Journal of Mining and Metallurgy, 39 (1–2) B (2003) 343 - 352.

SOME ASPECTS OF THE ELECTROCHEMICAL FORMATION OF CARBON MICRO-TUBES FROM MOLTEN CHLORIDES

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(Received 4 January 2003; accepted 19 March 2003)

Abstract

Carbon nano/micro-tubes have been successfully synthesized by an electrochemical way from the NaCl-KCl-5% $MgCl_2$ molten salt on the surface of a graphite cathode. The length of the tubes is above 100 μm, while their diameter ranges from hundreds of nanometers to 1-2 μm. A new cleaning procedure of the carbon tubes from the remaining salt has been developed, with acetone found to be the best cleaning agent. It has been shown that in addition to carbon micro-tubes, some tube-like or rod-like structures can be formed, which do not actually consist of carbon but of the remained salt.

Keywords: electrochemical synthesis, carbon nano/micro-tubes, molten salts, graphite

1. Introduction

Carbon nano-tubes were discovered in 1991 by Iijima [1]. Since then, several methods of their synthesis have been described [2-5], such as evaporation of carbon in arc discharge, laser ablation, catalytic chemical vapor deposition of carbon containing gases and catalytic decomposition of fullerens.

One of the most perspective ways to produce carbon nano-tubes in bulk quantities is based on the electrochemical deposition of liquid alkali metals from their molten halides

onto graphite cathodes, first described by Hsu et al [6-7]. This method has been developed further by Chen et al [8-11], later by our group [12-14] and recently by Bai et al [15] (for a comprehensive review see [16]).

As it was noted earlier [12, 14], in addition to nano-tubes, tubes of micrometer size are also formed [12, 14] during this process. As micro-tubes are somewhat closer to the engineering scale of our days, a sub-project on the synthesis of carbon micro-tubes from molten salts has been launched. Some preliminary results of this work will be shown in the present paper. Particularly, we have carried out the chemical identification of some tube-like structures, and also studied different cleaning techniques to improve the separation of the carbonaceous material from the salt.

2. Experimental conditions

The electrochemical system was similar to that described in [16]. As a source of carbon, graphite cathode of cylindrical shape (6.1 mm in diameter) immersed into the molten salt mixture of 95% *NaCl-KCl* and 5% $MgCl_2$ was used. Equimolar *NaCl-KCl* served as a solvent, while $MgCl_2$ was chosen because the atomic radius of *Mg* is almost identical with the distance between the graphite plates. The salt mixture was first dried for 24 hours at 100 ^{o}C under vacuum. After drying the system was filled with *Ar* and its pressure was kept at 1.2-1.25 bars during the whole duration of experiment. The temperature of the system was increased up to 850 ^{o}C and the salts were melted. After that the cathode and a glassy carbon rod, serving as reference electrode were immersed into the melt at a depth of about 5 mm, cyclic voltammograms were taken by means of a computer controlled potentiostat. Electrolysis was carried out in a potentiostatic way, by applying potential corresponding to the value of *Mg* deposition potential, in order to make sure that *Mg* is the only deposited metal. The duration of electrolysis was 1 hour.

After electrolysis the cathode was removed from the molten salt and the system was cooled down to room temperature. In literature and also in our previous works the toluene-water cleaning method was used, as it was believed that nano-tubes are concentrated at the water/toluene interface probably due to interfacial energies. In the present work, a new dialysis-based cleaning method has been developed. It was partly aimed to remove the salt as much as possible, and also to extract the micro-tubes by means of a membrane. The scheme of the dialysis-based cleaning method is shown in Fig. 1. The system was filled with distilled water and then water in the outer zone was changed every day until the concentration of Na^{+} was close to zero. The sodium ion concentration was measured by flame photometry. After the main cleaning period, four similar samples of 1-1.5 ml each were taken from the suspension. They were mixed with 6-8 ml of hydrochloric acid, acetone, toluene and distilled water respectively, and the four mixtures were treated by ultrasound for 6*15 min. Then a small “drop” taken from the sedimented part containing black carbonaceous particles was put onto an aluminum

plate. The resulting material was analyzed by SEM (Scanning Electron Microscopy). Some tube-like structures were also analyzed for their composition by EDS (Energy Disperse Spectroscopy).

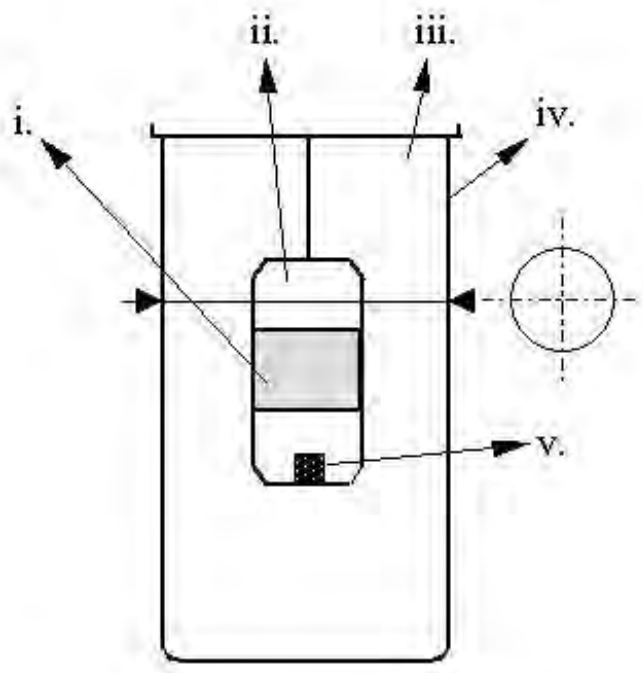


Figure 1. Illustration of dialysis-based cleaning system. i. - membrane, ii. - inner diffusion space, iii. - outer diffusion space, iv. - vessel, v. - solidified salt to be cleaned.

3. Results and discussion

In Fig. 2, sodium ion concentration of the water solution taken from the outer zone of the dialysis set-up is presented as a function of time. One can see that sodium ion content decreases rapidly during the first few days, but becomes negligible only after a month. This means that cleaning the carbonaceous material from salt is a difficult task.

In Fig. 3 a tube-like structure "growing out" of the cathode surface can be seen. As EDS analysis proved, it consists of almost pure carbon (Table 1). On the other hand, when washing was not performed accordingly, some other tube-like (or rod-like) structures appeared to be not carbon (see for example Fig. 4), but to consist of the remaining salt.

In Fig. 5 tubes of different diameters collected by the membrane of the dialysis

equipment are shown. One can see the curved, long cylinders with diameter of about 100 nm. Fig-s. 6.a-d show the SEM photographs of the sedimented parts prepared by combination water/toluene, water/hydrogen-chloride, water/water, and water/acetone solutions respectively. Interestingly, toluene is usually used as a separating agent for nano-tubes. However, at least for tubes with diameter above 100 nm, the best cleaning effect was achieved by using acetone. Probably it can wash away all undesired impurities remaining from the main cleaning period more strongly and it was proved to be the best cleaning agent for micro-tubes.

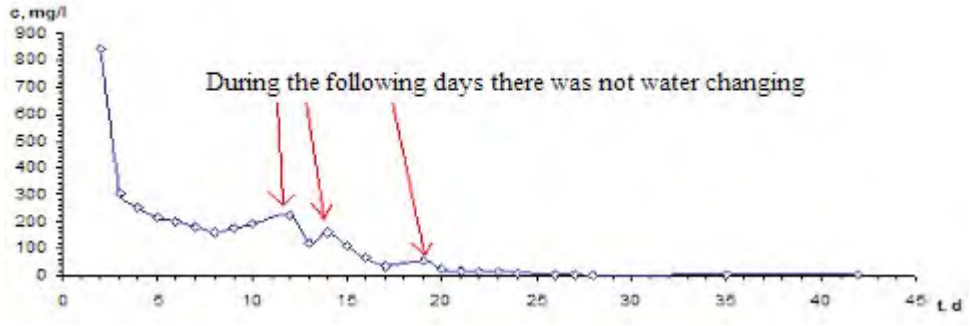


Figure 2. Concentration of Na^+ as a function of time during the main cleaning period.

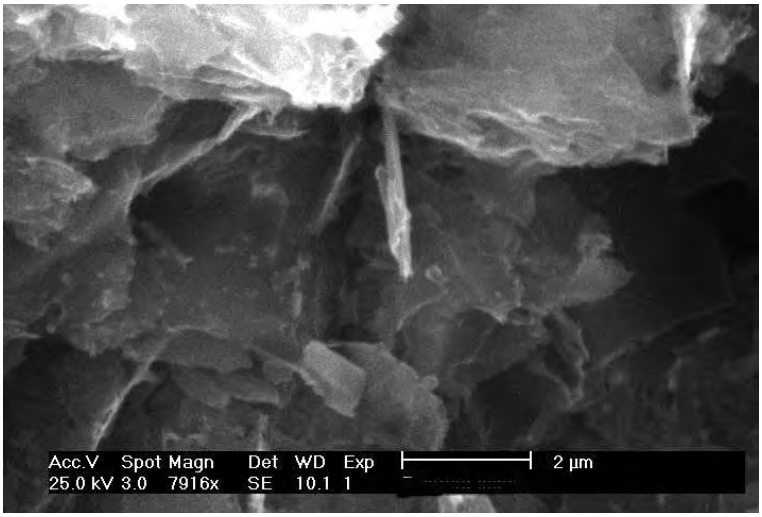


Figure 3. A spiral carbon tube formed on the surface of the cathode.

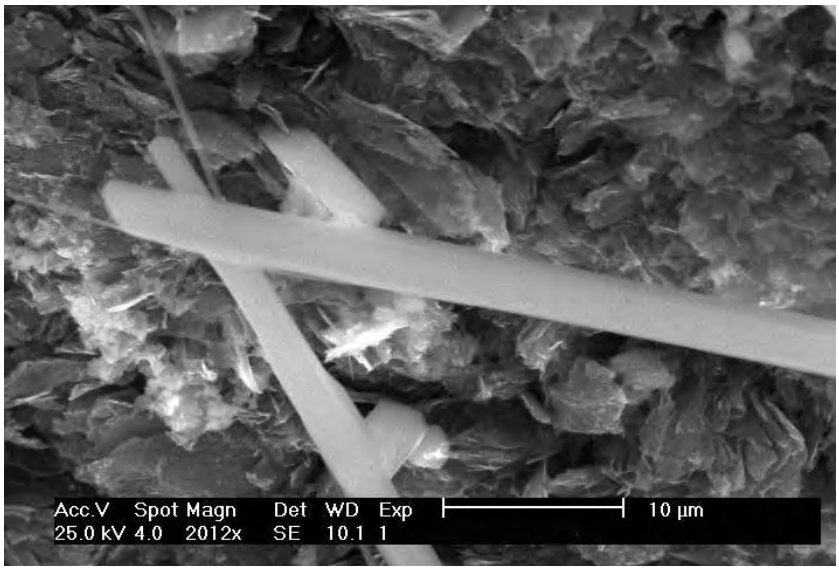


Fig. 4. A tube (rod) found on the surface of cathode, consisting of salt.

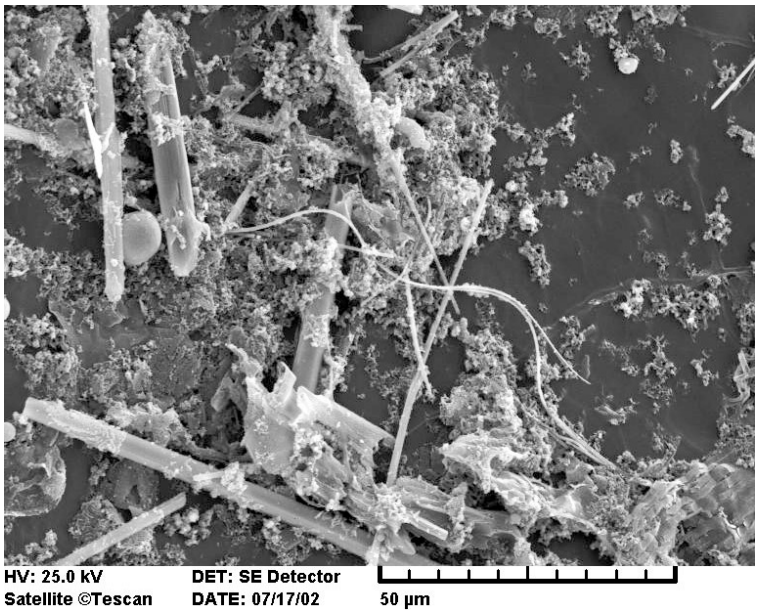
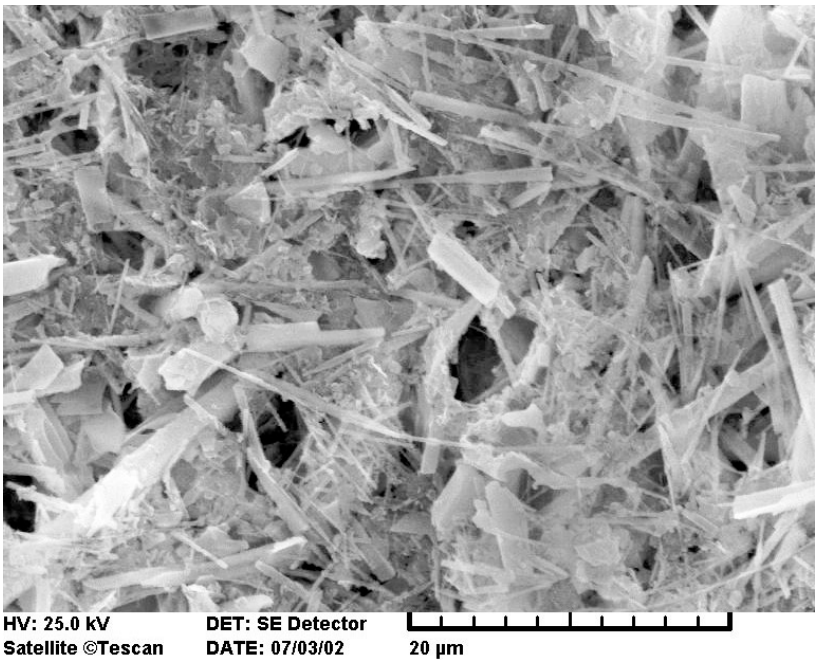
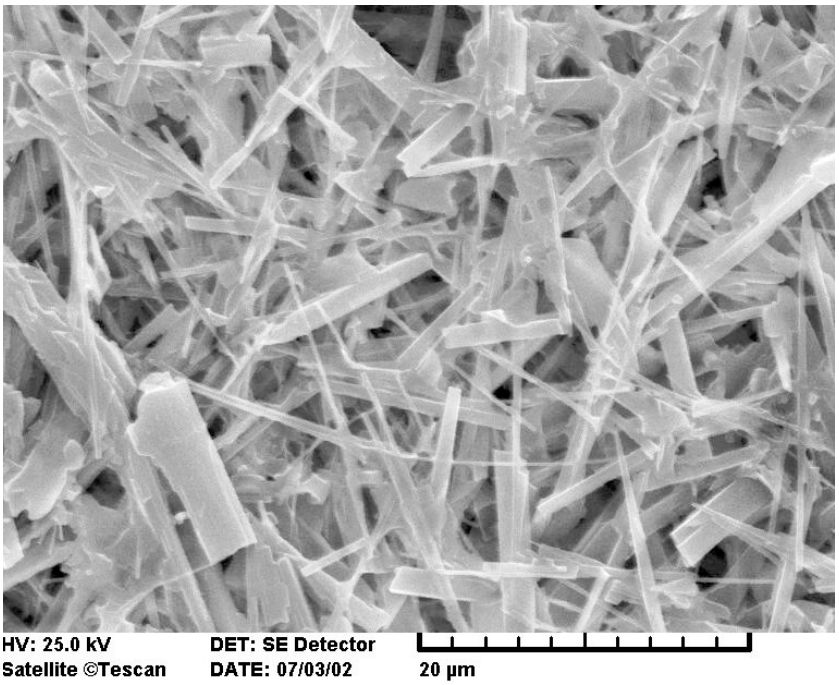


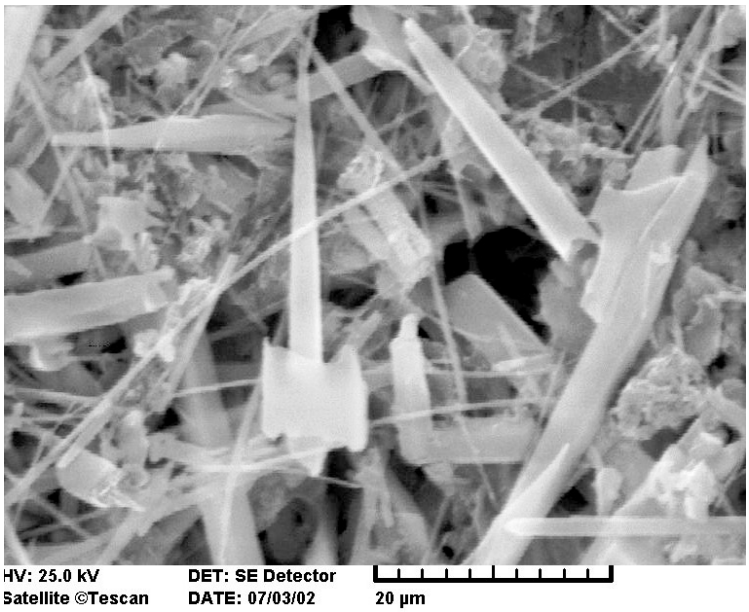
Fig. 5. SEM image of some carbon tubes remained on the membrane surface.


HV: 25.0 kV
Satellite ©Tescan
DET: SE Detector
DATE: 07/03/02
20 µm

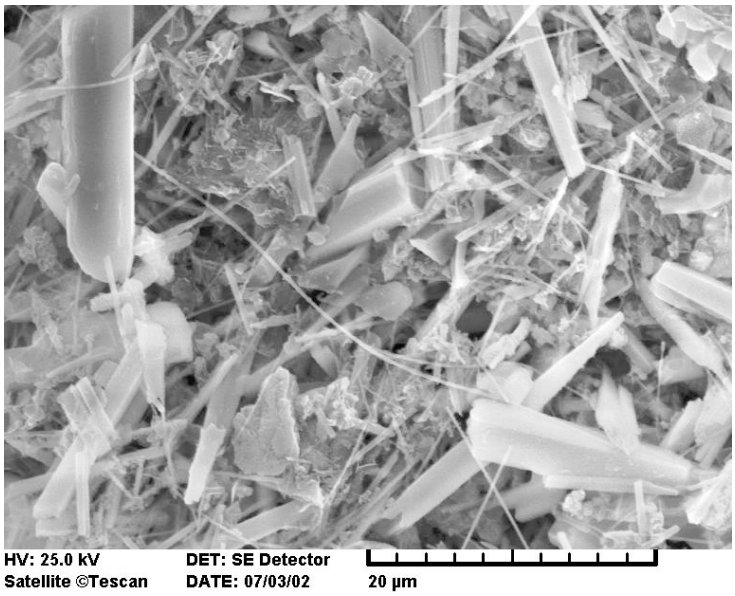
a)


HV: 25.0 kV
Satellite ©Tescan
DET: SE Detector
DATE: 07/03/02
20 µm

b)



c)



d)

Fig. 6. SEM images of the carbonaceous samples: a) water/toluene, b) water/hydrochloric acid, c) water/water, d) water/acetone.

Table 1. EDAX ZAF Quantification (Standardless)Element Normalized

Element	Wt. %	At. %
C*K*	96.13	98.78
Mg*K*	1.04	0.53
Cl*K*	0.53	0.19
Fe*K*	2.29	0.51
Total	100.00	100.00

4.Conclusions

Carbon nano/micro-tubes have been successfully synthesized by an electrochemical way from the *NaCl-KCl-5% $MgCl_2$* molten salt system on the surface of a graphite cathode. A new cleaning procedure of the carbon tubes from the remaining salt has been developed, with acetone found to be the best cleaning agent. It has been shown that in addition to carbon micro-tubes, some tube-like or rod-like structures can be formed, which do not actually consist of carbon but of the remained salt.

Acknowledgements

We are grateful to Mr. Árpád Kovács (University of Miskolc) for the SEM, and to Dr. Péter János Szabó (BME, Mechanical Technology and Material Structure Department) for SEM-EDS analysis. The authors are grateful to European Office of Aerospace Research and Development (EOARD) for the financial support of this work (grant No.FA8655-02-M4076).

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