

Improving the mechanical and thermal properties of semi-coke based carbon/copper composites reinforced using carbon nanotubes

S. Kumari^{1*}, A. Kumar¹, P. R. Sengupta¹, P. K. Dutta², R. B. Mathur¹

¹CSIR-National Physical Laboratory, Dr. K.S. Krishnan Marg, New Delhi 110012, India

²Motilal Nehru National Institute of Technology, Allahabad, India

*Corresponding author. Tel: (+91) 1145608285; FAX: (+91) 1145609310; E-mail: kumaris@mail.nplindia.ernet.in

Received: 29 October 2013, Revised: 07 December 2013 and Accepted: 08 December 2013

ABSTRACT

Multiwalled carbon nanotubes (MWCNT)- reinforced carbon/copper (C/Cu) composites were developed by powder metallurgy technique and mixed powders of C and Cu were consolidated into plates without using any extra binder followed by sintering at 1000°C in inert atmosphere. Samples were characterized for structural, mechanical, electrical and thermal properties w.r.t. different mass fraction of MWCNT in C-Cu matrix. In comparison to C/Cu composite, addition of minute amount (0.25 wt%) of CNT in C-Cu substantially improved the mechanical, electrical and thermal properties of composites. These composites were mechanically stable and strong and exhibited high bending strength of 162 MPa, indicating a homogeneous dispersion of MWCNTs in the C-Cu matrix. Maximum thermal conductivity of 37.60 W/mK perpendicular to the pressing direction was obtained for 0.50 wt% CNT reinforced C-Cu composite exhibiting an improvement of 45% over pure C-Cu composite processed under identical conditions. High thermal conducting and mechanically strong composites can be used as heat sink for long time. Copyright © 2014 VBRI press.

Keywords: Carbon nanotubes; carbon/copper composite; electrical properties; mechanical properties; thermal properties.



Saroj Kumari received her Ph.D. in the field of semiconductor based photoelectrochemical splitting of water for hydrogen production from Dayalbagh Educational Institute, Dayalbagh, Agra, Uttar Pradesh, India. She is presently working as a Scientist at CSIR-National Physical Laboratory, New Delhi, India. She has been involved in research pertaining to development of QI free pitch, high density graphite, copper reinforced graphite composites, semi-coke materials, mesophase pitch, mesocarbon microbeads, needle coke, carbon nanoparticles, carbon fibers and graphene for applications in mechanical, electrical, thermal, strategic and energy fields.



Anil Kumar received his M.Sc in Organic chemistry from Chaudhary Charan Singh University Meerut, Uttar Pradesh, India. He is presently working as a senior research fellow (SRF, Ph.D student) at CSIR-National Physical Laboratory, New Delhi, India and involved in development of advanced material such as. Graphene based metal composite, QI free pitch, high density graphite, copper reinforced graphite composites, semi-coke materials for various applications.



R. B. Mathur is presently associated with the CSIR-National Physical laboratory, New-Delhi, India as Chief scientist and Head, Physics and Engineering of Carbon. He specializes in Solid state Physics, X-ray spectroscopy; Advanced carbon products e.g. carbon fibres; carbon nanotubes, carbon fibre and CNT reinforced polymer and carbon-carbon composites, carbon materials for energy applications etc.. He has published more than 140 research papers in International Journals, developed and patented more than 15 technologies out of which five have been commercialized. Recipient of many National /International awards. Dr. Mathur has worked in several reputed Institutes and laboratories in Germany, France, U.K., USA, Russia and Australia and have established active scientific collaboration with them.

Introduction

Carbon (graphite)/copper (C/Cu) composites have been widely used in tribological engineering parts, e.g. carbon brushes for engines, sliding bearings and also in electrical and thermal devices [1-5]. These composites have been characterized for their high mechanical strength, friction, electrical resistivity and thermal conductivity. The C/Cu is a combination of unique characteristics of both elements, such as electrical and thermal conductivity from the copper and low thermal expansion coefficient and lubricating properties from the graphite. Diverse efforts have been made to produce C/Cu composites focusing on improving their mechanical, electrical and thermal properties useful for specific applications. Interfacial bonding between copper and carbon particles which make the interface strength of carbon-copper is very weak [6,7] resulting in poor mechanical, electrical and thermal properties as interfacial strength and wettability play a key role in processing as well as in the performance of C/Cu composites. To overcome this problem, many studies have been carried out on incorporation of various [6-7, 9-10] additives in the composites in order to increase the interface strength and improve the mechanical, electrical and thermal properties of the composites for various applications.

Various methods have been adopted to prepare C/Cu composites of excellent mechanical and physical properties, such as powder metallurgy [2-3, 5, 8-9], impregnation [10], hot isostatic pressing [11] and chemical reduction method [12]. Out of these methods, powder metallurgical route has shown many advantages over these methods for the possibility of obtaining good quality composites with low cost. Nowadays, carbon nanotubes (CNT) have received significant attention as a reinforcement material in the polymer [13], metal [14] and ceramic matrix [15] materials for the development of high quality composites, which is due to their excellent mechanical and electrical properties, extraordinary low coefficient of thermal expansion and outstanding axial thermal conductivity [16,17]. Several reports are available only on improvement in mechanical properties of CNT/Cu composites developed by mainly two new methods i.e. spark plasma sintering [18], molecular level mixing [19] and melt stirring [20]. However, very few results on the enhancement of thermal properties are available in the literature [21, 22]. Despite many efforts, to the best of our knowledge, effect of CNT in self-sintering semi-coke based carbon-copper composites on the mechanical, electrical as well as thermal properties is not reported so far in literature. Self-sintering semi-coke is one such carbonaceous material produced from heat treatment of coal tar pitch, which is a high quality material used for producing special carbon products of high density, high strength, low porosity and low electrical resistivity without using any extra binder [23]. When semi-coke is mixed with copper powder, it results in dense C/Cu composites with good mechanical and electrical properties [24]. Incorporation of CNT in these semi-coke based C/Cu composites is expected to further improve the mechanical, electrical as well as thermal properties of the composites.

Therefore, in present research work, we have studied influence of multiwalled carbon nanotubes (MWCNT) reinforced in self-sintering semi-coke based carbon and copper matrix and developed CNT/C-Cu composites through powder metallurgy technique without using any extra binder to produce high performance composites. CNT/C-Cu composites have been investigated for structural, mechanical, electrical and thermal properties.

Experimental

Materials

Coal tar pitch (CTP) with quinoline insoluble (QI) content of 0.2% used in the present study, was procured from procured from Konark Tar Products Ltd, India. Copper powder (99%), was procured from Merck, India. MWCNT (90% pure) used as an additive was purchased from Nanocyl, Belgium. The other chemicals were of reagent grade and used as received.

Synthesis of semi-coke and development of CNT/C-Cu composites

Self-sintering semi-coke material used as carbon source was prepared from commercially available coal tar pitch (CTP) by heating at temperatures in the range of 400-500°C in inert atmosphere. Detailed methodology has been described in our previous research paper [24]. The coke thus prepared was then ground into fine powder using planetary ball mill at 250 rpm for 5h. Similarly, commercially available copper powder was also ball milled alone for 15h.

To investigate the influence of CNT on different properties of C/Cu composites, a series of samples with formula $\text{CNT}_x/(\text{C-Cu})_{100-x}$, where x is mass fraction of CNT varying from 0 to 5 wt% (0, 0.25, 0.50, 0.75, 1.0, 3.0, 5.0 wt%) were prepared. Prior to mixing, CNT were dispersed in ethanol using ultra sonicator for 30 min. The dispersed CNT in different amounts were mixed with semi-coke and copper powders in the fixed copper to carbon ratio of 1:1 through stirring in ethanol. After oven drying at 50-70°C, mixtures of CNT, semi-coke and copper were ball milled for 15h. Finally, the ball milled powders of $\text{CNT}_x/(\text{C-Cu})_{100-x}$ were moulded into rectangular plates (without using any extra binder) of the size $30 \times 15 \times 5 \text{ mm}^3$ using a conventional hydraulic press at a pressure of 150 MPa. These green plates (as such moulded plates) were sintered at 1000°C in nitrogen atmosphere to obtain consolidated CNT reinforced C-Cu composites.

Characterization of materials and CNT/C-Cu composites

The precursor CTP and semi-coke powder were characterized for quinoline insoluble (QI), toluene insoluble (TI), softening point, specific gravity, coking value (at 1000°C in inert atmosphere) and volatile matter. Thermogravimetric analysis (TGA) was carried out by heat treating CTP and semi-coke at different temperatures in inert atmosphere. Weighed quantity of CTP and coke were heat treated in nitrogen from 100 to 950°C to determine residual mass upon heat treatment.

The consolidated and sintered CNTx/(C-Cu)100-x composites were characterized by X-ray diffraction analysis (D-8 Advanced Bruker) using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$), and scanning electron microscopy and energy dispersive X-ray spectroscopy (EDX) using SEM, ZEISS-EVO MA10. Further, all composites were characterized with respect to bulk density, weight loss and volume shrinkage after heat treatment at 1000°C. Bending strength was measured by three point bending test using Instron Universal Testing Machine (model 4411). Electrical conductivity was also measured for all the samples using a laboratory developed four-probe apparatus. For this purpose a Keithley 2602A programmable sourcemeter was used for providing constant current (I) and measuring voltage drop (V) between two points. Thermal conductivity was measured by Linseis GmbH (LFA-1000), Germany.

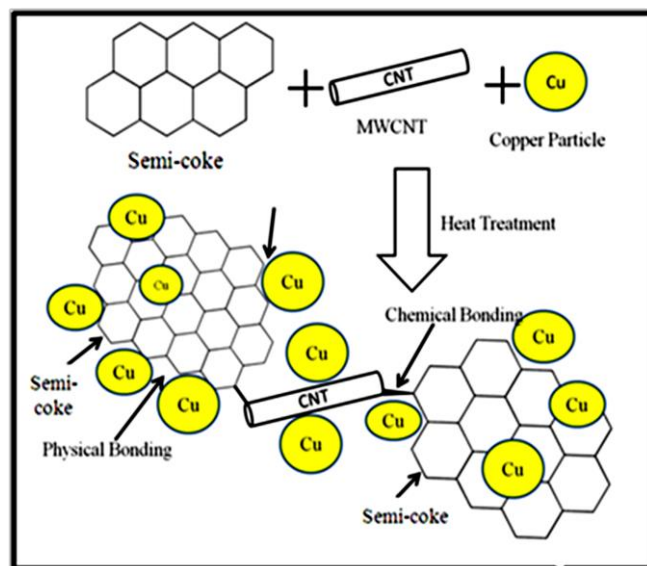


Fig. 1. Schematic illustration of CNT/C-Cu composite (colour online) synthesis process.

Results and discussion

Fabrication strategy of CNT/C-Cu composites

Fig. 1 shows the basic fabrication strategy of CNT/C-Cu composite. It shows semi-coke material get attached with carbon nanotubes via chemical bonding on heat treatment at 1000°C in inert atmosphere. This may improve the mechanical, electrical and thermal, properties of the composites; detail has been given in forth coming sections.

Characteristics of CTP and semi-coke

CTP used in this study to synthesize self-sintering semi-coke was observed to have low softening point of 86.2°C and specific gravity of 1.27. Further, precursor CTP possessed a QI content of 0.2%, TI content of 22.3% and coking value of 43.3%, which are lower as compared to those of semi-coke powder which showed QI of 97.0%, TI of 99.0% and coking value of 91.2%. The increase in QI and TI for coke powder is attributed to the removal of volatile matter (51.1%) on pyrolysis of precursor CTP at

the temperature upto 500°C during self-sintering semi-coke preparation and also to the dehydrogenative condensation and polymerization reactions between various molecular species of the CTP. This observation is confirmed by the hydrogen content and C/H atomic ratio of CTP and semi-coke as hydrogen content decreased from 4.8% for CTP to a value of 2.7% for semi-coke and C/H atomic ratio was increased significantly from a value of 1.6% for coal tar pitch to 2.9% for semi-coke derived therefrom. TGA study was carried out to monitor the thermal stability of CTP and semi-coke by recording the change in mass of the sample with respect to temperature. TGA results of CTP and semi-coke under nitrogen atmosphere are shown in **Fig. 2A**. The pitch used in this study started losing weight above 150°C which is related to the removal of moisture and drying of residual washing solvent. A sharp weight loss around 40% for CTP occurred from 300 to 500°C because of above 500°C up to 950°C, removal of volatile matter weight loss was only 5%. On the other side, in semi-coke, the total weight loss upto 950°C was 8%.

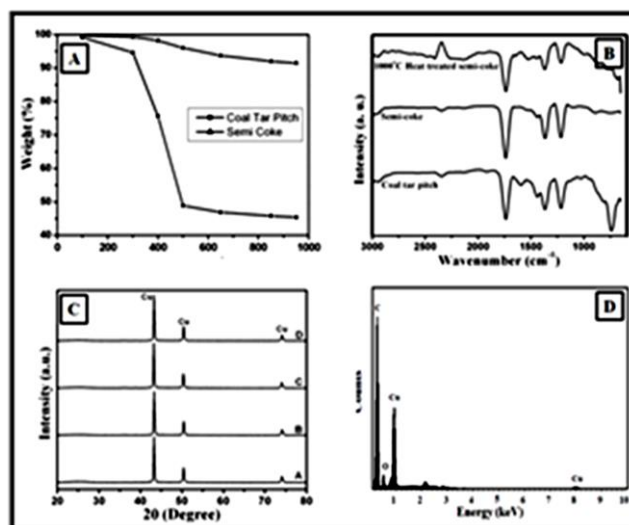


Fig. 2. (A) TGA curves for coal tar pitch and semi-coke at different temperatures. (B) FTIR spectra of coal tar pitch, semi-coke, 1000°C HT semi-coke. (C) XRD patterns of (a) C/Cu composite without CNT, (b) 0.25, (c) 1.0 and 5 wt% CNT- reinforced C/Cu composites heat treated at 1000°C. (D) EDX pattern of 5.0 wt% CNT- reinforced C/Cu composite.

Fig. 2B shows the FTIR spectra of coal tar pitch, as such synthesized semi-coke powder and 1000°C heat treated semi-coke powder. In case of CTP, peak positions at 741, 1214, 1366, 1439, 1737, and 3026 cm^{-1} correspond to the mono substituted benzene, aromatic ether (C-O), aromatic nitro(NO_2) compound, aromatic C=C (SP^2) ring, cyclic ether with conjugation in ring and methene (C=CH). For semi-coke, peak position at 741 cm^{-1} is absent due to removal of mono substituted on heat treatment of CTP. Peak positions at 1214, 1366, 1439 1737 and 3026 cm^{-1} are common but there is a shifting in peaks from CTP to 1000°C HT semi-coke. This phenomenon also indicates the removal of functional groups on heat treatment of semi-coke at 1000°C. The presence of aromatic ring and their derivative peaks prove formation of polyaromatic hydrocarbon structure.

Phase analysis and microstructures of CNT/C-Cu composites

The X-ray diffraction (XRD) analysis results are shown in **Fig. 2C**. The main diffraction peaks in the composites for $x=0, 0.25, 1.0$ and 5.0 wt%, correspond to the phase of copper are very sharp due to the crystalline nature of copper. The major diffraction peaks at 2θ values of 43.29° , 50.45° , and 74.17° corresponding to (111), (200), and (220) planes of copper, respectively were observed through JCPDS data. There was no change in these diffraction patterns by addition of CNT in different mass fractions. No peak of copper oxide was observed in the X-ray pattern (**Fig. 2C**), which confirms that copper is present in the metallic form in the matrix even after ball milling. The (002) peak at $2\theta=26.55^\circ$ corresponding to graphitic structure of carbon was not observed. This suggests that carbon (semi-coke material) in all composites is amorphous in nature due to their heat treatment at low temperature of 1000°C because crystalline phase of carbon forms above temperature of 1400°C . It was also observed that the peaks of CNT in the composites were absent, which may be due to much lesser amount of CNT (0.25 to 5 wt%) in the mixture. The EDX result of CNT/C-Cu composite for $x=5$ wt% is shown in **Fig. 2D**. Peaks due to carbon and copper elements with a small oxygen peak were present in the EDX spectrum. The presence of oxygen peak was probably due to the formation of copper oxide phase by the surface oxidation of the Cu particles at the room temperature.

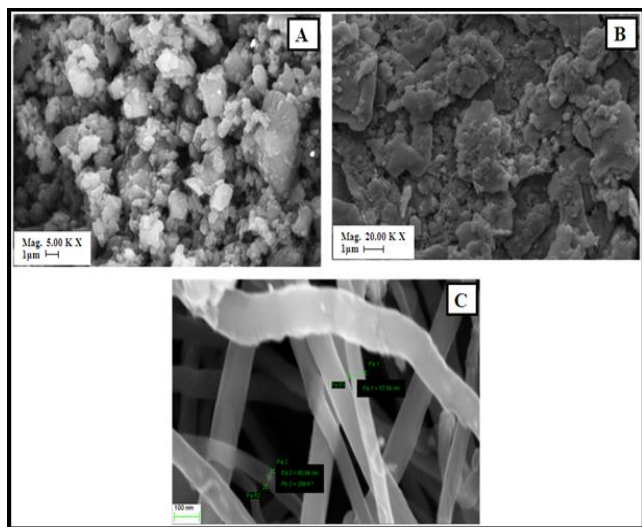


Fig. 3. SEM images of (A) semi-coke material, 5 h ball milled, (B) copper powder, 15 h ball milled and hydrogenated and (C) as received MW-CNTs.

Fig. 3 shows the morphology of individual materials used to prepare the composites such as semi-coke material prepared from heat treatment of CTP in **Fig. 3A**, pure copper powder after ball milling in **Fig. 3B** and CNTs in **Fig. 3C**. The microstructure of coke powder showed the homogeneous distribution of particles of size varying from 0.5 to $3\mu\text{m}$ (**Fig. 3A**), on the other hand, physically synthesized (ball milled) copper particles had flake like structures (**Fig. 3B**) with grains and grain boundaries. Ball milling is mainly responsible for the rough texture of the

copper particles and flaky structure. **Fig. 3C** shows the SEM image of morphology of commercially obtained MWCNTs. The diameter of MWCNT was in the range of $50\text{--}70$ nm with very little damage on the outermost layer.

The surface morphology of composite heat treated at 1000°C for $x=0$ was smoother than that of the CNT/C-Cu composites (**Fig. 4A and 4B**). Upto $x=0.25$ wt%, the microstructure of composites shows homogeneous structure (**Fig. 4C**), but when the amount of CNT is increased to 5 wt% in the composites, dispersed bulges can be seen on the surface of the composite (**Fig. 4D**). This may be due to the fact that addition of CNT into C-Cu matrix introduces additional nucleation sites that cause rough surfaces. It can also be seen from the fractured surface (**Fig. 5A**) that CNT added in small amounts (0.25 wt%) were dispersed homogeneously in the C-Cu mixed powder. But, when the CNT content was higher (5 wt%), clusters of CNT were formed resulting in a non-uniform distribution and formation of some large pores in the C-Cu matrix, **Fig. 5B**. These pores may be responsible for the reduction in physical and mechanical properties, as discussed in following sections.

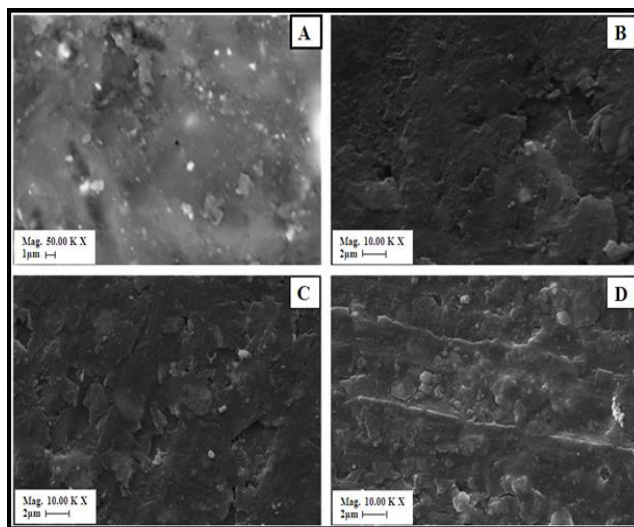


Fig. 4. SEM images of (A) C/Cu composite without CNTs, (B) 0.25, (C) 0.50 and (D) 5.0 wt% CNT-reinforced C/Cu composites heat treated at 1000°C .

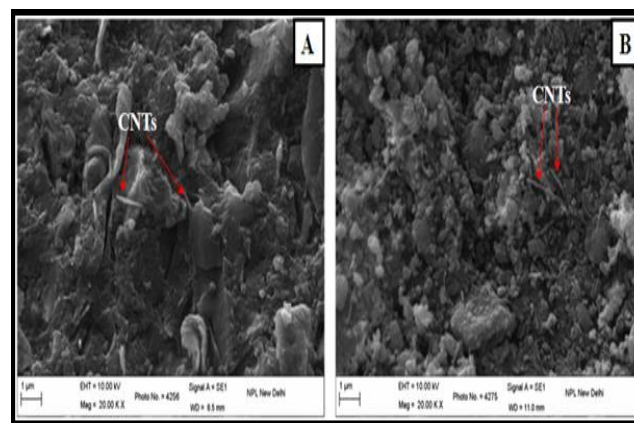


Fig. 5. SEM images of fracture surface of (A) 0.25 and (B) 5.0 wt% CNT-reinforced C/Cu composite heat treated at 1000°C .

Bulk density of composites

Fig. 6 presents bulk densities, before and after sintering for all composites. It was observed from the **Fig. 6** that green densities of all composites were lower than that of densities measured after heat treatment at 1000°C. This increase in bulk density is only due to the self-sintering property of coke resulting in high volume shrinkage of the order of 28% with a relatively low weight loss during the sintering of plates, i.e. heat treatment from room temperature to 1000°C. Because the CNT and Cu present in composites do not undergo any significant volume shrinkage, the volume shrinkage can be attributed entirely to sintering of coke particles. The weight loss is due to gradual removal of volatiles (poly aromatic hydrocarbons) during the solid transformation from coke to carbon. The effect of CNT on density of composites can also be seen from **Fig. 6**. As the amount of CNT increases from 0 to 5 wt%, the densities of composites were found to decrease from 2.25 to 2.13 g/cm³ and 2.93 to 2.79 g/cm³, before and after sintering, respectively. It was also observed that at low concentration of CNT (upto 1 wt%), the decrease in bulk density was linear, but at higher concentrations, i.e. for x=3 and 5 wt%, density decreased drastically. This is because of CNTs which have a tendency to agglomerate due to their relatively high surface areas, their high aspect ratios and poor interactions with copper. At high loading, they get agglomerated into bundles by van der Waals forces which is responsible for pores created in the composites, thereby reducing the density [25], as also confirmed by SEM micrographs.

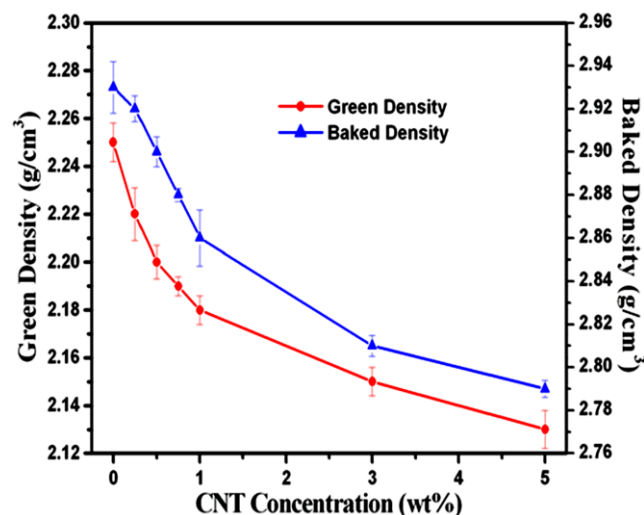


Fig. 6. Effect of CNTs with varied content on composite densities (before and after carbonization) (Colour online)

Mechanical properties of composites

The mechanical properties of all sintered composites were studied using bending and compressive tests. As shown in **Fig. 7**, bending and compressive strength of C/Cu composite without CNT were found to be 100 MPa and 215 MPa, respectively. This strength in C/Cu composite is due to the self-sintering property of semi-coke powder prepared from heat treatment of CTP. Minute addition of CNT (x=0.25 wt%) in C-Cu matrix showed maximum

bending strength of 162 MPa as well as compressive strength of 260 MPa, which are much higher (61.73%) than those composites prepared without CNT and with higher amount of CNTs. These values are much higher than the values reported by others in Ref 3, 24 and 26 for different types of copper-carbon composites without CNT. This remarkable strengthening of the composite by CNTs reinforcement may be firstly due to intrinsic strength of CNT and secondly due to uniform dispersion of CNT and better interfacial strength between CNT and Cu. It is also known that the reaction between C and Cu does not form any inter-metallic compound (carbide) and the solubility of C in molten Cu is almost zero (0.0005% at 1773K) [27]. So the strength due to the chemical bonding between carbon and copper would be extremely low. Therefore, the strengthening obtained in the composite must be due to the homogeneous dispersion of CNTs in the C-Cu matrix and chemical bonding between semi-coke and CNT. With further increase in CNT concentration, the strength of the composites was found to decrease continuously which is due to the creation of porosity as a result of agglomeration of CNTs at higher concentration as explained earlier. Strengthening in CNT-Cu composites has also been reported in literature, for example a three times higher yield strength was reported by Cha et al. [19] for 10 vol% CNT reinforced Cu than that of pure Cu. The CNT-Cu composite, prepared by cold rolling of sandwiched layers of metal and SWCNT showed an 8% improvement in tensile strength and a 12.8% increase in elastic modulus [28]. Our results for CNT/C-Cu composites are better than the reported by others as mentioned above. These results are suitable for various commercial applications because, methodology adopted in the present study is economically viable and straightforward.

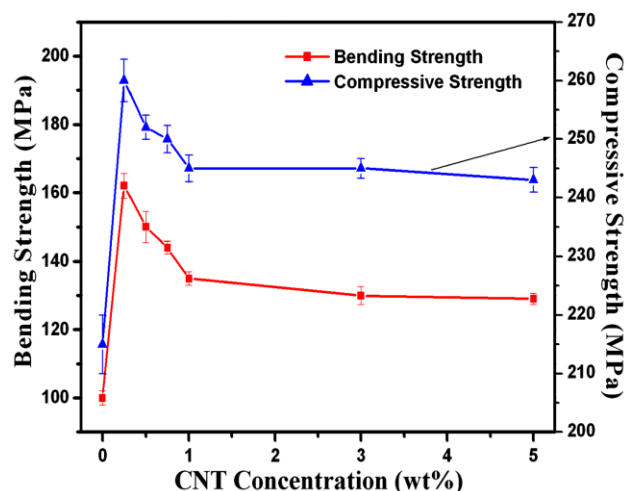


Fig. 7. Comparison of bending and compressive strengths of C/Cu composites as a function of CNTs (Colour online).

Electrical and thermal conductivity of composites

The room temperature electrical resistivity of all consolidated composites, measured by four probe method is presented in **Fig. 8**. The calculated electrical resistivity of the samples decreased significantly with increasing CNT mass fraction upto 1%. Beyond this amount, the value of

electrical resistivity marginally decreased. As mentioned earlier, the copper to carbon ratio in all the composites was kept constant and amount of CNTs was varied. Therefore, it is clear that decrease in electrical resistivity of CNT/C-Cu composites is only due to the high electrical conductivity of CNT along with well dispersion at lower mass fraction upto 1 wt%. At higher mass fraction of CNT ($x=3$ and 5 wt%), the electrical resistivity was found to be almost constant. Very recently, one hundred fold increase in current carrying capacity in a carbon nanotube–copper composite has been reported by Subramaniam et al [29]. In this paper they developed CNT–Cu composite that combines the best electrical properties of CNT (high ampacity) and Cu (high conductivity) for high-performance electrical conductor. CNTs are also known as an effective reinforcing/filler material to improve the electrical properties of insulating ceramics, polymers while retaining other properties as reported in [30]. However, in our study, a little increase in electrical resistivity at higher mass fraction (5 wt%) of CNTs may be attributed to the agglomeration of CNTs, forming grain boundary which will increase the scattering of charge carriers at grain boundary. This may also be due to the increase in porosity at higher concentration of CNTs as discussed in earlier sections.

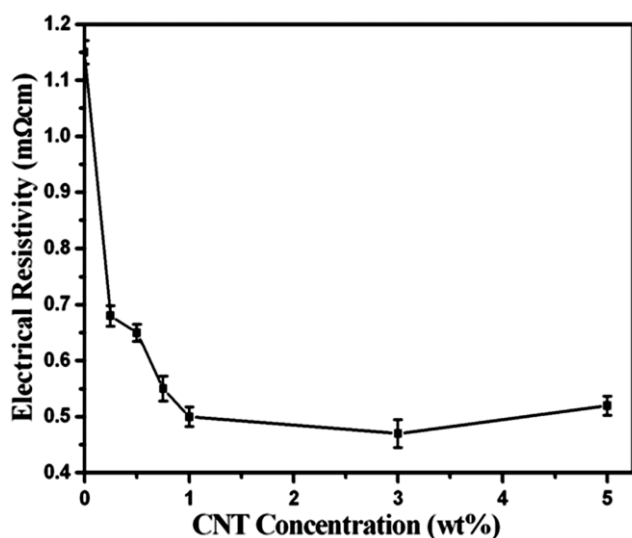


Fig. 8. Electrical resistivity ($\text{m}\Omega\text{-cm}$) vs. CNT concentration of C/Cu composites.

Thermal conductivity (all measured in the direction normal to the pressing) at room temperature (31°C) of different CNT/C-Cu composites as a function of CNT mass fraction is shown in Fig. 9. Thermal conductivity of the composite without CNT was 16.90 W/mK and increased to 24.50 W/mK for $x=0.25 \text{ wt\%}$ and further increased to 37.60 W/mK with $x=0.50 \text{ wt\%}$ of CNTs in the composite. Higher thermal conductivity of CNT/C-Cu composites than that of C/Cu may be due to the proper alignment of some CNTs in preferential direction and with well dispersion of CNTs. Since, CNTs have very high thermal conductivity along the tube direction but very low in the radial direction, as a result distribution of some CNTs normal to the pressing direction helps in heat transfer mechanism and increases the effective thermal conductivity of the composites.

Thermal conductivity decreased as the CNT mass fraction further increased to 3 wt%. This reduction is due to the lack of proper alignment of CNTs and agglomeration of CNTs creating pores. Pores are of two types: pores located at CNT/Cu interface and pores among the tubes [31]. Pores located at interface introduce additional thermal barriers by increasing the interfacial resistance value while pores among the tubes can efficiently scatter the heat flow. It is important to mention here that thermal conductivity of the composites was much lower as compared to Cu and CNTs. This is due to the semi-coke based carbon matrix used which is non graphitic form of carbon at 1000°C and has very low thermal conductivity and thus weakens the heat transferring. Effect of CNTs on mechanical, electrical and thermal properties of semi-coke based carbon-copper composites to the best of our knowledge is not reported anywhere in literature, however, effect of CNT concentration in copper matrix is reported by many researchers. The positive effect of CNTs on thermal properties of CNT/Cu composites has recently been reported for the first time by Cho et al. [21]. They reported increase in thermal conductivity for less than 3 vol% CNT/Cu composites prepared by mixing acid treated CNT and copper powder followed by consolidation through spark plasma sintering than the Cu alone. Next article was reported by Chai and Chen [22] on 180% greater thermal conductivity (average 604 W/mK) of CNT/Cu composites than that of pure copper (340 W/mK) prepared with a novel electrochemical co-deposition method. However, on the other side, there is large number of research papers [31-34] on CNT/Cu composites showing no enhancement in the thermal conductivity of the composites. The major problem was the dispersion and alignment of CNTs in preferential direction in the Cu matrix.

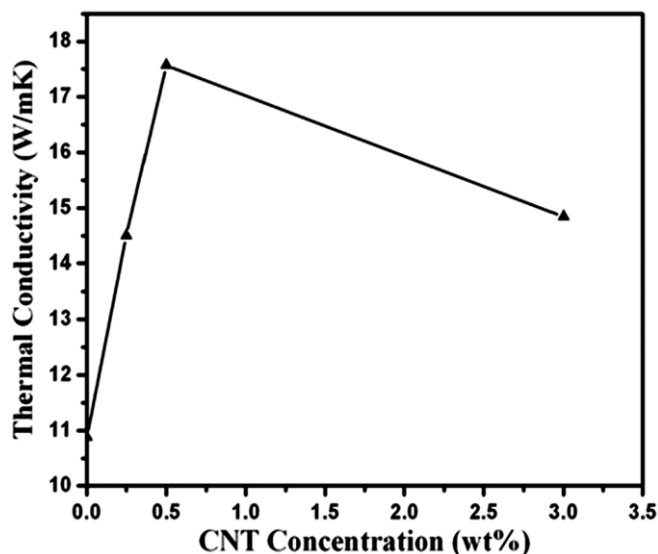


Fig. 9. Effect of CNT mass fraction on the thermal conductivity of C/Cu composites.

Conclusion

In this study, MWCNT- reinforced C/Cu composites were developed through powder metallurgy method by using CTP derived semi-coke material as carbon source and

copper powder followed by consolidation into plates without using any extra binder and sintering at 1000°C in inert atmosphere in order to obtain high performance composites. Mechanical, electrical as well as thermal properties were investigated as a function of CNTs concentration in C-Cu matrix. The consolidated composites developed by reinforcing CNT in C-Cu matrix showed high bending strength of 162 MPa, compressive strength of 260 MPa, low electrical resistivity of ~0.50 mΩ-cm with thermal conductivity of 37.60 W/mK.

Acknowledgements

Authors are thankful to Prof. R. C. Budhani, Director, National Physical Laboratory, for his kind permission to publish this article. The authors are also thankful to Dr. Chandra Shekher, Director and Dr. S. N. Joshi, Emeritus Scientist of Central Electronics Engineering Research Institute (CEERI), Pilani, India, for giving us an opportunity to co-operate in the 11th plan network project sponsored by Council of Scientific and Industrial Research (CSIR).

Reference

1. Futami, T.; Ohira, M.; Muto, H.; Sakai, M. *Carbon*. **2009**, 47, 2742–2751.
DOI: [10.1016/j.carbon.2009.05.034](https://doi.org/10.1016/j.carbon.2009.05.034).
2. Rohatgi, P.K.; Ray, S.; Liu, Y. *Int. Mater. Rev.* **1992**, 37, 129–152.
3. Ma, X.C.; He, G.Q.; He, D.H.; Chen, C.S.; Hu, Z.F. *Wear*. **2008**, 265, 1087–1092.
DOI: [10.1016/j.wear.2008.02.015](https://doi.org/10.1016/j.wear.2008.02.015).
4. Ma, W.; Lu, J. *Tribol. Lett.* **2011**, 41, 363–370.
DOI: [10.1007/s11249-010-9718-x](https://doi.org/10.1007/s11249-010-9718-x).
5. Garcia-Marquez, J.M.; Anton, N.; Jimenez, A.; Madrid, M.; Martinez, M.A.; Bas, J.A. *J. Mater. Process. Technol.* **2003**, 143(144), 290–293.
DOI: [10.1016/S0924-0136\(03\)00476-X](https://doi.org/10.1016/S0924-0136(03)00476-X).
6. Bakshi, S.R.; Lahiri, D.; Agarwal, A. *Int. Mater. Rev.* **2010**, 55(1), 41–64.
DOI: [10.1179/095066009X12572530170543](https://doi.org/10.1179/095066009X12572530170543).
7. Ichikawa, H.; Kanemaru, T.; Yamazoe, H. US Patent 3956568 A, **1976**.
8. Cho, K.H.; Hong, U.S.; Lee, K.S.; Jang, H. *Tribol. Lett.* **2007**, 27, 301–306.
DOI: [10.1007/s11249-007-9234-9](https://doi.org/10.1007/s11249-007-9234-9).
9. Polese, F.J.; Engle, G.B.; Ocheretyansky, V. US Patent 6238454 B1, **2001**.
10. Oku, T.; Oku, T. *Solid. State. Comm.* **2007**, 141, 132–135.
DOI: [10.1016/j.ssc.2006.10.013](https://doi.org/10.1016/j.ssc.2006.10.013).
11. Kováčik, J.; Emmer, Š.; Bielek, J.; Keleši, L. *Wear*. **2008**, 265, 417–421.
DOI: [10.1016/j.wear.2007.11.012](https://doi.org/10.1016/j.wear.2007.11.012).
12. Hu, Z.L.; Chen, Z.H.; Xia, J.T.; Jing, G.Y. *Trans. Nonferrous. Met. Soc. China*. **2007**, 17, s1060–1064.
13. Ci, L.; Suhr, J.; Pushparaj, V.; Zhang, X.; Ajayan, P.M. *Nano Lett.* **2008**, 8(9), 2762–2766.
DOI: [10.1021/nl8012715](https://doi.org/10.1021/nl8012715).
14. Tiwari, A.; Dhakate, S. R. *International journal of biological macromolecules*, **2009**, 44, 408.
Tiwari, A.; Gong, S. *Electroanalysis*, **2008**, 20, 2119.
15. Bakshi, S.R.; Agarwal, A. *Carbon*. **2011**, 49, 533–544.
DOI: [10.1016/j.carbon.2010.09.054](https://doi.org/10.1016/j.carbon.2010.09.054).
16. Tiwari, A.; Valyukh, S. (Eds), In *Advanced Energy Materials*, WILEY-Scrivener, USA, **2014**.
17. Samal, S.S.; Bal, S. J. *Minerals & Mater. Charac. & Engg.* **2008**, 7(4), 355–370.
Tiwari, A.; Mishra, A.K.; Kobayashi, H.; Turner, A.P.F. (Eds.), In *Intelligent Nanomaterials*, WILEY-Scrivener, USA, **2012**.
18. Treacy, M.M.J.; Ebbesen, T.W.; Gibson, J.M. *Nature*. **1996**, 381, 678–680.
DOI: [10.1038/381678a0](https://doi.org/10.1038/381678a0).
19. Dresselhaus, M.S.; Dresselhaus, G.; Charlier, J.C.; Hernández, E. *Phil. Trans. R. Soc. Lond. A*. **2004**, 362, 2065–2098.
DOI: [10.1098/rsta.2004.1430](https://doi.org/10.1098/rsta.2004.1430).
20. Guiderdoni, C.; Estournès, C.; Peigney, A.; Weibel, A.; Turq, V.; Laurent, C. *Carbon*. **2011**, 49, 4535–4543.
DOI: [10.1016/j.carbon.2011.06.063](https://doi.org/10.1016/j.carbon.2011.06.063).
21. Cha, S.I.; Kim, K.T.; Arshad, S.N.; Mo, C.B.; Hong, S.H. *Adv. Mater.* **2005**, 17, 1377–1381.
DOI: [10.1002/adma.200401933](https://doi.org/10.1002/adma.200401933).
22. Hippmann, S.; Li, Q.; Addinal, R.; Volk, W. Proceedings of the Institution of Mechanical Engineers, Part N: *J. Nanoeng. Nanosyst.* **2013**, 227, 63–66.
DOI: [10.1177/1740349912467730](https://doi.org/10.1177/1740349912467730).
23. Cho, S.; Kikichi, K.; Miyazaki, T.; Takagi, K.; Kawasaki, A.; Tsukada, T. *Scripta. Materialia*. **2010**, 63(4), 375–378.
DOI: [10.1016/j.scriptamat.2010.04.024](https://doi.org/10.1016/j.scriptamat.2010.04.024).
24. Chai, G.; Chen, Q. *J. Comp. Mater.* **2010**, 44(24), 2863–2873.
DOI: [10.1177/0021998310371530](https://doi.org/10.1177/0021998310371530).
25. Bhatia, G.; Aggarwal, R.K.; Mahur, J.S.; Bahl, O.P. Indian Patent 215804, **2008**.
26. Kumar, A.; Kaur, M.; Kumar, R.; Sengupta, P.R.; Raman, V.; Bhatia, G.; Sood, K.N. *J. Mater. Sci.* **2010**, 45, 1393–1400.
DOI: [10.1007/s10853-009-4097-0](https://doi.org/10.1007/s10853-009-4097-0).
27. Pham, V.T.; Bui, H.T.; Tran, B.T.; Nguyen, V.T.; Le, D.Q.; Than, X.T.; Nguyen, V.C.; Doan, D.P.; Phan, N.M. *Adv. Nat. Sci: Nanosci. Nanotechnol.* **2011**, 2, 015006–9.
DOI: [10.1177/002199831244339](https://doi.org/10.1177/002199831244339).
28. Queipo, P.; Granda, M.; Santamaría, R.; Menéndez, R. *Fuel*. **2004**, 83, 1625–1634.
DOI: [10.1016/j.fuel.2004.02.014](https://doi.org/10.1016/j.fuel.2004.02.014).
29. Saji, S.; Kadokura, T.; Anada, H.; Notoya, K.; Takano, N. *Mater. Trans. JIM*. **1998**, 39(7), 778–781.
DOI: [10.1023/A:100670170803](https://doi.org/10.1023/A:100670170803).
30. Li, Y.H.; Houston, W.; Zhao, Y.; Zhu, Y.Q. *Nanotech.* **2007**, 18, 205607(1–6).
DOI: [10.1088/0957-4484/18/20/205607](https://doi.org/10.1088/0957-4484/18/20/205607).
31. Subramaniam, C.; Yamada, T.; Kobashi, V.; Sekiguchi, A.; Futaba, D.N.; Yumura, M.; Hata, K. *Nature comm.* **2013**, 4, 2202–9.
DOI: [10.1038/ncomms3202](https://doi.org/10.1038/ncomms3202).
32. Ahmad, K.; Pan, W.; Shi, S.L. *App. Phys. Lett.* **2006**, 89, 133122–4.
DOI: [10.1063/1.2357920](https://doi.org/10.1063/1.2357920).
33. Chu, K.; Wu, Q.; Jia, C.; Liang, X.; Nie, J.; Tian, W.; Gai, G.; Guo, H. *Comp. Sci. and Tech.* **2010**, 70, 298–304.
DOI: [10.1016/j.compscitech.2009.10.021](https://doi.org/10.1016/j.compscitech.2009.10.021).
34. Firkowska, I.; Boden, A.; Vogt, A.-M.; Reich, S. *J. Mater. Chem.* **2011**, 21, 17541–17546.
DOI: [10.1039/C1JM12671G](https://doi.org/10.1039/C1JM12671G).
35. Chu, K.; Guo, H.; Jia, C.; Yin, F.; Zhang, X.; Liang, X.; Chen, H. *Nanoscale. Res. Lett.* **2010**, 5, 868–874.
DOI: [10.1007/s11671-010-9577-2](https://doi.org/10.1007/s11671-010-9577-2).
36. Kim, K.T.; Eckert, J.; Liu, G.; Park, J.M.; Lim, B.K.; Hong, S.H. *Scripta. Materialia*. **2011**, 64, 181–184.
DOI: [10.1016/j.scriptamat.2010.09.039](https://doi.org/10.1016/j.scriptamat.2010.09.039).

Advanced Materials Letters

Publish your article in this journal

ADVANCED MATERIALS Letters is an international journal published quarterly. The journal is intended to provide top-quality peer-reviewed research papers in the fascinating field of materials science particularly in the area of structure, synthesis and processing, characterization, advanced-state properties, and applications of materials. All articles are indexed on various databases including DOAJ and are available for download for free. The manuscript management system is completely electronic and has fast and fair peer-review process. The journal includes review articles, research articles, notes, letter to editor and short communications.

