Carbon structures formation in low current high voltage electrical discharge in hydrocarbon vapours

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Carbon structures formation in low current high voltage electrical discharge in hydrocarbon vapours

A T Sobczyk [1], **A Jaworek** [2]

[1)]Institute of Fluid Flow Machinery, Polish Academy of Sciences, Fiszera 14, 80-952 Gdansk, Poland

[2)]Institute of Physics, Pomeranian Academy, Arciszewskiego 22B, 76-200 Slupsk, Poland

E-mail: jaworek@imp.gda.pl

Abstract. The properties of carbon fibers and other carbon structures produced from hydrocarbon vapours decomposed in electrically generated plasma at atmospheric pressure are studied in this paper. The electrical discharge was generated between a stainless steel needle and a plate made of nickel alloy. The carbon fiber has grown at the tip of the needle electrode, while other microflower-like deposits were built at the plate. The physical properties of carbon fibers were investigated by SEM, Raman spectroscopy, XRD, and EDS methods.

1. Introduction

Electrical discharges are used in various industrial processes, for example, for surface modification, sterilization, noxious compound decomposition, particulate matter precipitation, micro- and nanostructures synthesis, plasma etching, or electric-discharge-machining. These processes, operating at pressures ranging from atmospheric to below one pascal, are generated by high voltage of various frequencies: direct-current (DC), alternating-current (AC), radio-frequency (RF), pulsed (PD), or microwaves (μW), supplying electrodes of different geometries.

In industry, carbon fibers are usually produced by thermal pyrolysis of polymer fibers (usually pitch) or by synthesis gaseous light hydrocarbons such as methane, benzene, or acetylene. In our experiments, carbon fibers were synthesized via the pyrolysis of vaporized liquid hydrocarbons in electrically generated plasma in oxygen-free atmosphere.

The aim of the present paper is to investigate the properties of plasma-synthesis carbon fibers, grown in a low-current high-voltage electrical discharge.

2. Experimental

A schematic of experimental set-up is shown in Figure 1. The experiments were carried out at normal pressure, in the atmosphere of argon and cyclohexane as carbon feedstock, in a reactor chamber of 0.6 dm^3, made of plexi glass. The hydrocarbon vapour was obtained by feeding liquid cyclohexane to a heated flask where it evaporated. Next, the vapours were removed to the reactor chamber by flowing argon. The concentration of hydrocarbon was controlled via dosing it by a syringe pump of costant flow rate. The argon-cyclohexane mixture flowed diagonally through the reactor chamber, from the

inlet at the ceiling to the outlet in the wall at opposite end of the chamber. The flow rate of the gas mixture was 0.08 dm^3/s. The discharge was generated between a stainless steel needle and a plate made of nickel alloy. The diameter of the needle was 1 mm, and the dimensions of the plate were 67x90 mm. The distance between the electrodes was 15 mm.

The discharge electrodes were supplied from high voltage DC source SPELLMAN HV SL 600W/40kV/PN of positive polarity. The discharge current was stabilized by a series resistance of the value of 5 MΩ. For the discharge current increasing from 1 mA to 3 mA, after the time of synthesis of 30 s, the length of produced carbon fibers changed from 0.5 to 7 mm, and their diameter from about 20 μm to 70 μm [1]. In the following experiments, the concentration of hydrocarbon in argon was kept at 5%, and the current was 2 mA. These conditions were the optimal for carbon fiber synthesis: the growth rate was the fastest (0.25 mm/s), and the surface of carbon fibers was smooth [1].

The as-made carbon fiber grown on the needle tip was carefully removed from the reactor and examined under scanning electron microscope (Zeiss EVO 40) equipped with energy dispersive spectroscope (EDS, Bruker), and next tested by X-ray diffraction method (XRD). The XRD pattern was recorded using Phillips X'Pert system with Cu Kα radiation. Renishaw inVia Raman Microscope with a 100x objective lens and a laser of wavelength of 785 nm of power 1.5 mW was used in order to analyse the Raman spectra.

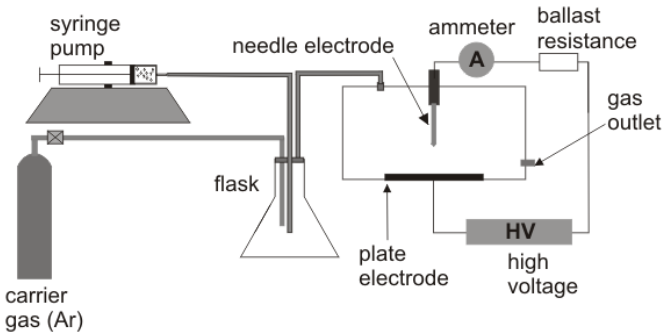

Figure 1. Schematic of experimental set-up.

3. Results

Fig. 2 shows SEM micrographs of a carbon fiber collected from the needle after 30 s of the discharge of the current of 2 mA. In Fig. 2a is presented the tip of carbon fiber, and in Fig. 2b a close-up view of its surface. The surface of the fiber is build from grains of about 1 μm in diameter.

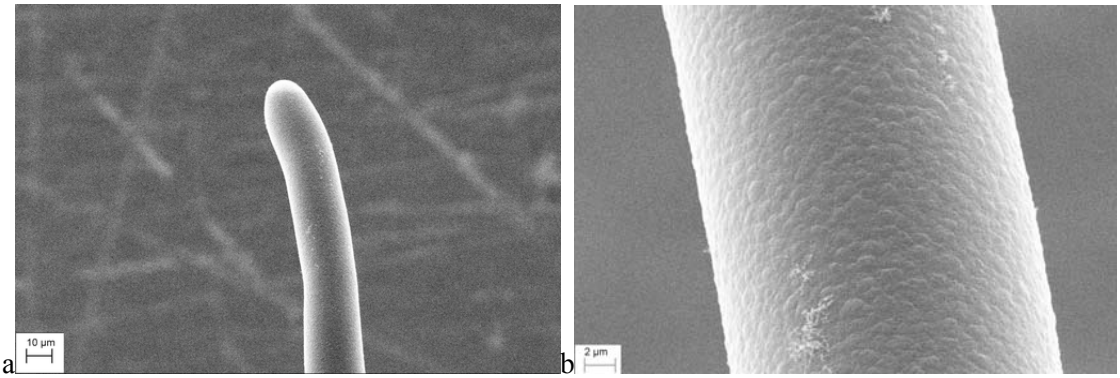

Figure 2. SEM images of carbon fiber obtained in $Ar+C_6H_{12}$ (95:5) mixture, for I=2 mA and U=3.8 kV. a. tip of the carbon fiber, b. surface of the carbon fiber.

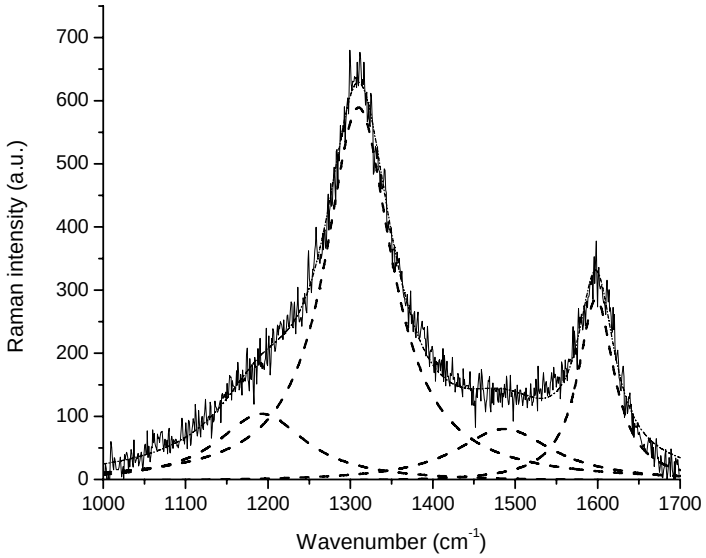

Figure 3. Raman spectrum of produced carbon fiber (I=2 mA).

The Raman spectrum of the as-made carbon fiber, emitted in the range from 1000 cm^{-1} to 1700 cm^{-1} is shown in Figure 3. Deconvolution of the spectra via using the Lorentzian fits (dashed lines in Figure 3) revealed the following peaks: 1192 cm^{-1}, 1309 cm^{-1}, 1486 cm^{-1} and 1598 cm^{-1}. The intense and sharp peaks at 1309 and 1598 cm^{-1} correspond to carbon D- and G-bands, respectively.

The G band is due to the Raman active E_{2g} vibration mode, which is related to the vibration of sp^2 bonded carbon atoms in a hexagonal graphite lattice. The D band is associated with dangling bonds of disordered carbons at the plane boundaries. The G band at 1598 cm^{-1} confirms the presence of graphitic carbon in the synthesized deposit [2]. Strong intensity of the peak at 1309 cm^{-1} implies the existence of large quantity of carbonaceous impurities.

The origin of peaks at 1192 and 1486 cm^{-1} is uncertain. The possible candidates for the 1192 peak are (1) sp^3 C–C stretching vibrations, (2) C–H bonds in the grain boundaries [3], and (3) mixed sp^2-sp^3- bonded carbon structure [4].

X-ray diffraction measurements showed that the carbon fibers obtained during the discharge were partially crystalline and partially amorphous. In Figure 4, the XRD peaks corresponding to 2θ values of 26.5°, 28.5°, 32.3°, 47.5° can be observed. In the case of carbon materials, an XRD peak with 2θ value of about 26.5° corresponds to the 002 plane of graphite. The peaks corresponding to 2θ values of 35.7° and 38.4° correspond to Si (which was the substrate) [5]. The nature of peak with 2θ value of about 32.3° is of unknown origin. Sharp and intense XRD peak at about 2θ=26.5° indicates graphitic nature of the fiber which is in good agreement with Raman spectroscopy investigations.

The elemental analysis was used to identify weight percentage of carbon and hydrogen in synthesized deposit. The analysis confirmed that carbon is the dominant element in the produced fibers. Comparing the concentration of carbon and hydrogen in cyclohexane (C — 85.7 wt.%, H — 14.3 wt.%) it is evident that highly carbonised products (C — 98.7 wt.%, H — 0.9 wt.%, the rest was N and O absorbed from the atmosphere) can be obtained from the decomposition of cyclohexane in electrically generated plasma.

The energy of electrons needed to dehydrogenate or decompose cyclohexane to simpler compounds of carbon and hydrogen should be in the range of 1.6 – 6eV [6]. In an electrical discharge at atmospheric pressure, only the electrons from the tail of energy distribution, which are those flowing near the sharp electrode (needle), could reach sufficiently high energy [7] required for decomposition of hydrocarbons. It can be supposed that carbon atoms can be produced only in the process of hydrocarbon fragmentation in collisions with fast electrons, for example in the following processes:

$$e^- + C_x H_y \rightarrow C_{x-1} H_{y-2} + H_2 + C + e^-$$

or

$$e^- + C_x H_y \rightarrow C_{x-1} H_{y-2} + H_2 + C^-$$

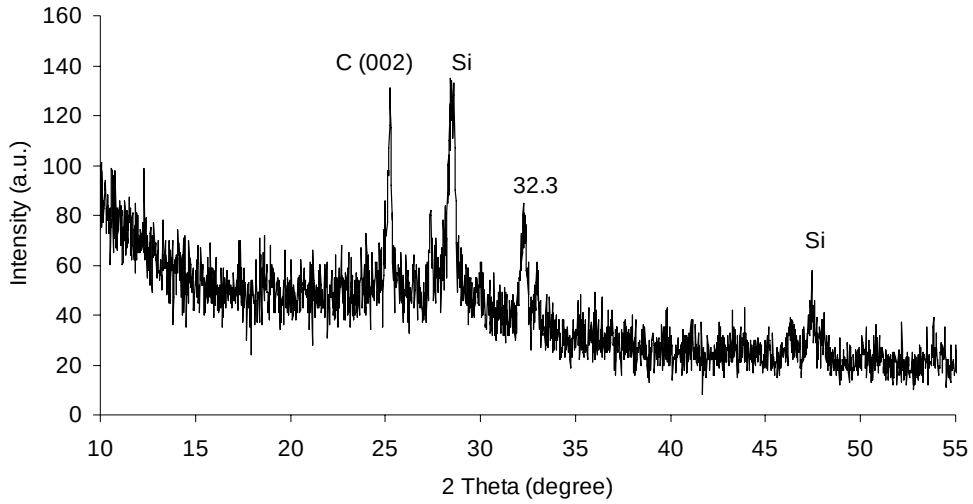

Figure 4. XRD of carbon fiber on silicon substrate.

4. Conclusion

The analysis confirmed that carbon is the dominant element in the produced fibers obtained in the electric-discharge plasma in point-plane geometry, for the discharge current I=2 mA. Raman spectroscopy and X-ray diffraction analysis confirmed the co-existence of crystalline and amorphous structures in the obtained deposit. It is evident that energy of the high-voltage low-current electrical discharge is sufficiently high to decompose cyclohexane to simpler compounds and atomic or molecular carbon from which the carbon fibers are built.

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