acta physica slovaca vol. 55 No. 4, 405 – 409 **August 2005**

ROLE OF DIAMOND ON CARBON NANOSTRUCTURE FORMATION IN THE ARC DISCHARGE

M. Sioda[1,a], **H. Lange**[a], **E. S. Ming**[b]
[a] *Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*
[b] *Department of Physics, National University of Singapore, Singapore*

Received 3 April 2003, in final form 4 March 2004, accepted 10 March 2005

The influence of diamond on carbon nanostructure formation in the arc discharge was investigated. The use of the electrodes made of graphite mixed with diamond micro-crystals and small admixture of catalysts (Ni, Co and Y) enhances the production of single-walled carbon nanotubes. The nanotubes form a web-like product. The presence of diamond drastically decreases the anode erosion rate, and thereby the C_2 radical content in the arc plasma zone, while the average plasma temperature remains unchanged.

PACS: 52.80.Mg

1 Introduction

Many elements like Fe, Co or Ni are well known to significantly influence the process of fullerenes and carbon nanotubes (CNTs) formation [1]. Multi-walled and single-walled carbon nanotubes (MWCNTs and SWCNTs, respectively), mostly found in the collected soot, can then be produced. In the case of pure graphite arc sublimation, only the MWCNTs are formed and they are found exclusively in the cathode deposit core [2]. In the present study, the influence of diamond on anode erosion rate, arc plasma parameters and formation of the carbon nanostructures was investigated. One should mention that fine diamond powder has already been used in the CNTs synthesis [3].

2 Experimental

The experimental system and the arcing procedure have been described in details elsewhere [4]. Heterogeneous graphite electrodes of 6 mm in diameter containing different mixtures of catalysts were used (Table 1). The drilled graphite electrode and filled with pure graphite powder was also sublimated for comparison. The electrodes were dc arced in He atmosphere under pressure 80 kPa. The buffer gas pressure in the discharge chamber (0.0133 m^3 in volume) was controlled automatically within $\pm$ 1 kPa throughout the runs. The arc current (53 A) was also kept constant within $\pm$ 0.25 A. The electrode gap and its position on the optical axis was controlled within

[1] E-mail address: masioda@chem.uw.edu.pl

Tab. 1. Anode composition, arc discharge conditions and anode erosion rate

Exp. run	Anode composition (at %)	Arc discharge conditions	Erosion rate mg s^{-1}
1	C (pure graphite)	p(He) = 80 kPa I = 53 A U = 29 ÷ 31 V	2.12
2	C/D* (48)		0.42
3	C/Ni(0.23)/Co(0.23)/Y(0.27)		0.44
4	C/D(22.5)/Ni(0.13)/Co(0.13)		0.53
5	C/D(24)/Ni(4)/Y(1)		0.21

* - diamond

1 mm using an optoelectronic system [4]. During the arcing, optical emission spectroscopy of the arc zone was performed to determine plasma temperature and C_2radical distributions in the arc plasma cross-section. The method applied was based on the self-absorption phenomena within the $d^3\Pi_g$ – $a^3\Pi_u$ (0-0, 5165 nm) emission band [5]. The morphology of obtained carbon product was investigated by scanning electron microscopy (SEM). Additionally, measurements by Raman spectroscopy were performed to confirm the presence of SWNTs in the obtained products.

3 Results and discussion

It follows from the comparison of the processing variables that the dynamics of the evaporation process of pure graphite, graphite doped with metal catalysts, and graphite doped with a mixture of diamond and metal catalyst anodes are quite different (Table 1).

The erosion rate of the electrodes doped with metal catalysts (Ni, Co and Y) is lower than of the pure graphite one. However, the addition of diamond powder results in further erosion rate decrease. In the case of the electrode doped with diamond, Y and Ni powders the erosion rate was only ca. 0.2 mg s^{-1}, i.e. much lower than in the case of pure graphite electrode. This phenomenon may be related to the non-conducting character of introduced material. The influence of diamond doping on the whole process is also reflected in the morphology, length and abundance of the formed carbon nanotubes.

3.1 Plasma temperature and C_2 contents

The results of the spectroscopic measurements across a vertical section between the electrodes are shown in Fig. 1. The temperatures were derived from non-Abel inverted spectra. Therefore, the respective values can be interpreted as the average temperature along a given chord (observation path) in the arc cross-section. Let us note that despite of different erosion rates there is not great difference between the temperature distributions representing the different anode compositions. The deviation between the temperatures one should rather relate to an error resulting from the self-absorption phenomenon affecting the intensity distribution in the rotational structure of the C_2($d\ ^3\Pi_g \rightarrow a\ ^3\Pi_u$,0-0) band [5]. Generally, the temperature values are consistent with the values already obtained when influence of Co/Ni on carbon nanostructure formation was investigated [1]. The column densities of the C_2($a\ ^3\Pi_u$, v=0) radicals in the arc plasma zone were

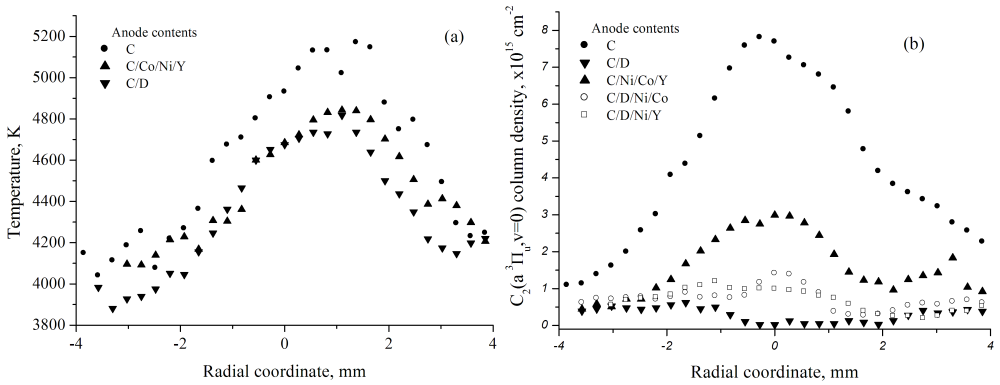

Fig. 1. Radial distributions of temperature (a) and column density of $C_2(a\ ^3\Pi_u$, v=0) radical across carbon arc plasma (b).

calculated on the basis of the temperatures and the integrated intensities of the normalized (0-0) vibrational band [5].

It is clearly seen that in the case of the diamond-containing anode, the C_2density is distinctly lower. This is due to the lower anode erosion rate. Thus, one can say that the C_2 content in the plasma phase roughly follows the amount of carbon species leaving the anode surface. These species, if complex, decompose subsequently towards the more simple ones, e.g. atoms and diatomic molecules. At the temperature prevailing in the anode tip ($>$ 3000 K), diamond crystals should convert into graphite very easily. However, graphitic species which are formed under such conditions are very likely of much lower size that those resulted from the arc ablation of ordinary graphite. This probably is the main reason of different behavior of diamond doped electrodes in respect to final products.

3.2 Product composition and morphology

The application of pure or mixed electrodes manifested itself not only in different anode erosion rate but also in different behavior with respect to the CNTs growth. For graphite mixed with Ni and Co, we did not observe high yield of CNTs. Under our experimental conditions they constitute at only a few percentage of total soot-product. When additionally Y was present, besides of soot a web-like material was formed. The example of SEM image of as- obtained product is shown in Fig. 2. However, there is still not to many elongated carbon structures. Surprisingly, the diamond drastically changed the product morphology. The final product appeared almost in form of a web-like material. The web can be easily recovered from the cover situated above the arc (Fig. 3). The SEM image of the web morphology is shown in Fig. 4. The effect of diamond on carbon nanostructures is evident. There are plenty of very thin and long CNTs. The analysis by HR TEM technique (results not presented here) confirmed that the obtained product consists mostly of SWCNTs.

A good indicator for the presence of SWCNTs is the Raman spectra shown in Fig. 5. For the sake of comparison, spectra of soot resulted from ablation of pure graphite and graphite mixed with Ni/Co are also shown. Only in the case of C/D/Ni/Y electrode, a characteristic low

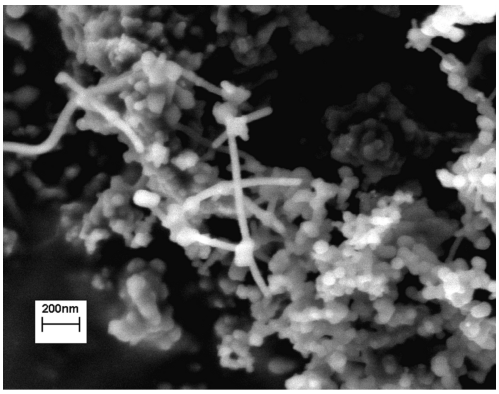

Fig. 2. SEM image of soot product. Anode: C/Ni/Co.

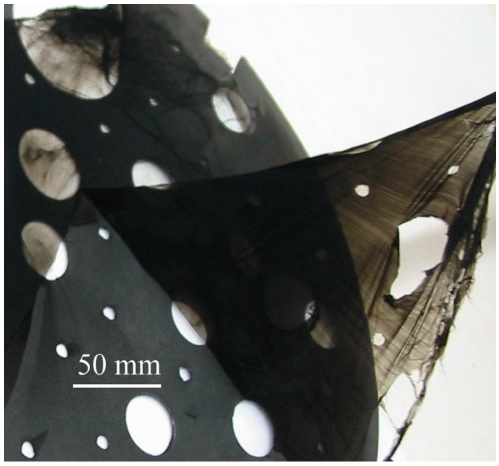

Fig. 3. Photo of web-like product. Anode: C/D/Ni/Y.

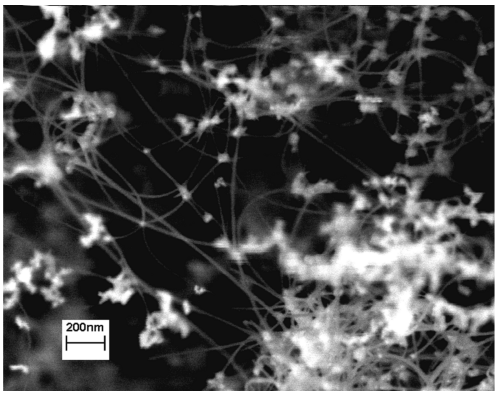

Fig. 4. SEM image of web-like product. Anode: C/D/Ni/Y.

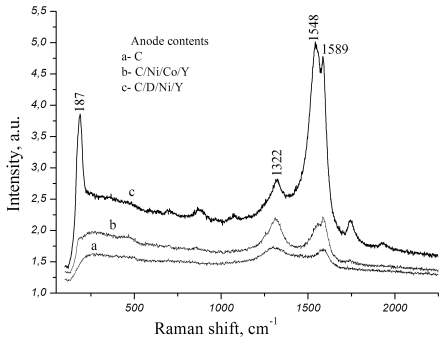

Fig. 5. Raman spectra of selected products.

frequency band at 187 cm^{-1} is present. This band corresponds to SWCNT breathing vibrational-mode [6]. Additionally, the band at 1590 cm^{-1} corresponding to the tangential stretching mode of well ordered graphite material is much stronger than the one at 1320 cm^{-1} which originates from a disordered carbon. Thus, in the case of C/Ni/Co/Y electrode only MWCNTs could be detected.

In summary, the presence of a diamond powder in addition to metal catalysts influences not only the plasma characteristics but also the morphology and quality of the obtained carbon nanotubes.

Acknowledgement: This work was supported by the funds of the State Committee for Scientific

Research through the department of Chemistry, Warsaw University within the project No. 4T08D 021 23.

References

[1] A. Huczko, H. Lange, T. Sogabe: *J. Phys. Chem. A* **104** (2000) 10708–10712

[2] S. Iijma: *Nature* **354** (1991) 56–58

[3] M. Pacheco, M. Monthioux, M. Razafinimanana, L. Donnadieu, H. Allouche, N. Caprais, A. Gleizes: *CARBON 2002*, 15-20 Septembre 2002, Beijing (China)

[4] H. Lange, P. Baranowski A. Huczko, P. Byszewski: *Rev. Sci. Instrum.* **68** (1997) 3723–3727

[5] H. Lange, K. Saidane, M. Razafinimanana, A. Gleizes: *J. Phys. D: Appl Phys.* **32** (1999) 1024–1030

[6] P.C. Eklund, J.M. Holden, R.A. Jishi: *Carbon* **33** (1995) 959–972