Moravsky and Loutfy in which a sulfur-containing Fe : Co : Ni mixture is co-evaporated together with carbon in an electric arc in the presence of H_2 .⁶ Sulfur promotes the formation of both DWNTs⁶ and the formation of metals in filled nanotube ‘impurities’⁷ although the mechanisms by which these processes occur remain uncertain. We used a computer automated arc evaporation machine and a Fe : Co : Ni : S catalyst prepared under an inert atmosphere. An atmosphere of 30 vol% H_2 and 70 vol% Ar at 100 mbar was applied as opposed to the 500 mbar used in the published method.⁶ The arc product was purified by acid and air oxidation and then refluxed in 70% HNO_3 at 110 °C for 1 h followed by a static air oxidation at 350 °C for 2 h. This was followed by refluxing in 35% HCl at 110 °C for 8 h and a final 1 h air oxidation at 380 °C. The products were examined in a 300 kV JEOL JEM-3000F High Resolution Transmission Electron Microscope (HRTEM; $C_s = 0.6$ mm). Images were acquired on a Gatan ($1k \times 1k$) CCD camera model 794 calibrated using the Si [110] lattice spacings. Energy Dispersive X-Ray microanalysis (EDX) was done with an Oxford Instrument ISIS EDX system. Image simulations were performed

with a standard multi-slice algorithm employing representative parameters for the 3000F.

When Hutchison *et al.*⁸ first published their results on the arc-evaporation synthesis of DWNTs they mentioned the formation of encapsulated catalyst particles (CPs) and SWNTs as the by-products of the synthesis procedure. The EDX analysis of the CPs showed a composition of Fe, Ni, Co and S. However no further studies were done on these structures nor was there any mention of the formation of MWNTs. In our attempt to reproduce the results with an optimised version of their method,⁶ we found that, we also obtained impurity MWNTs with various shapes and dimensions. Many of these MWNTs were found to have their inner cavities filled with alloy crystals as shown in Fig. 1(a). In this example, the nanotube has a length of approximately 100 nm and a diameter of 17 nm in the larger region narrowing down to 6 nm at the other end.

Multiple EDX spectra obtained from the example in Fig. 1(a) (Fig. 1(b)) indicated that the alloy filling was quaternary with the approximate composition $\text{Fe}_3\text{Ni}_4\text{Co}_2\text{S}_8$. Additionally, HRTEM lattice images (Fig. 2(a)) and FFTs (Fig. 2(b))

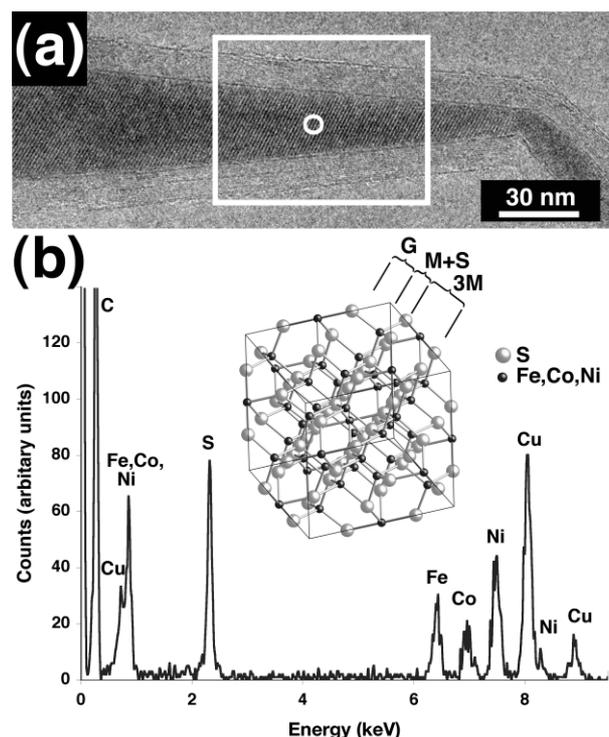


Fig. 1 (a) HRTEM image of a conical MWNT filled with a pentlandite-type crystal. The white rectangle represents the magnified image taken for analysis (see Fig. 2). The circle shows the area where the EDX was taken from. (b) EDX spectra of the filling material obtained with a *ca.* 3 nm probe (region indicated in (a)). The Cu peaks are from the copper support grid. The inset shows the unit cell of the pentlandite structure viewed along $[3\bar{2}1]$. Fe, Co and Ni are randomly distributed over the indicated metal sites.

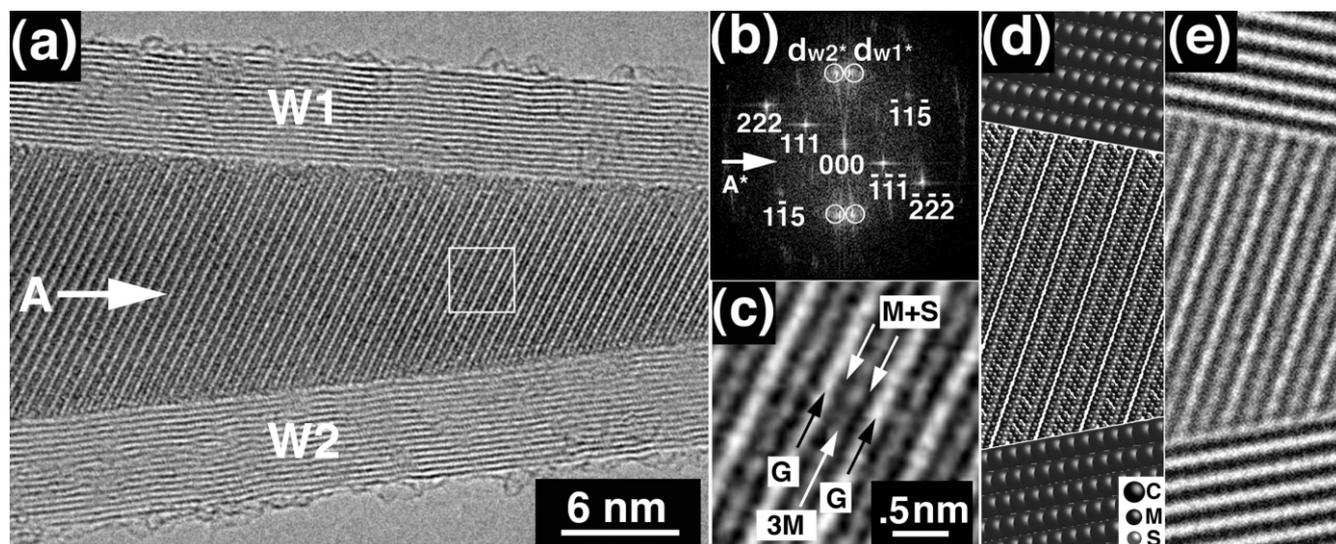


Fig. 2 (a) High magnification image of the boxed region in Fig. 1(a) showing a single crystal region of the alloy formed within a conical MWNT. (b) Fast Fourier Transform (FFT) of the composite in (a). Besides the reflections due to the crystal it is possible to observe the reflections from the MWNT {0002} wall layers (**W1** and **W2** in (a)) indicated as **dw1*** and **dw2***. (c) Enlarged image of the selected region in (a). The white stripes correspond to gaps in the structure (*i.e.* **G**), the black stripes to the mixed sulfur–metal layers (*i.e.* **M + S**) and the grey lines are due to the triple layers of metal (*i.e.* **3M**). (d) Extended structure model with the graphite layers (*cf.* Fig. 1(b) inset). (e) Image simulation obtained from the model in (d).

indicated that the microstructure corresponded to a lamellar alloy of the pentlandite form. In the example in Fig. 2(a), the crystal is located within a 15-layer conical MWNT in which the opposing walls imaged in projection (*i.e.* **W1** and **W2**) are arranged at an angle of *ca.* 10° to the MWNT axis (**A**). Several crystals with this microstructure type were observed in other conical MWNTs which exhibited similar metal ratios but varying sulfur content. The reason for the conical shape of the encapsulating nanotube is unclear but is probably related to the morphology of the alloy precursor particle as has been suggested for other encapsulates.⁹

The lamellar microstructure of the alloy (Fig. 2(c)) consists of alternating light (*i.e.* **G**) dark (*i.e.* **M + S**) and semidark (*i.e.* **3M**) layers which we attribute to the oblique [32̄1] projection through the cubic pentlandite unit cell (see inset in Fig. 1(b)). The **3M** layers are made up two layers of tetrahedrally coordinated 32(f) metal sites alternating with a central layer of octahedrally coordinated 4(b) sites which are staggered in projection. Either side of the **3M** layer are **M + S** layers which comprise one layer of tetrahedrally coordinated metal 32(f) sites and a pure sulfur layer. These are separated from adjacent **M + S** layers by a small gap (*i.e.* **G**) layer which also corresponds to the white lines in the lattice image (Fig. 2(c)).

In order to simulate the HRTEM image, a model was made based on atomic positions taken from the published pentlandite structure (Entry 2775, MDF database, Cambridge Structural Database).¹⁰ The variation of thickness in the crystal given its conical nature was taken into account and the overall thickness is consistent with that on the RHS of the main image (*i.e.* Fig. 2(a)). {0002} graphite planes corresponding to the walls of the nanotube were added and the overall simulation was based on a model containing *ca.* 20000 atoms (Fig. 2(d)). The image computed for Scherzer defocus (*i.e.* −47 nm for our instrument) provides an excellent match with the experimental image (*cf.* Fig. 2(e) with Fig. 2(a) and (c)). Consequently, we believe that the filling material is homogenous π -phase pentlandite with the approximate composition $\text{Fe}_3\text{Ni}_4\text{Co}_2\text{S}_8$.

The sulfur concentration in our initial catalyst was not high (~ 0.75 at%). Nonetheless, as Demoncey *et al.* have observed,^{7,11} even an impurity concentration level of sulfur is sufficient to catalyse the formation of sulfur-containing materi-

als inside MWNTs formed from catalyst precursors and also that it can be encapsulated in higher concentrations than the starting **M** : **S** composition. They further proposed that sulfur diffuses into the metal catalyst particle in the liquid state and assists the graphitisation of the nanotube. These observations are consistent with the high sulfur content produced in our alloy which contains simultaneously a homogenous mixture of Fe, Ni and Co in the condensed phase.

It has been shown that successful encapsulation of π -phase cobalt pentlandite has been achieved as a by-product of an arc evaporation process used to synthesize DWNTs. This filling represents the first example of a complex quaternary alloy within a MWNT.

We are grateful to Professor N. A. Kiselev and co-workers at the RAS, Moscow, and to Dr R. O. Loutfy of the MER Corporation, Tucson, Arizona, whose work⁸ inspired this experiment. P.C. acknowledges Fundação para a Ciência e a Tecnologia for a Graduate Scholarship (SFRH/BD/3103/2000) while J.S. is indebted to the Royal Society for a University Research Fellowship.

Notes and references

- 1 D. Lundqvist, *Ark. Kemi, Mineral. Geol. A*, 1947, **24**, No. 22.
- 2 O. Knop and M. A. Ibrahim, *Can. J. Chem.*, 1961, **39**, 297.
- 3 A. J. Brearley, *Science*, 1999, **285**, 1380.
- 4 V. Rajamani and C. T. Prewitt, *Can. Mineral.*, 1973, **12**, 178.
- 5 N. Grobert, M. Mayne, M. Terrones, J. Sloan, R. E. Dunin-Borkowski, R. Kamalakaran, T. Seeger, H. Terrones, M. Rühle, D. R. M. Walton, H. W. Kroto and J. L. Hutchison, *Chem. Commun.*, 2001, **290**, 2280.
- 6 A. P. Moravsky and R. O. Loutfy, Intern. Pat. WO 02/30816 A1.
- 7 N. Demoncey, O. Stephan, N. Brun, C. Colliex, A. Loiseau and H. Pascard, *Synth. Met.*, 1999, **103**, 2380.
- 8 J. L. Hutchison, N. A. Kiselev, E. P. Krinichnaya, A. V. Krestinin, R. O. Loutfy, A. P. Moravsky, V. E. Muradyan, E. D. Obratsova, J. Sloan, S. V. Terekhov and D. N. Zakharov, *Carbon*, 2001, **39**, 761.
- 9 V. D. Blank, I. G. Gorlova, J. L. Hutchison, N. A. Kiselev, A. B. Ormont, E. V. Polyakov, J. Sloan, D. N. Zakharov and S. G. Zybtev, *Carbon*, 2000, **38**, 1217.
- 10 <http://www.cds.dl.ac.uk>.
- 11 N. Demoncey, O. Stephan, N. Brun, C. Colliex, A. Loiseau and H. Pascard, *Eur. Phys. J. B*, 1998, **4**, 147.