Acta Agrophysica, 2002, 80, 25-37

CARBON ARC PLASMA: PARAMETRIC AND SPECTRAL STUDIES

M. Sioda, P. Baranowski, H. Lange

Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland
masioda@chem.uw.edu.pl

A b s t r a c t. Unique electrical, magnetic, nonlinear optical and mechanical properties make carbon nanostructures fascinating and attractive. The application of these structures demands the investigation and optimizing of their formation processes.

K e y w o r d s: carbon arc plasma, plasma spectroscopy, carbon nanostructures.

In the presented work we examined the influence of the carbon arc operational parameters such as: pressure, electrode composition, geometry, and erosion rate on the properties and characteristics of the obtained carbon sooth (fullerene and carbon nanostructure content). We also examined an arc discharge in water, which as recent studies have shown is a source of interesting carbon structures, for example the so-called carbon onions.

The solid products were characterized using SEM and TEM techniques and UV-VIS absorption spectroscopy. Diagnostic analyses were also performed on carbon arc plasma using optical emission spectroscopy. The concentration of C_2 radicals and the plasma temperature was determined.

INTRODUCTION

Pure carbon can exist in four different crystalline forms: diamond, graphite, fullerenes, and nanotubes.[1].While graphite and diamond have long been known, fullerenes [2] and carbon nanotubes (CNTs) [3] were discovered only recently, in 1985 and 1991, respectively. Since then, many techniques have been developed to produce these fascinating nanocarbons [4], which form efficiently during carbon gas coalescence. C_{60} was first discovered in vapor resulting from laser ablation of graphite [2]. However, since Krätschmer et al. developed a commercial method in 1990 [5], carbon vapors have been generated in an arc discharge between graphite electrodes. CNTs were first identified by Iijima [3], who was looking for the round football-shaped C_{60} molecules in a cathode arc deposit. Later [6], efficient methods of producing both multiwalled (MW) and single-walled (SW) CNTs, also based on

carbon arc technique, were developed. However, one should mention here that long before Iijima's discovery, carbon nanotubes were reported [7] to be a product of the catalytic thermal decomposition of CO. Also, Endo [8] in his study (which, in fact, is frequently neglected) presented, in 1988, SEM images of MWCNTs formed during the catalytic pyrolysis of hydrocarbons.

Thermal carbon plasma has been widely used to produce fullerenes and nanotubes in bulk, and the application of pulsed-mode arc operation [9] proved recently to distinctly improve the process performance.

One of the greatest open questions in the field of nanocarbons is how such intriguing structures form so efficiently from carbon species, which must be understood to enable scaling-up and optimization of the synthesis process. Process optimization has been based entirely on the relationship between operation parameters and the process output.

Additionally spectroscopic diagnostics can reveal details of the formation mechanism. Optical emission spectroscopy (OES) offers a simple, in situ diagnostics of plasma species.

OPTICAL EMISSION SPECTROSCOPY OF CARBON PLASMA

Despite of the high complexity of a soot material formed during ablation of graphite electrode in the electric arc, comprising various fullerenes and carbon microstructures, the presence of only several species may be registered directly with the use of OES. These include: carbon atoms (CI: 247.8 nm, ...), ions (CII: 392, 657.8 nm,..) and diatomic carbon radicals (C_2: $d^3\Pi_g \rightarrow a^3\Pi_u$, $C^1\Pi_g \rightarrow A^1\Pi_u$,...). There are also excited atoms of buffer gas He (e.g. 388.8 nm), however, under conditions of high carbon vapor pressure Helium lines intensity dramatically drops down. Generally it is consistent with thermodynamic considerations of equilibrium composition of carbon vapor. From thermodynamics it follows that the major components of plasma at temperatures exceeding 4500 K, i.e., such as inside the arc are carbon atoms and diatomic molecules. In temperatures between 4000 and 3000 K, i.e, at the edge of the plasma zone, C_3 molecules should prevail. However, despite the fact that C_3 is easily detectable in a graphite furnace, [10] so far it was impossible to explicitly identify the characteristic spectrum $A\ ^1\Pi_u \rightarrow X\ ^1\Sigma_g^+$ (405 nm) of these molecules. The thermodynamic calculations show also that in temperatures below 3000 K, i.e., in areas distant from the discharge zone, the prevailing structures should be in form of polyatomic C_4, C_5,... molecules, including fullerene clusters. Thus, estimation of the carbon vapor pressure in the arc should be related with the determination of temperature and partial pressure of at least one of the listed components.

The C_2 radicals in the arc emit wide spectrum of high intensity (Swan bands), which is linked with the ground triplet level, a $^3\Pi_u$. Just due to transition to the ground electronic states, the OES can provide also, under some conditions, direct information on ground state species concentration. It is possible when carbon plasma is sufficiently dense. Thus, in such a case fullerenes and CNTs are formed. Then, the self-absorption phenomenon takes place affecting the measured along the observation path emission intensity distribution in the rotational structure of the bands. As a result of self-absorption the intensity of P(0-0) band head drops with the increase of the volume density values more profoundly than the intensity of resolved rotational lines.

A simple and unconventional method based on this effect was elaborated by Lange et.al [11-12] and used for the determination of C_2 content in the carbon arc plasmas [13-18]. The method consisted in registration of the (0,0) vibrational band. A given experimental spectrum, normalized to the P(0-0) band head, is fitted to the computed spectra for various volume C_2 densities and temperatures. It has been shown that such a direct fitting can provide instantaneously values of temperature and volume density of C_2. Volume density is defined as the product of radical concentration (N) and a column length (L) along a line of sight. Thus, a column density divided by the path of self-absorption (L) represents an average radical density along the line of sight.

As mentioned above there are few papers dealing with OES with the use of self-absorption therefore here we refer to our works only, which were systematically carried out using an automatic system and digitally controlling the arc gap, pressure and power supply, described elsewhere.

EXPERIMENTAL SETUP

Pure graphite

Here the attention is focused on the influence of Helium pressure on the C_2 content in the arc zone. Under each pressure, the arc current discharge was adjusted to obtain approximately the same sublimation rate of the graphite anode: 4.0 ± 0.2 mg s^{-1}. Therefore, in the pressure range from 0.3 to 90 kPa the discharge current was changed from 60 to about 105 A, and the anode-cathode voltage drop increased from 16 to 32 V. The results regarding the plasma temperature shown in Fig. 1 indicate that within the arc zone ($\pm$ 3 mm) the temperatures are between 3500 and 5500 K (without a clear functional dependence on pressure). With the Helium pressure increase, however, a distinct increase of C_2 density in the arc takes place as is also shown in Fig. 1. Obviously, under higher pressure, the diffusion of the carbon species out of the arc zone is hampered by Helium, which causes the increase of local C_2 densities.

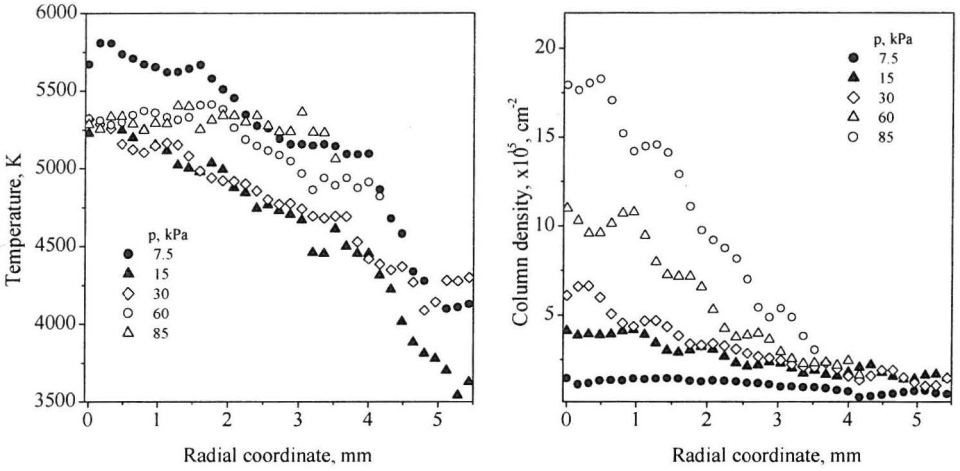

Fig. 1. Radial distributions of temperature and C_2 ($a\ ^3\Pi_u$, v''=0) column density under different Helium pressure at constant anode erosion rate equal to 3.6 ± 0.2 mg s^{-1}.

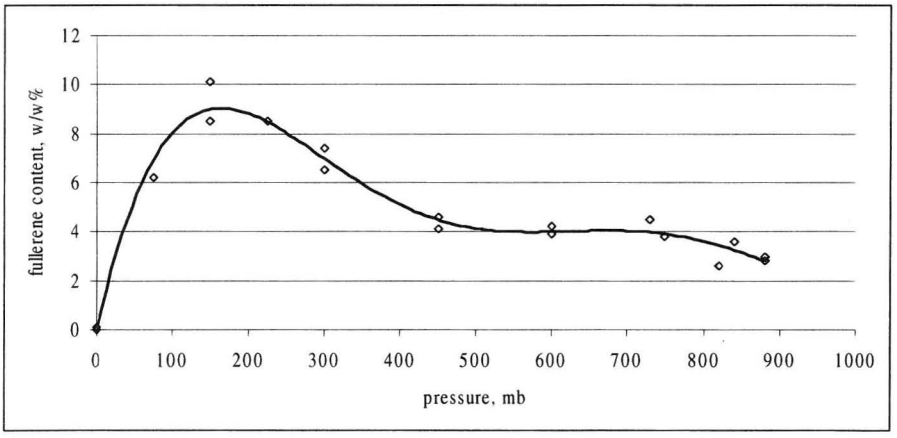

Fig. 2. Fullerene content as a function Helium pressure.

This experimental series showed that the optimal pressure for fullerene production is 133 mb, as seen on Fig. 2. Therefore we decided to perform another experimental at 133 mb with different arc currents. The aim of this series was to find an optimal erosion rate for the formation of carbon fullerenes. In this set C_2 densities are correlated with erosion rates.

Figure 3 presented below shows the fullerenes content as a function of anode erosion rate, which is a derivative of the arc current.

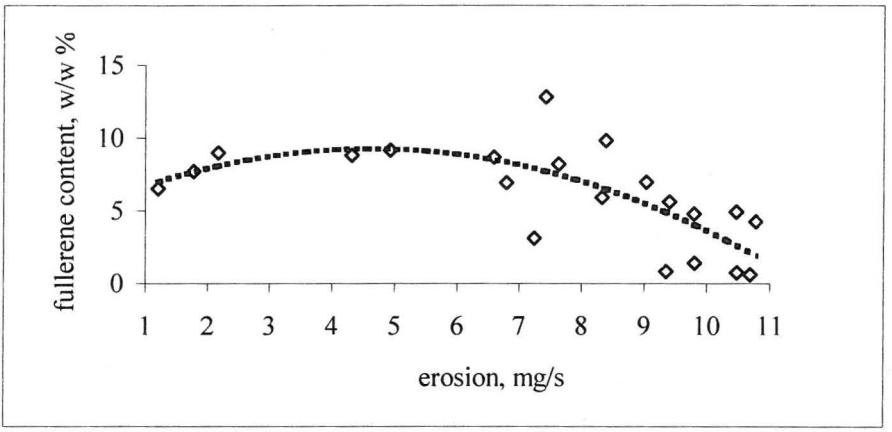

Fig. 3. Fullerene content as a function of anode erosion.

As can be seen for a given type of electrode there is optimal erosion at which the largest amount of fullerenes is formed. This can be explained by the following reasoning. At low currents the erosion is very small and the C_2 density is not high enough to form C_{60} molecules. C_2 density rises together with the erosion rate giving favorable conditions for the formation of fullerenes. At high currents the C_{60} yield drops because as we believe large graphite clusters, instead of individual atoms, erode from the anode. These large particles can not form the desired carbon nano-structures.

Figure 4 presents how the anode erodes and cathode deposit grows in time. The pressure changes in time are presented on the right hand axes. The automatic experimental set up allows a constant erosion rate as seen on figure. Also the pressure is restricted to a given value 133 mb and changes within a small degree. Therefore the parameters are optimized and kept constant.

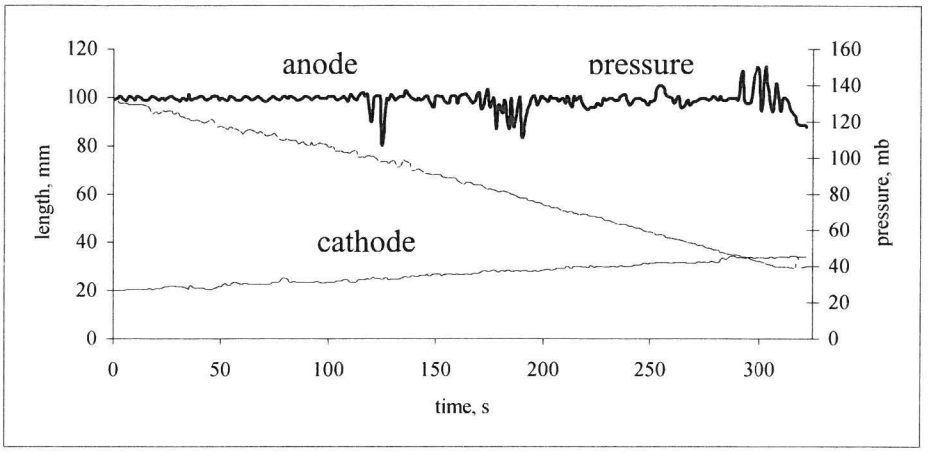

Fig. 4. Electrode lengths and pressure changes during discharge.

Catalyst-doped graphite

Examples of C_2 radial distributions in the arc when anodes doped with metal catalysts like Gd, Fe or Co/Ni (each of 0.8 %at) were used are shown in Fig. 5. The listed catalysts are routinely used in the arc plasma synthesis of SWCNTs.

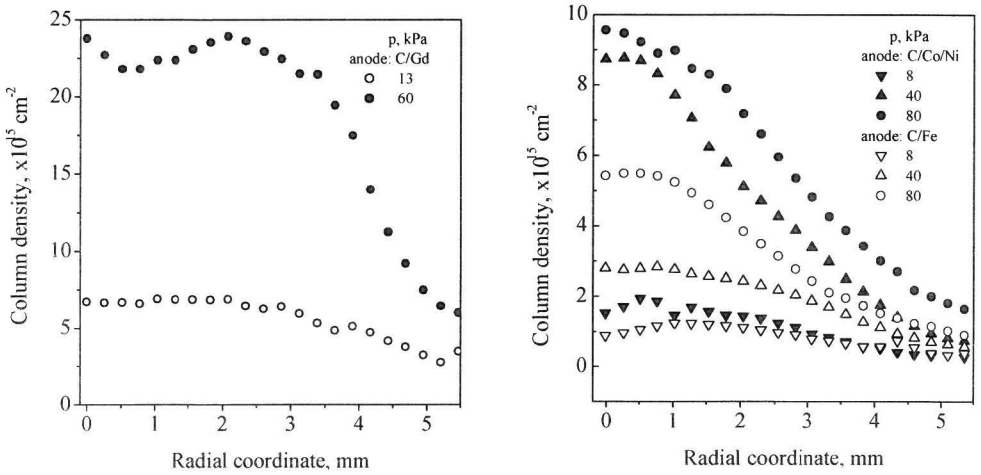

Fig. 5. Radial distributions of temperature and $C_2(a\ ^3\Pi_u, v''=0)$ column density under different He pressure and anode composition. Anode erosion rates: (a) 11 – 15 mg s^{-1}; (b) 4 mg s^{-1}.

As in the case of pure graphite anode (Fig. 1), C_2 densities are correlated with pressure. However, the nature of the catalyst specifically influences the C_2 content

and distribution profiles. It must be admitted, however, that because of the small arc gap, the accuracy of the positioning of the target plasma cross section onto the entrance slit was within ± 0.2 mm. Thus, even small displacement can yield results from a different arc cross section than was intended.

However, from many carried out experiments the trend like above was observed. The temperature values, not presented here, were similar to those in Fig. 1.

During the dc arc discharge multiwalled carbon nanotubes (MWCNTs) are formed efficiently on the anode surface, when the He pressure is great enough (> 40 kPa) Co-evaporation of carbon and catalyst (mostly metals) in the arc also results in the formation of CNTs, including single-walled, but they are mostly found as a component of the soot. Also a web-like material is often found on the discharge chamber wall [19].

The presence of the catalyst though greatly diminishes the fullerene content on the collected soot. In the case the average content was about 7 w/w %, while in the case of doped electrodes the content was less then 1 percent.

In 1978 Wiles and Abrahamson [20] described the formation of carbon fiber layers on the surfaces of graphite or carbon anodes, as a result of a low current, ca. 10 A, arc operated under nitrogen. Recently we discovered similar phenomenon while arcing the doped by Ce, Y and Gd graphite electrodes. On the anode face and side surface we noticed formation of novel elongated nano- and microstructures under 'fullerene' and 'nanotube' conditions, i.e. under lower and higher pressures, respectively. The anode picture and SEM images of the "hair-like" deposits in the case of (C + 0.8 %at Y) are shown in Fig. 6.

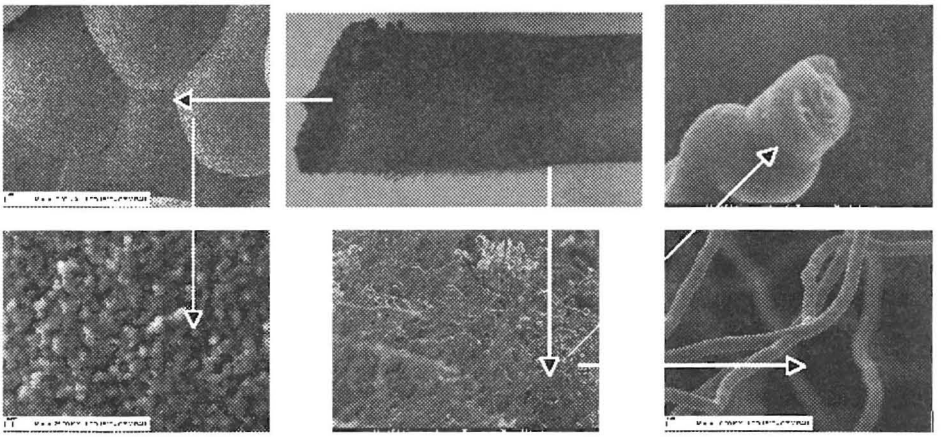

Fig. 6. Nano- and microstructures deposited on the anode during arcing of doped by Yttrium graphite elctrode. p = 13 kPa.

Empty and filled nanotubules and nanocrystallites were confirmed by HRTEM observations. The study is under way to relate the temperature of deposit growth with its morphology.

The unusual fibers growth on the side anode surface stimulated the OES observation of this zone. The results related to the use of Ce-doped graphite, are shown in Fig. 7. Similar longitudinal distributions of C_2 were observed when under the presence of Gd or Y. It is worth noticing that C_2 distribution along the anode is irregular with a maximum shifted off the anode tip. However, the most surprising is a fact that quite far from the anode tip, about 6 or 7 mm, the column density of C_2 is still very high and is similar to that close to that arc gap.

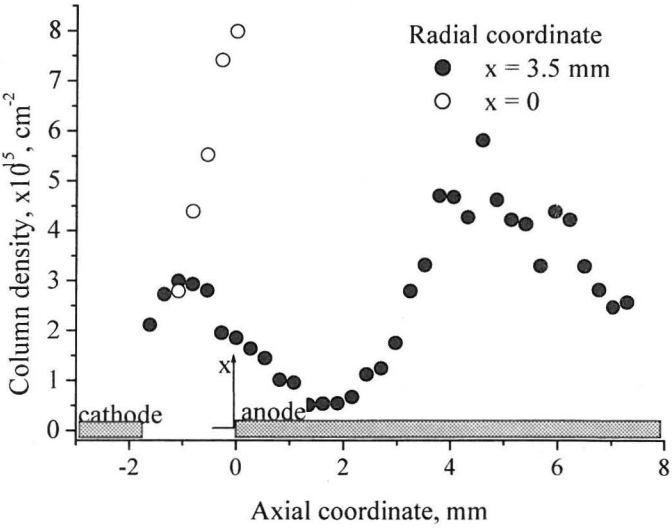

Fig. 7. Distribution of C_2 close to the anode surface (solid markers) and inside the arc gap (open markers). Anode composition C+ 0.8at% Y, pressure 13 kPa.

Carbon arc in liquid

Various electric discharges in liquid media were tried in order to produce nanocarbons. Rosseter Holding Ltd. (Limassol, Cyprus) developed and patented a commercial-scale technology to produce CNTs based on the decomposition of hydrocarbons driven by a low-voltage contact auto-regulated arc discharge in aromatic based hydrocarbon liquids. CNTs [21] were also obtained during the electrolysis of molten salts. In an intriguing study Sundaresan and Bockris [22]

presented the results of arcing between carbon rods in water. However, they did not focus on the possibility of carbon nanostructure formation but on cold fusion.

Recently, Sano *et al.* [23] reported the formation of carbon nano-onions during arc discharge between carbon electrodes immersed in water. These nanoparticles of 25-30 nm in diameter on average are composed of C_{60} cores surrounded by onion-like graphenes and were found mostly floating on the water surface. High-yield, easy and low cost fabrication of such carbon nanostructures seems to be a great boost not only for current basic research but also for future application, e.g., in lubrication technology. Therefore it was of interest to undertake more detailed studies on carbon arc discharge in water. Firstly we focused our attention on the discharge itself determining the temperature and C_2 radical content by the OES method as described above. Secondly we were looking also for other types of carbon nanostructures, e.g., CNTs. So far, it has never been done. The carbon arc discharge in water of 30 – 40 A in current intensity under atmospheric pressure was investigated.

First of all one has to note that the OES revealed nearly similar emission as in the case of arc discharge in Helium, i.e. the strongest emission remains to be C_2 radical bands and carbon atomic lines. A new feature was the presence of hydrogen lines, e.g., H_α and a broad continuum. The characteristic OH and CH bands were not spotted.

Figure 8 shows the results of OES studies, axial distributions of plasma temperature and C_2 radicals content (in column density units). It is noteworthy that the plasma temperature (*ca.* 4000-6500 K) in water is slightly higher than that in He. Despite much lower arc current there are also similar values of C_2 column densities.

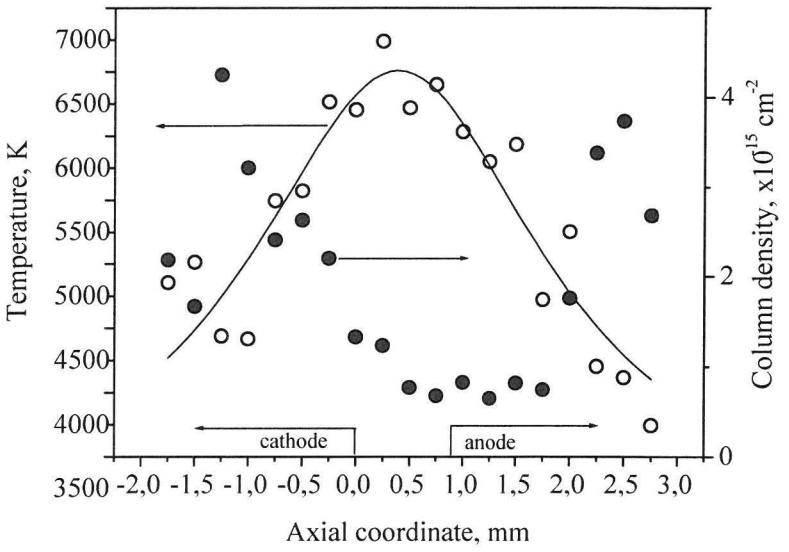

Fig. 8. Axial distribution of temperature and $C_2(a\ ^3\Pi_u, v = 0)$ in arc discharge generated in water. I = 40 A.

It results from the fact that the arc plasma is confined in much smaller volume, within a bubble surrounded by water. Hence, there is much higher energy density.

The SEM and HRTEM images of floating soot are shown in Fig. 9, which also presents a photographic image of the film formed during arcing (d). It is interesting to note that besides "nano-onions" (c) we detect quite lot of CNTs (a, b). It seems even that the bulk quantity of CNTs is at least of that of carbon balls.

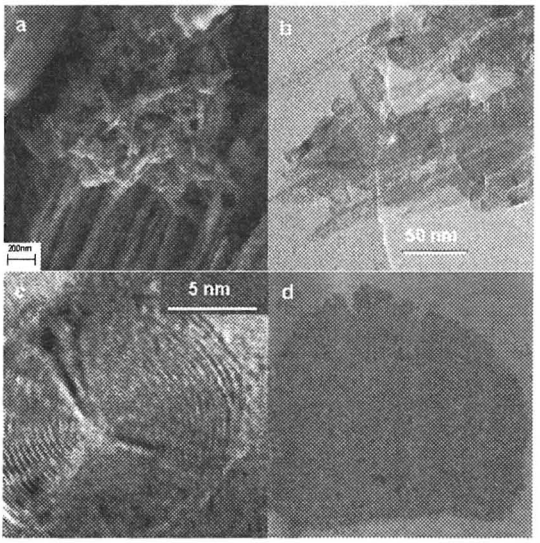

Fig. 9. SEM (a) and HRTEM (b,c) images of product of arc discharge in water floating on the surface.

The most striking is the fact that CNTs are formed at much lower than usual arc discharge current (only at 40 A or even less).

The carbon collected from the bottom of the tank revealed broken graphite layers.

Fullerenes (C_{60}) were not detected in the soot for all the samples, although C_2 radicals, according to our measurements, were formed in large amounts. We believe that the presence of hydrogen and oxygen, which was verified by spectroscopically, and also water vapour significantly, hindered the formation of C_{60}. This conclusion is supported by Vries *et al.*'s study that hydrogen hampers the formation of fullerenes [24].

The presented results indicate that the water arc technology is in a way a simplification of the traditional arc in Helium. First of all the system does not require any special preparation – like vacuuming. The reaction chamber can be open and the Helium atmosphere is not needed. Furthermore the system operates cleanly and the collection of dusty soot from the whole reaction chamber is avoided.

ACKNOWLEDGEMENT

The work was supported by the Committee for Scientific Research (KBN) through the Department of Chemistry, Warsaw University, under Grant No. 7 T09A 020 20 and BW-1562/12/2002.

REFERENCES

1. **Chen P., Lin J., Tan K. L.**: IUBMB Life 49, 105, 2000.
2. **Kroto H. W., Heath J. R., O'Brien S. C., Curl R. F., Smalley R. E.**: Nature 318, 162. 1985.
3. **Iijima S.**: Nature 354, 56, 1991.
4. *Science of Fullerenes and Carbon Nanotubes*, Eds. M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, Academic Press, New York, 1996.
5. **Krätschmer W., Lamb L. D., Fostiropoulos K., Huffman D. R.**: Nature 347, 354, 1990.
6. **Ajayan P. M., Iijima S.**: Nature 358, 23, 1992.
7. **Hofer L. J. E., Sterling E. McCartney J. T.**: J. Phys. Chem. 59, 1153, 1955.
8. **Endo M.**: CHEMTECH nr 9, 568, 1988.
9. **Sugai T., Omote H., Bandow S., Tanaka N., Shinohara H.**: J. Chem. Phys. 112, 6000, 2000.
10. **Afanas'ev D. V., Blinov I. O., Bogdanov A. A., Dyuzhev G. A., Karataev V. I, Kruglikov A. A.:** Mol. Mat. 5, 105, 1994.
11. **Lange H., Huczko A., Byszewski P.:** Spectroscopy Letters 29, 1215, 1996.
12. **Lange H., Saidane K., Razafinimanana M., Gleizes A.**: J. Phys. D: Appl. Phys. 32, 1024, 1999.
13. **Byszewski P., Lange H., Huczko A., Behnke J. F.**: J. Phys. Chem Solids 58, 1679, 1997.
14. **Huczko A., Lange H., Byszewski P., Popławska M., Starski A.**: J. Phys. Chem. A 101, 1267, 1997.
15. **Lange H.**: Full. Sci. Technol. 5, 1177, 1997.
16. **Saidane K., Lange H., Razafinimanana M., Huczko A.**: J. High Temp. Mat. Process. 5, 2, 2001.
17. **Lange H., Huczko A.**: Chem. Phys. Lett. 340, 1, 2001.
18. **Lange H., Huczko A., Byszewski P., Mizera E., Shinohara H.**: Chem. Phys. Lett. 289, 174, 1998.
19. **Takizawa M., Bandow S., Torii T., Iijima S.**, Chem. Phys. Lett. 302, 148, 1999.
20. **Wiles P.G., Abrahamson J.**, Carbon 16, 341, 1978.
21. **Hsu W.K., Hare J.P., Terrones M., Kroto H.W., Walton D.R.M., Harris P.J.F.**, Nature, 377, 687-689, 1995.
22. **Sundaresan R., O'M. Bockris J.**, Fusion Technology Vol 26, 261-265, 1994.
23. **Sano N., Wang H., Chhowalla M., Alexandrou I., Amaratunga G.A. J.**, Nature, Vol 414, 506-507, 2001.
24. **de Vries M.S., Wendt H.R., Hunziker H., Peterson E., Chang S.**, Proceedings of the XXII Lunar and Planetray Sciences Conference,315, 1991.

ŁUKOWA PLAZMA WĘGLOWA: BADANIA PARAMETRYCZNE I SPEKTRALNE

M. Sioda, P. Baranowski, H. Lange

Wydział Chemii, Uniwersytet Warszawski, Pasteura 1, 02-093 Warszawa, Polska
masioda@chem.uw.edu.pl

S t r e s z c z e n i e. Unikalne elektryczne, magnetyczne, z zakresu optyki nieliniowej i mechaniczne własności czynią nanostruktury węgla obiektem coraz większych zainteresowań. Zastosowanie tych struktur wymaga badań i optymalizacji procesów otrzymywania.

S ł o w a k l u c z o w e: plazma łuku węglowego, spektroskopia plazmy, nanostruktury węgla.