MULTI-WALL CARBON NANOTUBES INVESTIGATED BY POSITRON ANNIHILATION TECHNIQUES AND MICROSCOPIES FOR FURTHER PRODUCTION HANDLING

A. T. LUU[1*], ZS. KAJCSOS[2], N. D. THANH[1], T. Q. DUNG[1], M. V. NHON[3], K. LÁZÁR[4], K. HAVANCSÁK[5], G. HUHN[5], Z. E. HORVÁTH[6], T. D. TAP[3], L. T. SON[1], P. T. PHUC[1]

[1] Center for Nuclear Techniques -Vietnam Atomic Energy Commission, 217 Nguyen Trai, District 1, Ho Chi Minh City, Viet Nam
[2] KFKI Research Institute for Particle and Nuclear Physics H-1525 Budapest 114, P.O.B. 49, Hungary
[3] Department of Nuclear Physics, Faculty of Physics, University of Natural Sciences, 227-Nguyen Van Cu, District 5, Ho Chi Minh City, Viet Nam
[4] Inst. of Isotopes HAS, H-1525 Budapest, P.O.B. 77, Hungary
[5] Dept. of Mater. Physics, Eötvös Univ, Pázmány Péter sétány 1/A, H-1117 Budapest, Hungary
[6] Research Institute for Technical Physics and Materials Sciences, H-1525 Budapest, Hungary

* Corresponding author: e-mail: tuyenluuanh@gmail.com, Phone: +0841268129632, Fax: +084838367361

Abstract: Multi-wall carbon nanotube samples with various tube diameters produced by Thermal Chemical Vapor Deposition technique using various catalysts were studied by various microscopic methods and positron annihilation spectroscopy (PAS) with the aim of assessing the applicability of these methods for structural studies in these novel materials. Specifically, positron lifetime (LT) and Doppler broadening (DB) techniques, transmission electron microscopy (TEM) and atomic force microscopy (AFM) were employed, on iron-containing samples Mössbauer spectroscopy was also utilized. The PAS measurements were carried out on densely packed powder samples and on samples pressed into pills in atmospheric pressure and in vacuum as well. The lifetime values could be interpreted by assuming trapping of positrons, the low contribution from longer-living trapped positronium can be probably related to defects on walls of the tubes. Possibility of correlation of LT and DB data with the nanotube sizes and sample composition was also considered.

Keywords: *Positron, Multi-wall carbon nanotubes, positron lifetime, Doppler broadening.*

1. INTRODUCTION

Multi-wall carbon nanotubes, representing a class of promising technological material with a wide variety of possible applications in many fields, have been intensively studied by many different techniques since their discovery [1-6]. In this study, we aimed at evaluating the applicability of the conventional positron lifetime (LT) and Doppler broadening (DB) techniques

of positron annihilation spectroscopy (PAS) for structural studies on multi-wall carbon nanotubes (MWNTs) with various tube diameters produced by Thermal Chemical Vapor Deposition (CVD) technique using various catalysts. It was hoped that combined by transmission electron microscopy (TEM), atomic force microscopy (AFM) and Mössbauer spectroscopy (MS), PAS could give additional information on the diameter of tubes, defects and also the presence of possible catalyst.

2. EXPERIMENT

Powder-MWNTs with different quality and diameter, produced by CVD technique using various catalysts for synthesis were employed as samples, marked for reference as CNT-1(on Ni foils), CNT-2, CNT-3 (on Fe foils) and CNT-4, CNT-5, CNT-6 (on Fe foils, adding $Fe(NO_3)_3$ 3%, 3.5%, 5%, respectively). The growth of these MWNTs was carried out for 24 min by adding C_2H_2 to the reaction gas mixture (Ar and H_2) at 600 ^{0}C [4]. For the LT and DB measurements, the powder samples were packed densely and pressed by cca. 4 GPa into pellets of 13 mm diameter and cca. 1.5 mm thickness. The ^{22}Na source (cca. 20 MBq activity, kept between thin Al foils) was inserted between two pellets and this arrangement was packed into a sandwich covered with thin Al foil. The experiments were carried out in vacuum and at ambient atmospheric pressure, respectively, to compare the influence of air (oxygen) on the annihilation pattern. The LT measurements were carried out with a fast-fast coincidence setup with 240 ps FWHM time resolution [6], the DB studies were performed with a CANBERRA HPGe detector with 1.2 keV resolution at the annihilation peak [7]. The spectra were recorded in a Microfast 16k PC MCA with integral counts of 3.10^6 for LT and 10^6 for DB. Data evaluations of LT were carried out using the LT v. 9 program [8] applying a correction of 10% accounting for annihilation in the source and in the aluminium foils. For the calculation of S and W parameters from the DB spectra, the SP v.1.0 [9] computer code was applied. For MS, the spectra were collected at 77 K in transmission mode with constant acceleration regime on a pellet of CNT-2 sample (Fig. 1). TEM measurements were performed on a Philips CM20 TWIN microscope, operating at 200 kV voltages. AFM images using an NT-MDT (Russian made) Solver type scanning probe microscope were taken in order to get an impression on the surface morphology and size of the MWNTs. The surface scanning was performed in a semi-contact (similar to tapping) mode to avoid altering the sample. Cantilevers with a typical force constant of 5.5 N/m, curvature radius of 10 nm and resonant frequency of 130 kHz were used.

3. RESULTS AND DISCUSSION

The slight differences in both LT and DB measurements, respectively, found for all samples are shown in Fig. 2 (a) and (b). No difference was found between the spectra recorded in atmospheric pressure or in vacuum, i.e., the annihilation pattern was not modified by the presence of oxygen. The S and W parameters [10] are presented as the S-W plot [11] in Fig. 2 (c). A clear separation of the samples with different compositions is evident, the two groups of composites of materials reflect the two ways using the catalyst for the production of the VCD technique. In the first group, CNT-, CNT-2 and CNT-3, an increasing content of catalyst (2.% of Ni, 3.2% and 5% of Fe) determined by TEM leads to a decreasing S-W parameter correlation. Associating CNT-1 to this group might be justified by the not too different electron structure of Ni and Fe. For the second group, the increasing content $Fe(NO)_3$ 3%, 3.5% and 5% also results in a decrease of the S-W parameter correlation.

The LT spectra were decomposed into three components, data are shown in Table 1. The short lifetime component τ_1 ($0.216 \div 0.238 \pm 0.005$ ns) could originate from positron annihilation in the bulk (eventually amorphous) graphite structure, with intensity I_1 ranging from 38 to 66%. The

results of TEM and AFM also showed a different and significant contribution of graphite and amorphous phases in all samples. These results may reflect differences of samples which content of MWNTs is changed due to the presence of the above other phases, however, annihilation of positrons trapped inside vacancies could also give different contribution to different LT spectra and should be also considered. Size and length of different MWNT samples, measured by TEM and AFM, differs significantly in the samples (Fig. 3). Earlier PAS studies [3] showed that slowed down positrons could probably not diffuse too deep inside the innermost walls of tube, where there is a dense electron distribution, but annihilation on the surface of the tube (interstitial region) and outer walls may occur [5, 11]. The characteristic lifetime values τ_2 (0.379÷0.429 ± 0.003 ns) are quite close to the results reported in [3]. The size distribution of MWNTs ranges from about 40 nm to appr. 100 nm as also shown by TEM and AFM results on the samples. A correlation between the MWNT diameters measured by TEM and AFM and the characteristic lifetimes τ_2 calculated from LT data could be expected assuming that the larger the diameter of the tube, the larger the chance for the positron to get attached to the surface so the longer the resulting lifetime will become (Table 1). On the other hand, the surface morphology of the MWNTs in different samples is quite different. A relatively smooth surface of MWNTs was found for CNT-1 while rougher surface is seen for CNT-4 by AFM images (Fig. 3 (d) and (e)). This surface quality may probably also effect annihilation characteristics. However, this question could be addressed only by future slow positron beam studies. The I_2 values range from 33% to 61%, but as $I_1+I_2 \approx 98\%$ for all samples, it can be concluded that they are all consisting of two dominant phases, i.e., graphite (eventually amorphous) and MWNTs.

Earlier structural studies indicated that impurities originating from the catalyst used during the sample preparation can be built into the wall changing the properties of the tubes [12-15]. Our results of MS measurements showed the presence of Fe^{3+} and a component formed probably from the oxidation of the high dispersion metallic iron particles (Fig. 1). However, stabilized high dispersion zerovalent irons, probably located inside the nanotubes and for that very reason protected against oxidation, were found. Furthermore, the sample probably contains some dissolved carbon in the metallic phase, as the appearance of the weak quadrupole splitting indicates. This interpretation is in full accordance with the TEM images shown in Fig. 3 (a), (b) and (c) where dark dots appear in the tubes indicating probably traces of iron catalyst in high dispersion. Similar features were detected and reported on other MWNTs prepared by C_2H_2/CVD method [14]. The AFM images just give an impression on the complexity of the samples.

Table 1 The LT data and MWNTs diameter of some samples.

Sample name	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	I_1 (%)	I_2 (%)	I_3 (%)	Diameter (nm)
CNT-1	0.216	0.385	2.619	38.100	61.001	0.896	60÷90
CNT-2	0.203	0.379	2.543	34.500	64.510	1.078	40÷80
CNT-3	0.218	0.381	2.808	40.900	58.202	0.968	50÷90
CNT-4	0.196	0.386	2.594	66.501	31.800	1.682	
CNT-5	0.229	0.424	3.322	60.904	37.501	1.565	80÷100
CNT-6	0.238	0.429	3.607	66.080	32.621	1.300	
Coal	0.290	0.818	3.682	90.890	7.110	1.998	

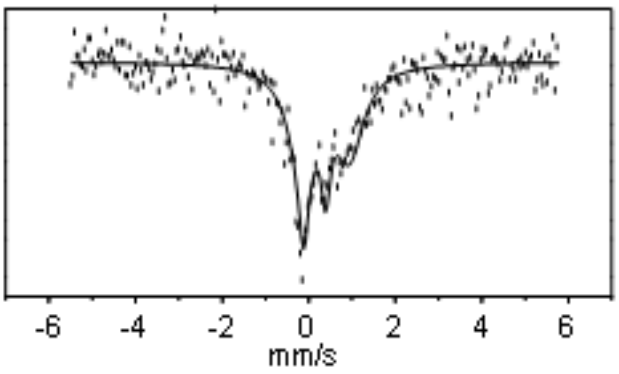
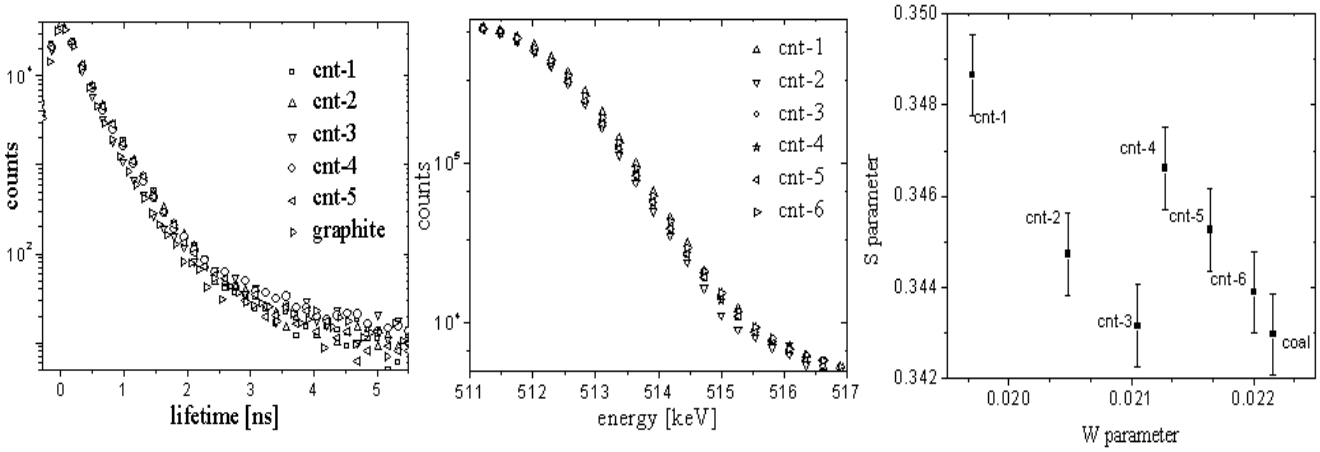


Figure 1 Mössbauer spectrum of CNT-2 sample.



a) The positron lifetime spectra of different samples.

b) The Doppler broadening spectra of different samples.

c) Correlation plot of S and W parameters of different samples.

Figure 2 The positron lifetime spectra, the Doppler broadening spectra and correlation plot of S and W parameters of different samples.

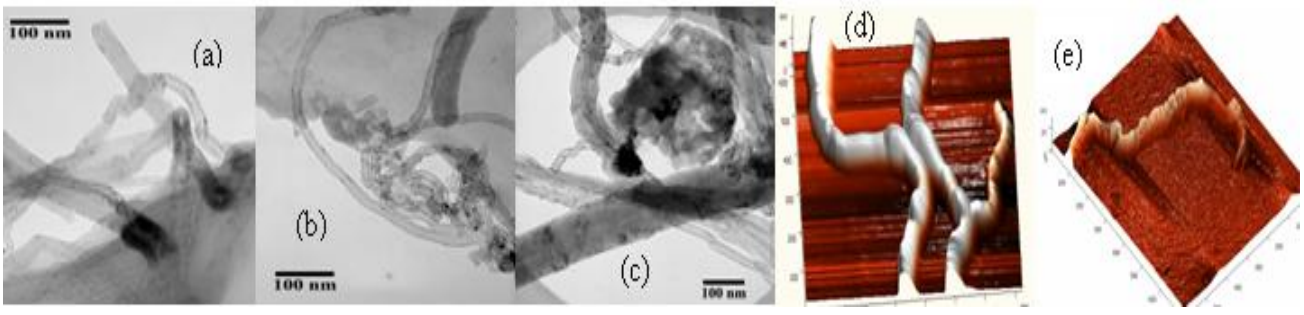


Figure 3 TEM images: (a), (b), (c) for CNT-1, CNT-2, CNT-3 and AFM images: (d), (e) for CNT-1, CNT-4, respectively.

Furthermore, defects can be formed at these composite sites which contribute to the dominant defects due to bond breaking (small voids) in the individual shells of the nanotubes [15]. The longer lifetime component τ_3 (2 - 3 ns) found in the LT spectra hints at the slight chance that

ortho-Positronium (o-Ps) might be also formed in the samples, probably trapped in those above-mentioned defects present with a comparatively low fraction of $I_3 \approx 2\%$.

4. CONCLUSIONS

A better understanding on the complex structure of MWNTs produced by CVD technique could be acquired from the combination of PAS with microscopies. Structure and features of MWNTs including C-bonding phases, size, length, defects and composites were expected to show up in LT data but further studies are still needed which could hopefully result in an improvement of the MWNT production techniques as well. The S-W plots show a small effect only but still reveal the specific sensitivity of the DB measurements for structural studies on MWNTs. Slow positron studies could seem highly desirable in the future on such samples.

ACKNOWLEDGEMENT

A.T.Luu and N.D.Thanh gratefully acknowledge the support from IAEA (VIE/07044 training fellowship and VIE/08 study trip, respectively). Partial support from OTKA K68414 is highly appreciated. The authors also express their sincere thanks to Dr. Nguyen Quoc Khanh (Research Institute for Technical Physics and Materials Sciences, Budapest, Hungary) and many colleagues at KFKI Research Institute for Particle and Nuclear Physics, Budapest, Hungary for discussions and help.

REFERENCES

[1] J. Gerard Lavin, S. Subramoney, R. S. Ruoff, S. Berber, D. Tomanek, Carbon 40 1123–1130 (2002).
[2] V. Klimov and V. S.Letokhov, Physica Scripta. Volume 56, 480-486 (1997).
[3] S. Ishibashi, J. Phys.: Condensed Matter 14 9753–9762 (2002).
[4] Pham Tan Thi, Gang Hee Han, Il Ha Lee, Lam Binh Thanh, Dang Mau Chien, Proceedings of IWNA 2007, Vung Tau, Vie Nam, (2007).
[5] T. Ohdaira, R. Suzuki, Y. Kobayashi, T. Akahane, L. Dai, Applied Surface Science V.194, 291–295 (2002).
[6] Zs. Kajcsos, C. Kosanovic, S. Bosnar, B. Subotic, P. Major, L. Liszkay, D. Bosnar, K. Lázár, H. Havancsák, A. T. Luu, N. D. Thanh, Materials Science Forum, Vol. 607, pp 173-176 (2009).
[7] Zs. Kajcsos L. Liszkay, G. Duplâtre, K. Lázár, L. Lohonyai, L. Varga, P.M. Gordo, A.P. de Lima, C. Lopes de Gil, M.F. Ferreira Marques, D. Bosnar, S. Bosnar, C. Kosanovic and B. Subotic, Rad. Phys. Chem. Vol. 76, Issue 2, 231-236 (2007).
[8] J. Kansy, Nucl. Instr. Meth. A 374, 235-244 (1996).
[9] J. Dryzek, The SP program Version 1.0, Institute of Physics in Krakow, Poland, (2007).
[10] Y. Ito and T. Suzuki, Phys. Rev. B, Vol. 60, No. 23 (1999).
[11] K.W. Chou, K. J. De Baerdemaeker, V. Peral, D. Ruiz, Y. Houbaert, D. Segers. Acta Phys. Polonica A, Vol. 107 (2005).
[12] Young-Kyun Kwon and D. Tomanek, Phys. Rev. B, Volume 58, Number 24, (1998).
[13] S. Krompiewski, R. Gutie´Rrez and G. Cuniberti, Phys. Rev. B 69, 155423 (2004).
[14] Z. Kónya, I. Vesselényi, K. Lázár, J. Kiss and I. Kiricsi , IEEE Trans. on Nanotechnology, 73-79 (2004).
[15] S. Agrawal, M. S. Raghuveer, H. Li and G. Ramanath, Appl. Phys. Lett. 90, 193104 (2007).