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► To cite this version:

Claire Arnaud, Florence Lecouturier, David Mesguich, Nelson Ferreira, Geoffroy Chevallier, et al.. High strength – High conductivity double-walled carbon nanotube – Copper composite wires. Carbon, 2016, vol. 96, pp. 212-215. 10.1016/j.carbon.2015.09.061 . hal-01486583

HAL Id: hal-01486583

<https://hal.science/hal-01486583>

Submitted on 10 Mar 2017

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Eprints ID : 16733

To link to this article : DOI:10.1016/j.carbon.2015.09.061
URL : <http://dx.doi.org/10.1016/j.carbon.2015.09.061>

To cite this version : Arnaud, Claire and Lecouturier, Florence and Mesguich, David and Ferreira, Nelson and Chevallier, Geoffroy and Estournès, Claude and Weibel, Alicia and Laurent, Christophe *High strength – High conductivity double-walled carbon nanotube – Copper composite wires*. (2016) Carbon, vol. 96. pp. 212-215. ISSN 0008-6223

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Letter

High strength – High conductivity double-walled carbon nanotube – Copper composite wires

A B S T R A C T

Double-walled carbon nanotube – copper composite macroscopic wires are prepared using a combination of spark plasma sintering and room-temperature wire drawing. The carbon content in the samples is low (0.5 vol.%). Compared to the corresponding pure copper wires, the electrical resistivity at 77 K of the composite wires is increased by only about 12% whereas their ultimate tensile strength at 293 K (560 MPa) and 77 K (710 MPa) is increased by about 10%.

Conducting copper wires are ubiquitous in today's world and there is a demand for stronger yet lighter ones, in fields such as aeronautics, space and power transportation as well as in niche applications such as materials for high-field magnets. Strengthening copper is achieved by alloying, by introducing another phase or through grain refinement, but these methods also usually increase scattering of the conducting electrons, i.e. they decrease the electrical conductivity. Tensile tests performed on macro- [1–4] or microscopic [5,6] dog-bone carbon nanotube - copper (CNT/Cu) composites showed that the presence of CNTs strengthens copper, but strongly decrease the electrical conductivity [2,3], which could in part reflect excessive carbon contents (typically 10–20 vol.%) in the samples. Here, CNT/Cu wires with a very low carbon content (0.5 vol.%) are prepared by a combination of spark plasma sintering (SPS) and room-temperature wire-drawing. Compared to pure Cu wires prepared by the same route, the presence of double-walled CNTs (DWCNTs) increases the ultimate tensile strength of the wires by about 10%, whereas their electrical resistivity at 77 K is increased by only about 12%. DWCNTs were used because there are more metallic CNTs in a DWCNT sample than in a single-wall CNT sample, although the tensile strength of the DWCNTs is lower. Multi-walled CNTs (MWCNTs) would also show high tensile strengths provided they are defect-free, but the number of defects tends to increase with the number of walls. Moreover, a given DWCNT weighs much less than a MWCNT of the same length [7] and therefore more CNTs are present for a given carbon weight loading when DWCNTs are used.

DWCNTs prepared in-house (average number of walls = 2, average outer diameter = 2.0 nm, length > 5 μm) [8] and a commercial Cu powder (Alfa Aesar, 99%, $1.0 \pm 0.5 \mu\text{m}$) were selected for the study. The DWCNTs were acid-functionalized to facilitate their dispersion. The required quantity of DWCNTs was soaked in a mixture of HNO_3 and H_2SO_4 aqueous solutions (1 h sonication in US bath, beaker placed in melting-ice vessel to avoid excessive heating). The resulting suspension was stirred for 24 h (magnetic stirring, room temperature) and an aqueous solution of HCl was slowly poured. The mixture was neutralized (ammonia aqueous

solution) and rinsed with distilled water, taking care of never drying the DWCNTs. A 1.1 g L^{-1} DWCNT suspension was obtained. An aqueous suspension of the Cu powder was poured stepwise into the DWCNT suspension under ultrasonic agitation (Bioblock Scientific VibraCell 75042). The vessel containing the DWCNT/Cu suspension was then frozen in liquid N_2 and was freeze-dried (Christ alpha 2–4 LD, Bioblock Scientific, $-40 \text{ }^\circ\text{C}$, 12 Pa, 48 h). The so-obtained powders were treated in H_2 ($214 \text{ }^\circ\text{C}$, 1 h) to reduce any present copper oxide and produce the DWCNT/Cu powders. The carbon content is equal to 0.5 vol.%. It was shown in a previous study using a similar preparation route [8] that the distribution of the DWCNTs in the DWCNT/Cu powders is homogeneous up to 5 vol.% carbon, even though the DWCNTs had not been functionalized. Therefore, although it is more difficult to assess for the present samples with a very low carbon content because there are large areas devoid of DWCNTs, it is reasonable to consider that the DWCNT distribution in the powder is homogeneous and that the applied functionalization avoided an excessive degree of bundling.

Cu and DWCNT/Cu cylinders, to be used as precursors to wire-drawing, were prepared by SPS (Dr. Sinter 2080, SPS Syntex Inc., Japan). 13.5 g of powder were loaded into an 8 mm inner diameter WC/Co die. A sheet of graphitic paper was placed between the punch and the powder and between the die and the powder for easy removal. The SPS run was performed in vacuum (residual cell pressure < 10 Pa) using the default pattern of the machine (12 on: 2 off current pulses). The temperature was controlled using a thermocouple introduced in a hole (5 mm deep) drilled on the outer surface of the die. The samples were heated ($100 \text{ }^\circ\text{C}/\text{min}$) up to either $600 \text{ }^\circ\text{C}$ (pure Cu) or $700 \text{ }^\circ\text{C}$ (DWCNT/Cu) where a 5 min dwell was applied. A uniaxial charge (corresponding to 25 MPa on the compact) was gradually applied within the first minute of the dwell and maintained during the remaining 4 min. Natural cooling was applied down to room temperature and the uniaxial load was gradually released during the same time. The SPS cylinders were 8 mm in diameter and 33 mm long. The graphitic paper remaining on the surface was removed by machining. The relative density of the cylinders, measured by Archimedes' method, is equal to $95 \pm 1\%$. No

attempt was made to achieve full density because some residual porosity will favor the deformation capability of the cylinders during wire-drawing by allowing for easier grain rotation. Electron microscopy images (not shown) observations of a transversal section of the cylinders revealed that the Cu grains have not grown significantly from the original size ($1.0 \pm 0.5 \mu\text{m}$), notably because of the short sintering times used in SPS in agreement with other works [8–10]. No phase change such as carbide formation was detected by X-ray diffraction, which is not surprising given the very low carbon content (0.5 vol. %) in these samples. Indeed, we have previously reported the absence of carbide formation for similar composites containing up to 16 vol.% in carbon [8].

The cylinders were wire-drawn at room temperature through conical tungsten carbide dies, in 40 passes, in order to obtain wires with decreasing diameters. Samples of wires were typically 700 mm or 1500 mm long. The 4 mm diameter wires have already achieved a relative density of $99 \pm 1\%$. For the sake of comparison, wires were also prepared using a conventional Cu cylinder (average grain size of the order of $10 \mu\text{m}$, relative density 99.3%) prepared from standard cast oxygen-free high conductivity (OFHC) copper. They are denoted OFHC-Cu wires. Transmission electron microscopy (TEM, JEOL JEM 2100F operated at 200 kV) observations of a longitudinal section, i.e. parallel to the wire-drawing (WD) direction, of the Cu wire 0.506 mm in diameter, show the so-called lamellar microstructure, consisting in Cu grains about 200–400 nm wide and elongated over several micrometers (Fig. 1a). No difference is observed between the microstructure of the pure Cu and DWCNT/Cu wires (Fig. 1b). Although it is yet to be confirmed by the study of higher magnification images, the DWCNTs are supposed to be aligned along the WD direction and thus along the elongated Cu grains.

Tensile tests (INSTRON 1195 machine) were performed at 293 K and 77 K on wires 170 mm long and 0.251–1.023 mm in diameter. The tensile direction was parallel to the WD direction. Precise stresses were measured by the stress gauge system (250 N , $1.6 \times 10^{-5} \text{ m s}^{-1}$). Typical stress–strain curves for the wires 0.506 mm in diameter are shown in Fig. 2. The ultimate tensile strength (UTS) was determined for all wires on similar curves. Note that the wide elastic domain observed on the curves is an artifact due to the experimental set-up (strain was determined from crosshead displacement without any correction of machine rigidity). Field emission gun-scanning electron microscopy (FESEM, JEOL JSM 6700F) images (not shown) revealed ductile fracture for all wires. The ultimate tensile strength (UTS) was determined for all wires on similar curves.

The UTS at 293 K (Fig. 3a) for the OFHC-Cu wires (*ca.* 450 MPa) is close to the value (460 MPa) reported [11] for a Cu wire deep-drawn at room temperature using a Cu cylinder with a comparable grain size ($9.4 \mu\text{m}$). This shows that both our wire-drawing and UTS measurement processes are valid. For the Cu wires, the UTS values are noticeably higher, increasing from 460 to 540 MPa upon the decrease in wire diameter, which could reflect the finer microstructure. The UTS values are still higher (490–560 MPa) for the DWCNT/Cu wires (reaching a plateau for wire diameters below 0.625 mm). These values are significantly higher than those reported for macroscopic dog-bone CNT/Cu samples [1–4], which could mainly reflect both the finer copper grain size and the probable alignment of the CNTs in the wires. The same trends are observed for the UTS measured at 77 K (Fig. 3b), with very high UTS (710 MPa) for DWCNT/Cu wires below 0.625 mm in diameter.

The higher UTS values for the DWCNT/Cu wires reflect the strengthening role of the DWCNTs, due to their very high resistance to elongation and because it is very likely that they are aligned along the WD axis, which is also the tensile direction. However, although it has yet to be investigated into more details, stresses developed during WD may have modified the structure of some

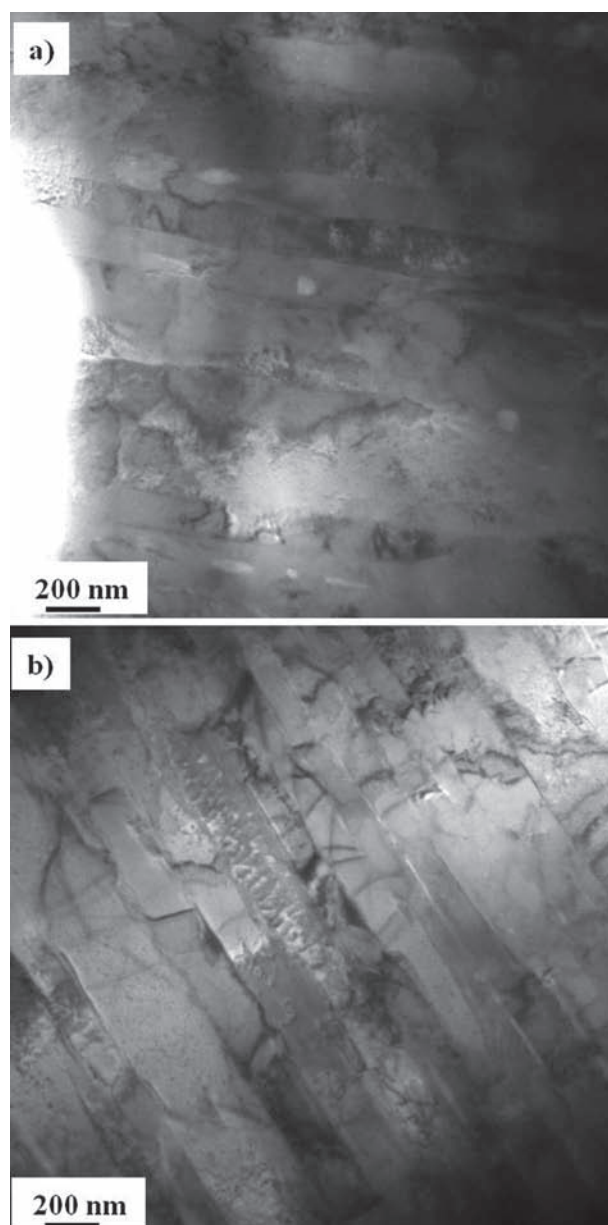


Fig. 1. TEM bright-field images of the longitudinal section of the wires 0.506 mm in diameter: Cu (a) and DWCNT/Cu (b).

of the DWCNTs in the Cu grains boundaries, by ovalization or collapse into ribbons (see Ref. [9] and references therein), which may be detrimental. It is possible that a certain degree of bonding between the DWCNTs and the Cu matrix is provided by the ex-carboxylate oxygen ions present at the surface of the DWCNTs since it is known that they resist H_2 reduction and SPS [12]. This strong Cu–O–C interface would favor charge transfer. Even if a good “wetting” has not been achieved in all areas, FESEM observations of the fracture surface reveal bridging DWCNTs and bundles, as shown in a typical image for the 1.023 mm wire (Fig. 4).

The electrical resistivity was measured at 293 K and 77 K (Fig. 5), using the four probe method with a maximum current of 100 mA to avoid heating the wires. The resistivity increases slightly upon the decrease in wire diameter, reflecting grain refinement and the corresponding increase in the density of grain boundaries acting as scattering centers for conduction electrons. At 293 K (Fig. 5), the values for the pure Cu and DWCNT/Cu wires are similar, only

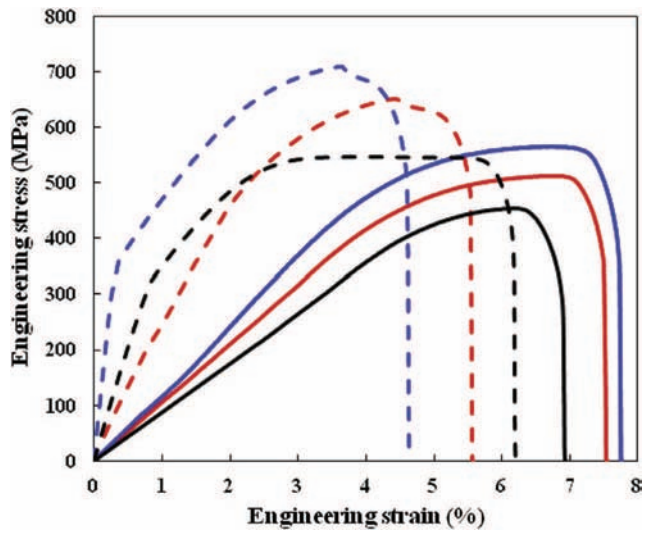


Fig. 2. Stress–strain curves at 293 K (full lines) and 77 K (dashed lines) for the wires 0.506 mm in diameter: OFHC-Cu (—), Cu (—) and DWCNT/Cu (—). (A colour version of this figure can be viewed online.)

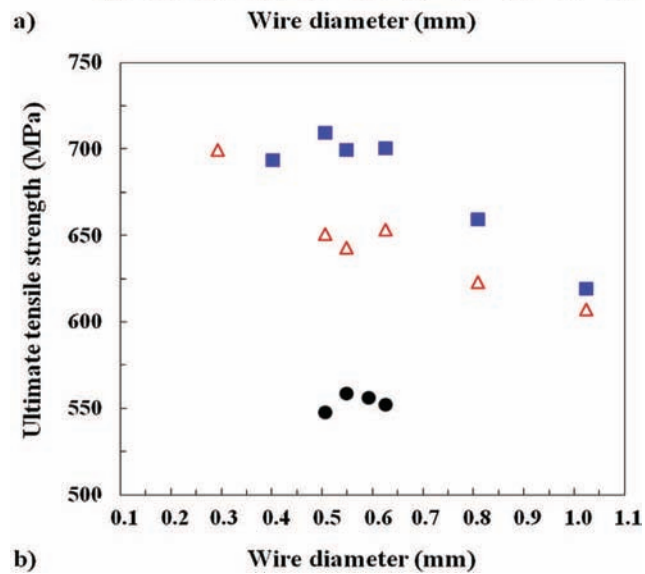
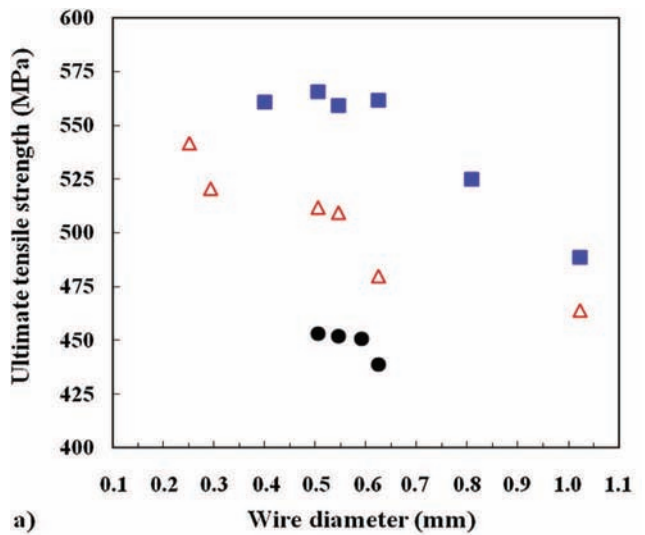


Fig. 3. Ultimate tensile strength versus wire diameter, at 293 K (a) and 77 K (b): OFHC-Cu (●), Cu (△) and DWCNT/Cu (■). (A colour version of this figure can be viewed online.)

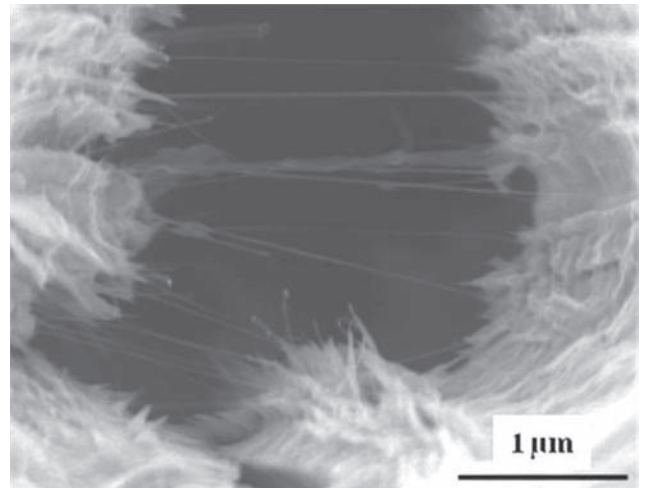


Fig. 4. FESEM image of the fracture surface for the DWCNT/Cu wire 1.023 mm in diameter.

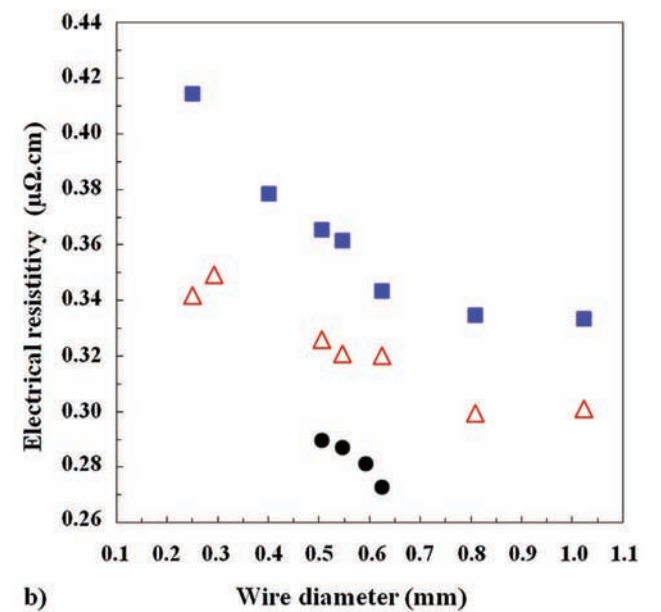
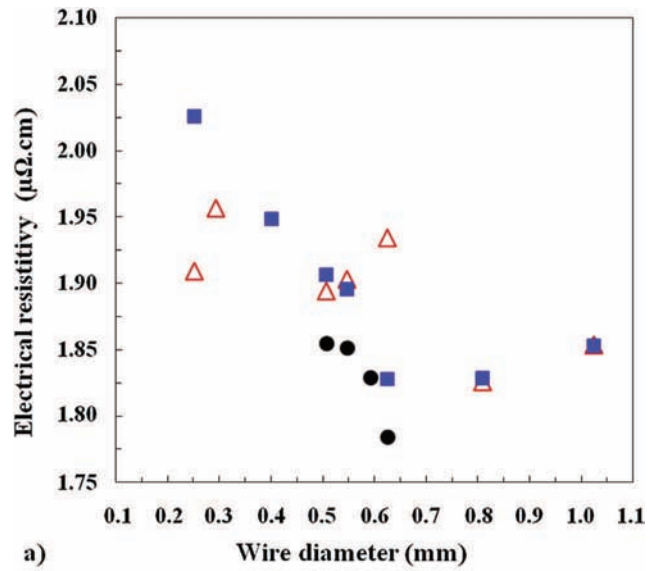


Fig. 5. Electrical resistivity versus wire diameter at 293 K (a) and 77 K (b): OFHC-Cu (●), Cu (△) and DWCNT/Cu (■). (A colour version of this figure can be viewed online.)

slightly higher than those for the OFHC-Cu wires, (1.78–1.85) $0.10^{-6} \Omega \text{ cm}$, corresponding to 93–97% International Annealed Copper Standard (IACS), in good agreement with reports [11] for same-diameter wires prepared from conventional cylinders (96.5% IACS) and higher than for dog-bone samples (about 82% IACS) [2–4]. The values measured at 77 K (Fig. 5b) are less scattered and are considered to reflect the evolutions more accurately because of the lower phonon contribution to the involved phenomena. Compared to the pure Cu wires, the DWCNT/Cu wires merely show a faint increase (about 12%) in electrical resistivity at 77 K.

Because the acid functionalization may have much degraded the electrical conductivity of the DWCNTs, applying a non-covalent functionalization treatment could be a direction for progress. Moreover, as noted above, a strong Cu–O–C interface may have been formed but this would also increase the electrical resistivity of the composite [12]. Note that the higher resistivities compared to the OFHC-Cu wires could reflect the higher oxygen content in the present wires, even though the DWCNT/Cu powder was hydrogen heat treated. Compared to Cu-based alloys with a similar strength (or a similar electrical conductivity) (see Ref. [13] and references therein), the present DWCNT/Cu wires show a significantly higher conductivity (or strength), respectively.

In conclusion, DWCNT/Cu composite wires are prepared by a combination of spark plasma sintering and room-temperature wire-drawing. The carbon content in the sample was kept very low (0.5 vol.%). Thus, compared to the corresponding pure Cu wires, the electrical resistivity at 77 K is only moderately increased (by about 12%) but it is sufficient to produce an increase of the ultimate tensile strength by about 10%. This arises because the DWCNTs, which are probably aligned along the elongated copper grains, have a very high tensile strength. Interestingly, such DWCNT/Cu composite wires are suitable for applications in their present form, as opposed to being laboratory test samples.

Acknowledgments

The authors thank L. Datas and L. Weingarten for assistance in TEM, performed at “Centre de microcaractérisation Raimond Castaing – UMS 3623” (Toulouse). The authors are grateful to Pr. A. Peigney and Dr. G. Rikken for fruitful discussions. This work was performed under contract NANO2C from Université de Toulouse and Région Midi-Pyrénées.

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