Diamond & Related Materials 85 (2018) 37–48

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Regularities of self-organization of technological conditions during plasma-arc synthesis of carbon nanotubes

Yuliia O. Kosminska*, Vyacheslav I. Perekrestov

Sumy State University, Rymsky-Korsakov Str. 2, 40007 Sumy, Ukraine

ARTICLE INFO

Keywords:
Nanotubes
Arc discharge
Self-organization
Low supersaturation

ABSTRACT

The emerging concept of self-organization under conditions of plasma-surface interaction is reflected in the present analytical study of the processes and causes of carbon nanotube formation in anodic arc discharge. Based on the energy balance and the interelectrode mass transfer, we created a mathematical model of self-organization of technological conditions required for carbon nanotube synthesis. The self-organization regularities of such parameters as carbon concentration, relative supersaturation above the growth surface and the surface temperatures of both electrodes have been determined by the phase portrait method. Unique possibilities of self-organized processes have revealed the ways of maintaining required synthesis stationarity. It has been shown that extremely low supersaturation of deposited vapors, substance accumulation above the growth surface and exposure to plasma are important factors for carbon nanotube formation. The structure formation mechanism under conditions of self-organized low supersaturation has been discussed. The stated self-organization regularities are also expected to take place in other fields of plasma nanoscience.

1. Introduction

Currently, it is known that a wide spectrum of various polymorphous, allotropic or molecular forms of carbon possess unique properties [1–3]. Therefore, researches keep constant interest in synthesis of various carbon structural forms. Most technological approaches related to synthesis of carbon nanotubes (CNT) are based on CVD techniques, plasma-arc evaporation, laser ablation, as well as on integrated physical and chemical techniques [4–7]. Similar carbon nanoobjects are generated by means of different technologies, indicating analogous thermodynamic and kinetic condensation conditions. However, no clear notions have been reached so far regarding the exact thermodynamic conditions common for all the technologies and necessary to generate 1D-nanoobjects. To address this problem, in the present work, we have set an aim to find out whether self-organization of synthesis conditions is the cause of CNT formation and, if so, to clarify the underlying mechanisms.

Thus, the study focuses on analyzing plasma-arc synthesis of multiwalled carbon nanotubes (MWCNT) in a cathode deposit. This method still remains promising since Iijima's work [8] as it allows generating CNTs with fewer structural defects as compared to other techniques [6,9]. The method is widely covered in the scientific literature, and certain technological parameters of the arc discharge have been reported to date. It gives the necessary prerequisites for developing a mathematical model that describes self-organization of thermodynamic parameters required to form a nanotube structure. Therefore, we consider this method to be appropriate to analyze thermodynamic conditions of CNT formation. Plasma-arc synthesis is also of interest, because the growth surface temperature and the depositing flux are not controlled directly during operation. Stated differently, we can suggest that self-organization of the above mentioned parameters should take place during operation in order CNTs to be formed. Thus, the example of plasma-arc CNT synthesis can reveal mechanisms of self-organization, help to understand nanotube formation and, moreover, to determine primary features of self-organized systems to be used in future to develop new self-organized systems based on other physical and chemical processes.

At the same time, the method is constantly being developed towards better understanding of the growth mechanism [10], larger scale synthesis [11], increasing yield and selectivity [12,13]. The recent progress deals with optimizing synthesis through adjusting geometry of the electrodes, working gas composition and pressure, direct current mode or pulse mode [10,11], applying external non-uniform magnetic field [14], studying high and low ablation modes [15], as well as rising focus on related self-organizing phenomena [16,17].

In general, realization of self-organized growth of nanostructures using plasma-based systems is considered as an important tool for emerging applications [18,19]. Mostly, self-organization is meant as

---

[*] Corresponding author.
E-mail address: y.kosminska@phe.sumdu.edu.ua (Y.O. Kosminska).

https://doi.org/10.1016/j.diamond.2018.03.032
Received 25 October 2017; Received in revised form 15 December 2017; Accepted 26 March 2018

Stranski-Krastanow growth of similar nanoislands or self-organized growth directed by surface effects [20]. However, if growth is accompanied by direct plasma interaction with the growth surface, it provides specific self-organization effects [19,21–23]. Plasma acts on the growth surface by joint action of many factors [21,24]. Among them, the electric field at the growth surface was found responsible for alignment of CNTs [25], narrowing size distribution of metallic nanodot arrays through polarization effects [26], and focusing of ionized deposited fluxes onto prominent surface parts that resulted in field-selective growth of highly porous metal layers and complex surface morphology [7,23,27–31]. For the first time, more general self-organization processes have been reported by us in [21] for the accumulative ion-plasma system (AIPS) based on dc magnetron discharge combined with hollow cathode. It has been shown that self-organization occurs through accumulation of substance by circular mass transfer mechanism and arises from self-consistent interdependence of the main technological parameters [21,32].

Self-organization in arc discharge plasma for CNT synthesis has recently been reported by other authors as well [16,17]. Circular type of carbon particles motion within near-cathode region has been accented [16], as well as interdependent physical processes of electrodes heating, electron emission, anode ablation and cathode deposit formation [17]. However, modern works only analyze processes related to self-organization of CNT formation conditions at a qualitative level. Existing energy balance equations lack correlation with flux balance equations and do not derive the concept of self-organization itself.

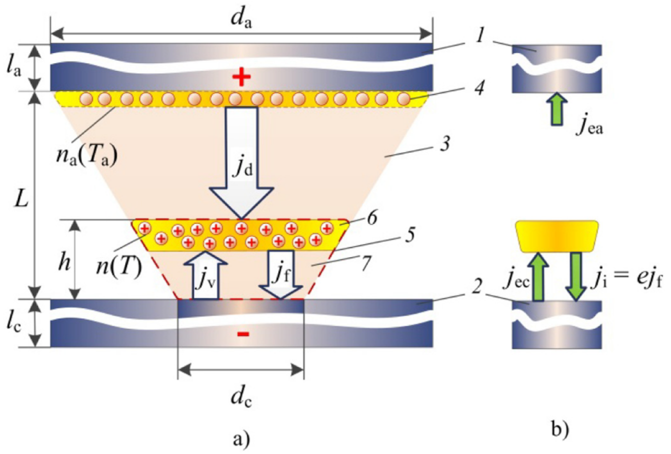
In the present work, we derive the concept of self-organization of the technological parameters that determine CNT growth in arc from the dynamical point of view. First, we analyze physical processes in arc involved in CNT synthesis and formulate a physical model (Section 2.1). On its basis, we develop a corresponding mathematical model in the form of complex interdependent differential equations (Section 2.2) which are solved by the phase portrait method (Section 3.1). We find the electrodes temperatures and regularities of evaporated carbon mass transfer when approaching steady-state operation mode and conclude that self-organization results in extremely low supersaturation of condensing carbon fluxes above the growth surface. Since the latter concept needs to be thoroughly understood, we devote Sections 3.2–3.4 to detailed discussion of the results and related physical and technological issues. Section 4 concludes the study.

2. Model representation of self-organized processes of MWCNT synthesis

2.1. *The physical model of arc discharge processes involved in MWCNT synthesis*

On the basis of experimental materials accumulated in large amount since S. Iijima's work [8], one can single out key processes and formulate a physical model and then derive a mathematical model of energy and mass transfer within the interelectrode gap. From now on, we focus upon those processes only that contribute to self-organization of the technological parameters and are available for experimental and theoretical determination.

The most widespread variant of plasma-arc MWCNT synthesis is realized by means of dc anodic arc between two graphite electrodes in helium ambient under pressure close to atmospheric pressure [6–8,10,16,44–57]. Currently, the cathode either is made of copper entirely or is combined of graphite in the center and copper in the periphery [16,17,44–47]. According to the published data, use of copper decreases CNT sintering and hence minimizes the number of defects [44], but, on the other hand, increases arc instability [54]. Fig. 1 schematically represents the electrode system and the fluxes of substance which illustrate the assumed physical model of the arc processes. As known, the cathode deposit contains MWCNTs in its central part onto which the greater part of the arc is focused, as well as ~95% of the total current [45,46,58]. To generate single wall nanotubes, one should place substrates in peripheral discharge areas [9,58] and use metal additives as catalysts as well [51,54,58] that is beyond our consideration.



a) b)

Fig. 1. Schematic representation of the electrode system, evaporated carbon mass transfer (a) and constituents of the electric current at the electrodes (b): 1 – the anode; 2 – the cathode; 3 – major part of the arc; 4 – evaporated carbon atoms; 5 – the cathode sheath (dashed line); 6 – the ionization layer with accumulation of positive carbon ions; 7 – the collisionless layer.

At present, it is generally assumed that the optimal conditions for the highest possible MWCNT yield are the following:

- the helium pressure close to 500 Torr [10,17,44,45,48–50,57];
- maintaining the constant low interelectrode gap (1–2 mm) [17,45,49,53,57];
- the interelectrode voltage ~17–26 V [10,45,47,48,55,56], the voltage below the first ionization potential of helium (24.5 V) being preferable to get more stable discharge [49].

Because of complex and interdependent real processes during arc synthesis, we should suggest some simplifications. So, we neglect the radial diffusive flux directed parallel to the end surfaces of the electrodes because ~90% of evaporated carbon is deposited on the cathode [4,17,44,58] and the interelectrode gap is much lower than the electrode diameters. We also assume the plasma temperature within the interelectrode gap to be constant and independent on the distance from the discharge axis. It is acceptable since the plasma heat capacity is low and its heating rate is much higher than that of the electrodes.

Under the above conditions, the arc discharge is typically maintained by thermo-field electron emission from the cathode. The electron current j_{ea} (Fig. 1b) heats the graphite anode up to high temperatures, and, as a result, the anode strongly evaporates or ablates. The ablation intensity depends on the anode sheath processes and the anode voltage drop sign [15–17,46,59], i.e. there are high and low ablation modes. Within the framework of our model, we bring the anode sheath role only to electron acceleration towards the anode. Evaporated carbon atoms move towards the cathode through the arc plasma column which is typically described by local thermodynamic equilibrium [51,54,59–62]. All plasma constituents have approximately the same temperature T_p being equal to several thousand K (4000–7000 K) [9,49,50,55,63,64]. We assume that evaporated carbon moves diffusively, and the degree of carbon ionization is substantial only near the cathode [65]. The cathode sheath (pos. 5 in Fig. 1a) can be divided into the following three layers [63,66]: i) the collisionless layer with no collisions between carbon and working gas, and the electric field strength is high; ii) the ionization layer; iii) the thermal relaxation layer. Let us simplify the cathode sheath structure and omit the transitional thermal relaxation layer since its role consists in temperature