 DOI 10.1002/mawe.201300084 Mat.-wiss. u. Werkstofftech. 2013, 44, No. 2–3

Magnetic properties of N-doped multi-walled carbon nanotubes

Magnetische Eigenschaften von mit Stickstoff dotierten mehrwandigen Kohlenstoffnanoröhren

G.E. Grechnev[1], V.A. Desnenko[1], A.V. Fedorchenko[1], A.S. Panfilov[1], Y.A. Kolesnichenko[1], S.V. Khrapatiy[2], Y.I. Prylutskyy[2], L.Y. Matzui[2], U. Ritter[3], P. Scharff[3]

The magnetic properties of nitrogen-doped multi-walled carbon nanotubes (N-MWCNTs) were studied in the temperature and magnetic field range of (4.2–290) K and (0.05–30) kOe, respectively. Also magnetic properties of the reference MWCNTs without nitrogen doping were investigated on the same footing for comparison. The presence of iron-based particles inside N-MWCNTs was detected. The low temperature SQUID (Superconducting Quantum Interference Device) magnetization measurements were supplemented with thermogravimetric analysis. The magnetic characterization provided the saturation magnetic moment M_S and residual magnetization M_R of N-MWCNTs to be, respectively, 4.5 emu/g and 0.9 emu/g, whereas for the reference MWCNTs the corresponding parameters are found to be about twice higher. The coercive field value amounts to 800 Oe for both systems at low temperatures, then decreasing to about 450 Oe at 200 K.

Keywords: carbon nanotubes / magnetization / susceptibility

Die magnetischen Eigenschaften von mit Stickstoff dotierten mehrwandigen Kohlenstoffnanoröhren (N-MWCNTs) wurden sowohl bei unterschiedlichen Temperaturen als auch Feldstärken untersucht. Dabei wurden die Messwerte zu Vergleichszwecken auch von nichtdotierten Kohlenstoffnanoröhren gemessen. Es konnte ebenfalls gezeigt werden, dass auch die N-MWCNTs Eisenpartikel im Inneren der Röhren enthalten. Die bei niedrigen Temperaturen gemessenen SQUID (Superconducting Quantum Interference Device) Magnetisierungen wurden durch thermogravimetrische Messungen ergänzt. Die magnetische Charakterisierung der N-MWCNTs ergab ein Sättigungsmagnetmoment M_S von 4,5 emu/g und eine Restmagnetisierung M_R von 0,9 emu/g, während für die nichtdotierten CNTs doppelt so hohe Werte gefunden wurden. Der eingeschränkte Feldwert beträgt für beide Spezies bei niedrigen Temperaturen 800 Oe und sinkt dann auf 450 Oe bei 200 K.

Schlüsselwörter: Kohlenstoffnanoröhren / Magnetisierung / Suszeptibilität

1 Introduction

Carbon nanotubes (CNTs) exhibit unique electrical, thermal and mechanical properties which allow to employ them in a variety of applications. In particular, CNTs are chemically and thermally stable, characterized by high mechanical strength, thermal and electrical conductivity, large specific surface area. Now CNTs are regarded as the most attractive building blocks for nanoelectronics, since they are able to form an almost perfect spin-transport medium, since electron transport in them is one-dimensional and ballistic with a long spin relaxation time and weak spin-orbital effects. Also, even pure CNTs, which are non-magnetic materials, are characterized by a giant magneto-resistance [1]. On the other hand, it is quite obvious that modification of CNTs (intercalation and filling the internal cavities with different elements) can lead to significant differences in their electronic structure and physical properties. In particular, it is known that nitrogen (N) doping causes significant changes in morphology, hardness, electrical conductivity and chemical reactivity [2–4]. The N-doped CNTs are especially interesting, since they exhibit metallic properties independent of their chirality [5]. Despite the great attention devoted to the N-doped multi-walled CNTs (N-MWCNTs), the understanding of the structure-property relationship of this nanosystem is one of the most challenging problems in material science [6–7].

[1] B. Verkin Institute for Low Temperature Physics and Engineering of the NAS of Ukraine, Kharkiv, Ukraine
[2] Taras Shevchenko National University of Kyiv, Kyiv, Ukraine
[3] Ilmenau University of Technology, Ilmenau, Germany

Corresponding author: Y.I. Prylutskyy, Taras Shevchenko National University of Kyiv, Volodymyrska Str., 64, 01601 Kyiv, Ukraine
E-mail: prylut@ukr.net

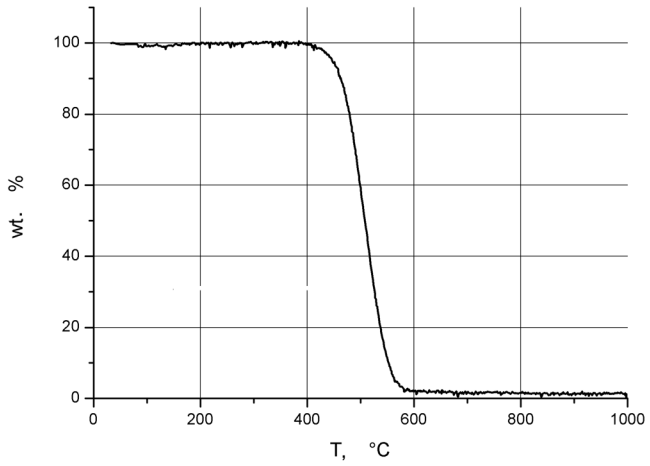

Figure 1. TG measurements of N-MWCNTs (heating rate 1 K/min in air).

Bild 1. TG-Messungen an N-MWCNTs (Heizrate 1 K/min in Luft).

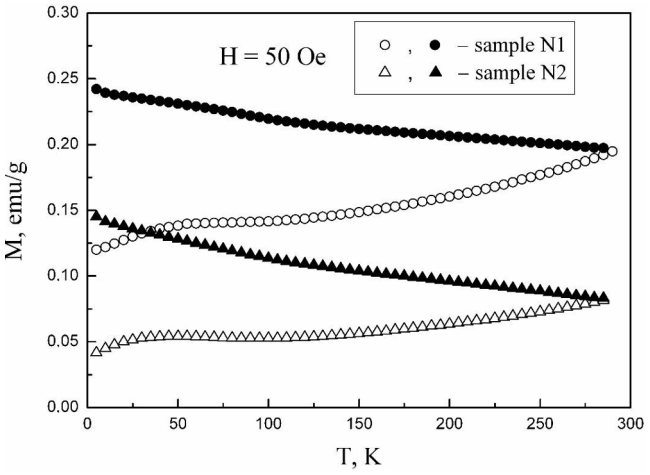

Figure 2. Temperature dependence of magnetization in H = 50 Oe for samples MWCNT (ferrocene, cyclohexane, N1) and N-MWCNT (ferrocene, acetonitril, N2). Open and full symbols correspond to ZFC and FC regimes, respectively.

Bild 2. Temperaturabhängigkeit der Magnetisierung bei H = 50 Oe für MWCNTs (Ferrocen, Cyclohexan, N1) und N-MWCNTs (Ferrocen, Acetonitril, N2). Offene und geschlossene Symbole korrespondieren mit einem ZFC und FC Regime).

In this work, the MWCNTs and bamboo-like MWCNTs doped with nitrogen (N-MWCNTs), were synthesized by the same method, catalytic vapor decomposition, and under the same experimental conditions. The magnetic properties of N-MWCNTs and MWCNTs (magnetic susceptibility and magnetization) were investigated in the temperature range (4.2–290) K and in magnetic fields up to 30 kOe.

2 Experimental

N-MWCNTs were synthesized by means of catalytic chemical vapor deposition (CVD) technique [7]. Acetonitrile was applied as a feedstock material for the synthesis process while ferrocene was used as catalyst. The inner diameter of N-MWCNT was between 30 and 40 nm, whereas the outer diameter was about 45 nm and the length was up to 15 μm. The N-doped MWCNTs show bamboo-like morphology. For comparison, another set of MWCNTs was prepared within the same procedure but without doping with nitrogen. In this case cyclohexane was employed as the carbon source for the synthesis process with ferrocene used to catalyze the growth of the aligned CNTs. In fact, both CNT materials were synthesized under the same experimental conditions, and the only difference was the reactant mixtures. As a result, rather different structures were obtained (see Ref. [7]).

The thermogravimetric (TG; Sartorius MC5) results show that the overall nitrogen amount in synthesized N-MWCNTs is about 3.5 wt%, *Fig. 1*. The decomposition of the N-MWCNT starts at temperature about 420 °C.

In the temperature range of 4.2 to 290 K, the magnetic properties of the CNT samples were measured by a SQUID (Superconducting Quantum Interference Device) magnetometer [8–9] in fields up to 30 kOe with an absolute error less than 10^{-6} emu for the measured magnetic moments. For the magnetization studies the samples were prepared by compacting the CNT powder (mass about 10 mg) inside of an elongated aluminum foil cylinder with 1.5 mm and 7 mm in diameter and height, respectively. Cylindrical shape of the samples fits the experimental setup and also reduces the effect of demagnetization factor in magnetization data obtained in the magnetic field applied for all measurements along the cylinder axis. The measurements were made after cooling the sample from room to helium temperature in a zero magnetic field (zero-field-cooling regime, ZFC). Then the temperature dependences of the magnetization $M(T)$ were measured under a slow heating with the rate of about 1.5 K/min in the applied magnetic field H = 50 Oe. The field dependencies of the magnetization were also measured in ZFC regime in magnetic fields up to 30 kOe at temperatures T = 10 and 200 K.

3 Results and discussion

The measured temperature dependences of the low-field magnetization are presented in *Fig. 2*. These data demonstrate the absence of distinct decay of magnetization with temperature, which takes place for super-paramagnetic systems. This temperature behavior of magnetization also points to a large energy of magnetic anisotropy, as well as a substantial fraction of magnetic nanoparticles. The discrepancy between ZFC and FC curves may imply a complex magnetic state at low temperatures. One can expect that the studied MWCNTs are not pure paramagnetic phases, but include ferromagnetic particles imbedded in the paramagnetic matrix, forming e. g. a spin-glass cluster state.

Due to the presence of ferromagnetic clusters, a hysteresis effect in the magnetization was observed in both N-MWCNT and MWCNT samples, which is presented in *Fig. 3* for the temperature T = 10 K. The hysteresis loops clearly show that the studied samples are ferromagnetic materials with a comparatively high value of coercive field H_C about 800 Oe for both systems. Since the value of H_C for a small particle is determined by the product

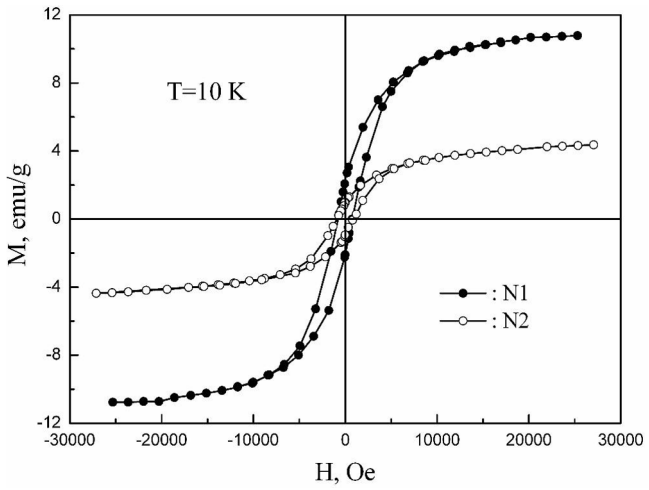

Figure 3. Magnetization curves at T = 10 K for samples MWCNTs (ferrocene, cyclohexane, N1) and N-MWCNTs (ferrocene, acetonitril, N2).

Bild 3. Magnetisierungskurven für T = 10 K für MWCNTs (Ferrocen, Cyclohexan, N1) und N-MWCNTs (Ferrocen, Acetonitril, N2).

of the particle volume and anisotropy energy, this result must be a consequence of high anisotropy energy. With increasing temperature H_C values decrease, being about 450 Oe at T = 200 K. The quantitative analysis of the experimental data for the N-MWCNT sample provides the saturation magnetic moment and residual magnetization to be, respectively, $M_S \approx 4.5$ emu/g and $M_R \approx 0.9$ emu/g. For the reference MWCNT sample the measured saturation magnetic moment and residual magnetization amount to $M_S \approx 11$ emu/g and $M_R \approx 2$ emu/g.

At the present, we can assume that for both samples the main magnetic phase might be the Fe_3C compound (cementite), undergoing a transition from ferromagnetic to paramagnetic state at the Curie temperature of approximately 480 K. This phase is characterized by the saturation moment value M_S = 163 emu/g (1.75 μ_B/Fe). Therefore, based upon the measured values of M_S, one can roughly estimate the content of Fe_3C phase as about 6.5 wt.% and 2.8 wt.% for the MWCNT and N-MWCNT samples, respectively.

4 Conclusions

MWCNTs modified with nitrogen and the reference nitrogen-free MWCNTs were investigated with respect to their magnetic properties. Magnetization studies revealed the presence of ferromagnetic particles in these systems, at least up to 300 K. At T=10 K the coercive field amounts to 800 Oe in both samples, and with increasing temperature H_C values decrease to about 450 Oe at T = 200 K. Based upon the assumption that the main magnetic phase can be Fe_3C, its quantity is estimated to be twice smaller in the N-MWCNT sample than in the reference MWCNT sample, 2.8 wt.% and 6.5 wt.%, respectively. One can assume, that the nitrogen doping, which causes significant changes in morphology of MWCNT, also reduces precipitation of magnetic particles in the course of the synthesis process.

Acknowledgements

This work was partly supported by the STCU (N 4908) and DFG grants.

5 References

[1] A. Cottet, T. Contos, S. Sahoo, H.T. Man, M.S. Choi, W. Belzig, C. Bruder, A.F. Morpurgo, C. Schonenberger, *Semicond. Sci. Techn.* **2006**, *21*, 78.

[2] L.G. Bulusheva, A.V. Okotrub, A.G. Kudashov, Y.V. Shubin, E.V. Shlyakhova, N.F. Yudanov, E.M. Pazhetnov, A.I. Boronin, D.V. Vyalikh, *Carbon* **2008**, *46*, 864.

[3] A.A. Koos, M. Dowling, K. Jurkschat, A. Crossley, N. Grobert, *Carbon* **2009**, *47*, 30.

[4] F.R. Garcia-Garcia, J. Alvarez-Rodriguez, I. Rodriguez-Ramos, A. Guerrero-Ruiz, *Carbon* **2010**, *48*, 267.

[5] S.H. Lim, H.I. Elim, X.Y. Gao, A.T.S. Wee, W. Ji, J.Y. Lee, J. Lin, *Phys. Rev. B* **2006**, *73*, 045402.

[6] A.A. Koos, F. Dillon, E.K. Obraztsova, A. Crossley, N. Grobert, *Carbon* **2010**, *48*, 3033.

[7] U. Ritter, N.G. Tsierkezos, Y.I. Prylutskyy, L.Y. Matzui, V.O. Gubanov, M.M. Bilyi, M.O. Davydenko, *J. Mater. Sci.* **2012**, *47*, 2390.

[8] V.Y. Lyakhno, A.V. Fedorchenko, O.B. Kivirenko, V.I. Shnyrkov, *Cryogenics* **2009**, *49*, 425.

[9] U. Ritter, P. Scharff, G.E. Grechnev, V.A. Desnenko, A.V. Fedorchenko, A.S. Panfilov, Y.I. Prylutskyy, Y.A. Kolesnichenko, *Carbon* **2011**, *49*, 4443.

Received in final form: November 23th 2012 T 83

