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# ELECTRIC ARC METHODS TO SYNTHESIZE CARBON NANOSTRUCTURES

The (mainly authors') publications on the problems of electric arc synthesis (EAS) of different carbon nanostructures (CNS) are reviewed. EAS of CNS can be carried out in both gas and liquid environments. EAS in a gaseous environment has a number of advantages such as high productivity and speed of the condensation process as well as ease of mode control. However, this method of synthesis has also disadvantages; it requires complex vacuum and cooling systems, which make the installation bulky. In addition, this method does not solve the problem of agglomeration of synthesized CNS and has a synthesis by-product in the form of an incrustation (deposit) on the electrode. EAS in a liquid environment is characterized by a more compact equip-

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ment, since it does not need vacuum (the process proceeds at atmospheric pressure) and cooling (the liquid environment plays the role of a heat sink) systems. With this method of synthesis, various types of dielectric liquids are used: from distilled water and liquid nitrogen to hydrocarbon solvents, which can serve as a source of carbon in the synthesis zone. By changing the composition of the liquid phase, it is possible to achieve the synthesis of various types of CNS. In addition, this method involves the using of metal electrodes, which, in addition to a long service life, can act as catalysts. In this case, metal particles can be encapsulated with CNS, forming composites with different magnetic properties. In some works, it was shown that, when metal electrodes are used in the process of EAS in a liquid environment, the mixtures of metal carbides could form. The liquid environment after EAS of CNS is also of scientific interest. Probably, the liquid environment contains new modifications of soluble organic compounds, which are being searched by researchers all over the world. Thus, scientists found that, after EAS in a liquid environment using graphite electrodes, the working solution ( $C_6H_6$ ) changed its colour. This indicates the formation of soluble organic compounds in it. In the review, based on the literature data, a table of modes for the industrial synthesis of single-walled CNS was created, and a list of modes (regimes) for creating defective CNS as a method of increasing the adsorption area of nanoparticles is given. The solutions to important problems of the EAS method are fixed: agglomeration of CNS, problem of deposit formation, productivity improvement.

**Keywords:** plasma-chemical synthesis, electric arc discharge, carbon nanostructures (CNS), carbon nanoclusters (CNC), carbon nanotubes (CNT), cryogenic media, liquid dielectrics.

### 1. Introduction

The production of different cheap carbon nanostructures (CNS) is an important task of the modern scientific world. The basis for the production of CNS is the development of various methods for the synthesis of carbon nanostructures using catalysts. To date, modern soluble [1-16] and insoluble [17-20] carbon nanostructures are being synthesized, from which modern materials can be created [21-26]. In some cases, synthesized CNS are able to store hydrogen [27, 28] and to compete with existing materials [29-40] for hydrogen storages [41, 42]. Products made from such materials are technological masterpieces [43-46] of the modern world.

A lot of time has passed since the discovery of the first multi-walled carbon nanotube (MWCNT) [47] in the structure of soot obtained by the thermal decomposition of carbon monoxide on an iron catalyst [48]. At present, carbon nanotubes (CNT) are produced in an electric arc discharge as a by-product of fullerene synthesis. In addition to electric arc plasma-chemical synthesis, in which graphite is evaporated in an electric arc of an inert environment at low pressure [49], there are other methods for CNT producing. For example, the pyrolysis method [50, 51], laser evaporation [52, 53], detonation method [54]. Each technique for obtaining of nanodispersed substances has both advantages and disadvantages.

### 2. CNS Production Methods and Their (Dis)Advantageous

Pyrolysis has previously been widely used as the cheapest method for the synthesis of various carbon pyrofibres and multiwalled nanotubes, and for this reason it has been fairly well studied.

Electric arc synthesis (EAS) in a gaseous environment as a method for obtaining CNT attracted the deserved attention of scientists only after the work of Iijima in 1991 [49], and today it is one of the most common methods. In 2016, Ukrainian and American scientists were nominated for the Nobel Prize in Chemistry for their studies of CNS by the method of their hydrogenation [55].

The electric arc method of synthesis in a gaseous environment is considered the one of the most reliable and productive methods with a number of advantages:

- high productivity;
- high rate of condensation process;
- dispersion of particles is from 1 nm to 100–200 nm;
- initial raw materials can be purified directly during the reaction;

• the possibility of obtaining of complex substances and composites at the output by mixing of the initial vapours;

• the zone of the interelectrode space has a temperature of about 12000 K (Fig. 1) [56];

• it is easy to change modes (current strength, precursor supply rate, *etc.*) during the experiment.

However, despite the obvious advantages, the method of plasmachemical electric arc synthesis is not without disadvantages, which include the following:

- wide range of particle size distribution;
- high, uncontrollable degree of particle agglomeration;
- bulkiness of equipment;
- necessity of a vacuum system presence;
- the need for an efficient cooling system of reactor.

In addition, in this method of synthesis, great number of incomprehensible points requires explanation. Uncertainty in understanding the mechanism of nanotube growth and fullerene formation hinders the progress in the development of more controlled technologies for the synthesis of these nanomaterials. However, the first attempts to study and explain these processes are already being made today [57–61].

For the leading of a metal (Me) catalyst in the electric arc method of CNS producing, special hollow graphite electrodes are made. The equipment has a complex system of automatic control of the electric arc and electrode feed rate.

The need to improve the technique of plasma-chemical synthesis of nanopowders and create a new plant for the synthesis of nanodispersed

Fig. 1. Location of temperature zones along the axis of the electric arc [56]

substances led to the development of an electric arc method in the liquid phase. The results of this development were first reported at the International Scientific Conference 'Carbon' in the USA in 2000 [62] by Ukrainian scientists from the I.M. Frantsevych Institute for Problems of Materials Science of the N.A.S. of



Ukraine (department of hydrogen materials science and chemistry of carbon nanostructures). The method of electric arc synthesis in the liquid phase is free from the disadvantages of EAS in the gas phase and significantly expands the range of synthesized products.

EAS of nanostructures in a liquid phase is no more expensive than EAS in a gaseous environment and is characterized by much less bulkiness of equipment. The arc synthesis of nanostructures in the liquid phase does not require the presence of vacuum systems, since the process is carried out at atmospheric pressure [63–65]. The choice of hydrocarbon solvents for the liquid phase as carbon sources for the CNT synthesis ensures the continuity of the process [60]. Metal electrodes, which have a long service life, can play the role of both catalysts and sources of reagents during synthesis. At the same time, metal nanoparticles can be encapsulated by carbon nanoparticles, forming nanocomposites [66–72, 75, 83]. Another advantage of EAS in a liquid phase is the solution of the problem of heat removal from the high-temperature reaction region of the plasma (>4000 K).

However, the question of the particle agglomeration degree in an electric arc method in a liquid environment remains unresolved, although it significantly decreases when a liquid phase replaces the gas one.

Advantages of carbon nanostructures electric arc synthesis in a liquid environment in comparison with EAS in a gaseous environment follow below.

• Possibility to create a continuous electric arc synthesis of nanostructures, which excludes the synthesis stop to replace the electrodes.

• Small conglomeration of nanostructures. Predominantly singlewalled nanostructures are formed due to the short synthesis time and low concentration of the initial reactants.

• No expensive and difficult to operate vacuum system.



Fig. 2. Schematic diagram of the device for arc synthesis with water protection [73]

• For the synthesis of carboncontaining nanostructures, it is possible to use not only electrodes (anode, cathode), but also the liquid phase. It is permissible to select the synthesis conditions in such a way that the electrodes will practically not be consumed, but the liquid phase will be used as a source of

synthesis reagents. This will make the process of carbon nanomaterials synthesis uninterrupted.

• The CNS synthesis process is safer than other methods, such as arc discharge in the gas phase, pyrolytic method, *etc*.

• The absence of water-cooled jackets used as a heat-removing element of electric arc reactors for the synthesis of carbon nanostructures in a gaseous environment. The liquid phase in the method of EAS in a liquid environment plays the role of a heat sink, and the solution temperature decreases due to the evaporation of the liquid dielectric phase. This is important, considering the fact that the temperature of the electric arc reaches up to 12000 K [56].

• Synthesis in the liquid phase makes it possible to obtain a wider range of nanomaterials than a similar process in the gaseous phase, and most importantly -this method is less laborious.

Currently, the synthesis of nanostructures by the electric arc method in a liquid environment is widespread all over the world. Various substances are synthesized by this method [57-60, 73, 63-65, 74-83]. For example, Chinese researchers succeeded in creating the synthesis conditions for the growth of CNT in a gaseous environment under a graphite cap immersed in distilled water [73] (Fig. 2). Synthesis was carried out with a vertical arrangement of electrodes with a direct current source. In this case, during the formation of an electric arc, gases are exuded: carbon and hydrogen monoxides [77, 84]. They, in turn, pushed out the water from the nanotube growth chamber. To CNT growing, metal groups (Fe, Co, Ni) were used as a catalyst [78–82]. In this case, the catalyst for CNT growth is introduced in the form of a mixture of metal and carbon powder (5:1) into the internal cavity of the evaporated electrode. The process lasted one minute, while the output of the nanoproduct is of 10 g/h. The main product is a solid deposit (300 mg) collected from the cathode electrode. This method, according to the authors, makes it possible to synthesize nanoproducts containing more than 50% of CNT, while in the case of synthesis by the same method, but without a graphite cap in a liquid environment (H $_2O$ ), less than 20% of CNT will be synthesized in the nanoproduct.

Numerous attempts are being made all over the world to develop the newest inexpensive processes for the synthesis of CNS, and the electric arc method in deionized water (H<sub>2</sub>O) is recognized as one of the most promising [63, 74, 84–90]. Therefore, today, the new methods are being perfected and developed to improving and reducing the cost of the process of carbon nanomaterials (CNM) obtaining by the considered method in the H<sub>2</sub>O environment. Chinese scientists who reported on the production of fullerenes and carbon nanotubes from Chinese coals [91-94]made an unusual contribution to this area. Expensive graphite electrodes have been replaced with carbon-based carbon rods [95]. Coal has been crushed and dried before use. The crushed coal sample was mixed with nickel powder ( $\approx 2.5 \text{ wt.}\%$ ) and coal resin ( $\approx 20 \text{ wt.}\%$ ), which served as a binder substance. After that, the mixture was pressed and carbonized in a stream of nitrogen  $(N_2)$  at a temperature of 1170 K for five hours. This type of rod was used as a vaporizable anode. Synthesis time varied from 20 to 40 min depending on the length of the manufactured carbon consumable electrode. The interelectrode gap was of 2-3 mm.

The authors of [73] report that the predominant amount of a singlecrystal metal (f.c.c.-Ni) lattice) is encapsulated in a carbon shell. Nickel nanoparticles coated with carbon retain their magnetic properties.

Carbon electrodes are a cheap alternative source of carbon. One of the main advantages of carbon electrodes compared with graphite one is their low cost and eases of introducing of any volume of catalyst (Me) into the electrode for the synthesis of carbon nanoparticles (CNP).

Graphite electrodes also came under close scrutiny by researchers from Great Britain [58] and Ukraine [96]. The only difference between graphite electrodes, which undergo preliminary cleaning in the form of calcination, is their grades. Grades of graphite rods differ mainly in maximum grain size, apparent density and final bending strength. To evaporation of graphite rods of a grade with worse characteristics requires higher current strengths and more time to overcome the intergranular space, because of which instability occurs in the electric arc, leading to crystalline defects in the CNM. This has also been experimentally proven, but UK researchers do not consider structural defects as a negative phenomenon, since the higher the structural defects of the lattices, the larger the particle adsorption area will be, and this is important for storing various gases in the CNS.

Ukrainian researchers also tried to replace the high-quality 'Finegrained dense graphite' (FGDG-7) graphite grade with a cheaper 'Special Impregnated Graphite Electrodes' (SIGE) grade for electric arc synthesis [96] in an inert gas (He) environment. As a result of the experiment, carbon nanostructures (CNS) of various types were obtained, and a com-

parative analysis of their characteristics was performed. The paper defines the optimal technological conditions for the synthesis of CNS from anode graphite electrodes of comparable grades. Using scanning and transmission electron microscopy, the structure of the synthesized carbon materials was studied and it was shown that during the evaporation of SIGE graphite grade, single-walled (SWCNT) and multi-walled carbon nanotubes (MWNT) are formed even without using of a catalyst (*Me*). According to the results of differential thermal, thermogravimetric and differential thermogravimetric analyses, the temperature of the beginning of the interaction of the formed CNS with oxygen ( $O_2$ ) of the air was established. According to the data of photospectral analysis of the synthesis products, calculations were made, and it was shown that the fullerene component obtained by evaporation of SIGE graphite grade contains 10–12% of C<sub>60</sub> and C<sub>70</sub> fullerenes, which is no worse than that of FGDG-7 graphite [96].

Taking into account the cheapness of graphite of SIGE grade compared to FGDG-7, it can be argued that carbon nanostructures (carbon nanotubes, fullerenes and fullerene-like structures) synthesized from SIGE graphite grade have a lower cost. This fact is an important result of the experiment on the synthesis of carbon fullerene molecules, since today new modern nanotechnologies are being created on their basis.

Hungarian scientists in the field of studying the synthesis of CNT [63, 84, 97] decided to combine the synthesis in a liquid environment using of an alternating current source with computer control [74]. With this method of synthesis, in the second half of the cycle, the cathode becomes the anode, and the deposit, accumulated on the cathode, evaporates in the plasma. Thus, the issue of deposition and etching of nanotubes on the cathode was solved, since the deposit formed on the cathode is self-purifying in the next half of the cycle.

For the same reason, the method using alternating current is suitable for continuous work and automation. For such synthesis, graphite electrodes were used, which were evaporated in deionized water under the action of an alternating current varying within the limits of 85-45 A at a voltage of 40 V. This method makes it possible to obtain 10-5 mg/min of a carbon nanoproduct and is accompanied by the permanent formation of gas bubbles of carbon monoxide CO and hydrogen (H<sub>2</sub>) [77, 84]. The experiments were carried out at different values of the current strength. The results of the tests indicate that, at low values of the current strength, oxidative processes are activated, and, at high values, carbon is formed in elemental and solid forms (soot, graphene packages).

Some of the first experiments on the evaporation of graphite electrodes (C/C) by the electric arc method in a cryogenic environment were carried out in liquid nitrogen (N<sub>2</sub>) [98] (Fig. 3), and then it was proved that deionized water (H<sub>2</sub>O) can also be an alternative environment [63, 84]. Fig. 3. Electric arc plant for the synthesis of CNS with automatic supply of liquid nitrogen  $(N_2)$  and a consumable anode [98]

The difference between the syntheses of CNP in these two environments was explained by researchers from Great Britain [58]. The experiments were carried out in deionized water and liquid nitrogen with graphite electrodes of different grades at the same direct current of 10 A [58]. Deionized water and liquid nitrogen equally well perform the function of holding and condensing the vapour generated during the arc discharge process. However, the surface evaporation of these liquids is different. This factor is significant in the analysis of the influence on the stability and uniformity of gas bubbles around the electric arc space during synthesis process.



MWNTs + Liquid Nitrogen

During the action of an electric arc, gases are formed in the liquid. They are exuded in the form of bubbles. In gas bubbles, the process of CNP quenching takes place in the same way as it occurs at the vapour/ liquid electric arc interface; therefore, the formation of nanoparticles continues in them. In liquid nitrogen, inside a gas bubble, the values of pressure and density exceed those of a bubble in water, since nitrogen is in a boiling state under normal conditions even when the electric arc breaks, and evaporates faster than water at contact with hot steam.

Therefore, the electric arc in liquid nitrogen will be less stable than in water. This was proved by British scientists who synthesize in liquid nitrogen various CNP with numerous structural lattice defects, since such defects occur mainly in particles obtained under conditions of unstable parameters of electric arc synthesis.

In addition, British scientists [58], as well as Ukrainian scientists [61], suggested a possible mechanism of the CNT formation. The volume of carbon plasma can be conditionally divided into two areas: the first one is the core (region 1) that covers the space near the electric arc cord. In this region, the temperature reaches  $\approx$ 4000 K, coming up to the melting point (3823 K) and boiling point (4203 K) of graphite. It is assumed that the electrons move in a direction, parallel to the electric

field. As the amount of carbon removed from the anode increases, the plasma expands, pushing the liquid away, resulting in gas bubbles formation. Region 2 is the volume between the core and the steam/liquid interface. According to this assumption, the core is the most suitable region for nanotube growth. On the other hand, the carbon onions are formed during the condensation of vapour at the steam/liquid interface, where the movement of carbon particles is less directed.

Ukrainian researchers [61] made a step towards studying the regularities of the carbon nanostructures formation during the electric arc evaporation of graphite. One of the main conclusions can be considered the fact that micro- and macroquantities of carbon nanomaterials are formed at the stage of nucleation, *i.e.*, a nanostructured product consists of nuclei of various structures [61].

The paper also describes the physicochemical processes occurring in the synthesis reactor at plasma temperatures [56], taking into account the behaviour of particles in electromagnetic fields at extreme temperature and pressure gradients. It was proposed a sequence of substance organization levels during the formation of carbon structures according to the size level, and the self-organization of systems during electric arc evaporation of graphite or graphite-containing electrodes was also studied. The mechanisms of formation of soluble (fullerenes and fullerene-like structures) and insoluble (nanocomposites, CNT, graphene sheets) carbon nanostructures [61] are considered. It is important for understanding the nature of the electric arc method of CNS synthesis and the possibility of predicting the products obtained by this method in advance.

In 2004, scientists from USA and Japan in a joint work [57] also asked the question about the role of a liquid phase in EAS process, as well as the difference in the properties of CNP obtained in liquid nitrogen and deionized water. The studies were carried out at direct current on an electric arc plant in a liquid environment using of graphite cathode and a composite anode containing Ni ( $\approx 0.7 \text{ mol.}\%$ ). The duration of one synthesis cycle was 97 s, while the output of CNP powder was 0.57 mg/s, and the deposit output was 4.5 mg/s.

During the analysis of CNP synthesized by the electric arc method in liquid nitrogen, new particle structures were discovered: carbon nanohorns (CNH) hybridized with carbon nanoclusters (CNC) containing Ni (CNH-CNC) [57]. When deionized water was used as a liquid phase, CNH-CNC particles were not detected, but CNC containing nickel were found. Therefore, the liquid nitrogen environment can play an important role in the formation of carbon horn structures.

The proposed theoretical model for the formation of a complex of CNH-CNC particles containing nickel (Fig. 4) considers the chemical inertness of nitrogen ( $N_2$ ). The model under consideration implies a three-stage process of CNH-CNC formation. At the first (I) stage, car-



Fig. 4. Schematic model of the formation of CNH hybrid particles including CNCs containing Ni [57]: (a) stage I — high temperature zone; dissolution of carbon in a nickel nanoparticle; carbon steam; (b) stage II — cold gas bubble; the formation of CNC; the nucleation of the complex; (c) stage III — rapid quenching of synthesis products; synthesis of the CNH-CNC complex; stabilized product

bon and nickel evaporate from the anode under the action of high-temperature electric arc plasma. Evaporated carbon and nickel turn into the gas phase and are spent on the synthesis of carbon nanostructures in the arc zone (Fig. 4, a). At the second (II) stage, nickel nanoparticles and formed carbon nanoclusters supersaturated with carbon vapour are transferred to the cold zone inside the gas bubble. When atomic carbon or carbon nanoclusters collide, nanohorns (CNH) are formed [99]. At the moment of catalytic growth of carbon nanostructures, CNC are formed on the nickel surface in the synthesis zone (Fig. 4, b). At the third (III) stage, the horns aggregate around the CNC, which serves as the nuclei (Fig. 4, c) of the CNH-CNC particle.

Thus, each type of liquid environment, at influence of an electric arc, can stimulate the growth of various hybrid modifications, which requires scientists to study in detail any suitable environment for CNP electric arc synthesis.

Japanese researchers raised the question of the effect of the catalyst vapours concentration during EAS in a liquid environment [100]. Electric arc syntheses were carried out in liquid nitrogen using a graphite cathode and a composite anode containing various amounts of nickel (0-28.1 mol.%). At a constant current value, an electrode was fed horizontally into a volume of a liquid environment (300 ml) with an interelectrode gap of 1 mm. After electric arc synthesis in liquid nitrogen for 45 s, a bulk deposit was obtained.

When the anode was evaporated without a catalyst (Ni), high-purity single-walled carbon nanohorns (SWCNH) were observed in the synthesis products. CNH were encapsulated in several graphite shells. The concentration of nanotubes and multifaceted wireframe particles was very low. For the synthesis of SWCNH containing nickel particles, it is necessary to evaporate an anode, which contains >0.64-7 mol.% Ni

(Table 1). Such nickel particles usually have an f.c.c. lattice [57]. However, to detect CNS containing nickel particles, it is necessary to perform a thorough scanning. During evaporation of an anode with 1.8-4.6 mol.% Ni, most of the synthesized SWCNH contain nickel nanoparticles. In addition to nickel-containing SWCNH, single-walled carbon nanotubes (SWCNT) are also observed in this group of products. SWCNT form a network between catalyst particles (*Me*) and in many cases, they are combined into bundles.

The deposit formed at the end of the cathode during the evaporation of the anode containing 0.64-4.6 mol.% of the catalyst (Ni) (Table 1) is the main nanostructured product. The presence of multi-walled carbon nanotubes (MWCNT) was fixed in its volume. In addition, SWCNH with inclusions of nickel particles were found in the deposit as a by-product of synthesis, but the presence of SWCNT was not detected. During evaporation of the anode with 6.4-28.1 mol.% of the catalyst (Ni), no SWCNH and SWCNT are observed in the synthesis products (Table 1). Instead, only agglomerated, almost spherical structures containing nickel particles are identified. This means that an excessive nickel vapour concentration in the electric arc zone inhibits the formation of single-walled carbon nanostructures.

Japanese scientists carried out similar studies. When performing the synthesis in deionized water, the SWCNT were not detected [100]. Repeated experiments were carried out with a composite graphite anode containing  $\approx 1.8 \text{ mol.}\%$  Ni, but SWCNT were never found [100]. At the same time, SWCNT were obtained by the method of synthesis in liquid nitrogen using a cathode with similar nickel content. Thus, the researchers concluded that a relatively inert environment in the elec-

Synthesis product	MWCNT, SWCNH (10%)	CNH	SWCNH, SWCNT	Nanocomposites (spherical particles)
Anode material	Graphite	Graphite	Graphite	Graphite
Cathode material/ catalyst content (Ni)	Graphite with Ni (0.64-4.6 mol.%)	Graphite with Ni (≥0.64-7 mol.%)	Graphite with Ni (1.8-4.6 mol.%)	Graphite with Ni (6.4-28.1 mol.%)
Synthesis environ- ment	Nitrogen	Nitrogen	Nitrogen	Nitrogen
Synthesis time, s	45	45	45	45
Volume of liquid environment, ml	300	300	300	300
Interelectrode gap, mm	1	1	1	1
Deposit	+	+	+	+

 Table 1. Synthesis of carbon nanostructures [57]

tric arc region plays a significant role in the formation of single-wal led structures.

The scientific community of Japan and Ukraine returned to the analysis of platinum (Pt) catalyst vapours, motivated by the energy produced by a fuel cell with a polymer electrolyte for hydrogen energy [101–104]. Carbon nanoparticles are an excellent carrier of a platinum catalyst. They have a developed surface, which is used to convert hydrogen into a proton, oxidize a proton, and produce water, which leads to the generation of electricity in a fuel cell with polymer membranes [105, 106]. Currently, many tries have been made to obtain carbon nanoparticles with a platinum load [101–108]. Typically, such particles are produced chemically in two steps. At the first (I) stage, carbon particles with a developed surface are obtained. At the second (II) stage, a solution of platinum compounds  $(H_2PtCl_6)$  is prepared and the carbon material is moistened with it. If the carbon material impregnated with the solution is treated at high temperature in a hydrogen environment, the  $H_2PtCl_6$  compound is reduced to metallic platinum (Pt) on the surface of the carbon particles.

When considering CNP as potential carriers of platinum, it can be assumed that it is more profitable to obtain single-walled carbon nanostructures. This will significantly increase the advantage in the mass production of platinum-containing structures for fuel cells.

The authors of [101] carried out electric arc synthesis in liquid nitrogen (3000 ml) using a graphite cathode and composite anodes containing a small amount of platinum (0.4 at.%) and 1.3 at.%). The interelectrode gap was 1 mm. At the same time, Ukrainian scientists focused on the creation of CNS that already contain a platinum catalyst in their structure [102–104, 106, 109]. To do this, vaporization of graphite of FGDG-7 grade using a catalyst (Pt) was carried out in a helium environment. Hollow consumable graphite anode electrodes containing a platinum wire catalyst fixed with graphite dust were used in this work. Thus, carbon nanomaterials containing platinum were created: fullerenes, nanocomposites, graphenes, single-walled carbon nanotubes (SWCNT) and multi-walled carbons. Scientists have conducted investigations at the micro- and nanolevels of the morphology and structure of materials formed on the cathode, and also studied the influence of platinum vapour on the processes of nanostructures formation. Using x-ray microanalysis method, it was found that most amount of the platinum with the condensate flow settles on the reactor walls. According to the data of emission spectral analysis, the largest amount of platinum (>1% wt.%) is accumulated in wall soot. A part of platinum (less than <1 wt.%) in the cationic state under the action of a strong electric field, together with carbon vapour, moves to the cathode, forming a Pt-containing deposit. It was found that platinum is present in the deposit despite the

high temperature of the deposit formation zone (up to  $11727 \,^{\circ}$ C) [56], which significantly exceeds the boiling point of Pt (3800  $^{\circ}$ C). Platinum in the synthesis products is distributed as follows: the deposit core — less than 0.001%, the deposit shell — less than 1%, and the wall soot — more than 1%.

For Japanese researchers, the main problem of synthesis only in liquid nitrogen  $(N_2)$  was the formation of a deposit [100]. Received deposit was formed at the edge of the cathode with MWCNT and the presence of SWCNH in the synthesized powder product [100]. It was also found that with a higher concentration of platinum (Pt), the output of powders and the volume of the deposit increase. Platinum nanoparticles were observed in the volume of the deposit. In the powder product, particles of amorphous carbon and SWCNH were found, on the surface of which platinum was dispersed. It has been shown that the particle size of platinum depends on the concentration of Pt in the anode. In addition, it was found that at a concentration of 0.4 at.% Pt in the anode, the percentage of platinum particles with a diameter of less than 5 nm is 90%. While when the anode with a Pt concentration of 1.4 at.% evaporates, the concentration of the catalyst vapour increases, and the content of fine platinum particles is about 60%. The particle size of platinum in the last evaporation method is slightly larger than the particle size of platinum received in the first evaporation method. Thus, the Japanese scientists found that the particle size of platinum could be controlled by adjusting the concentration of platinum in the anode. Moreover, in the cited work, MWCNT agglomerates with a platinum load in the form of a deposit were obtained.

In most cases, the issue of agglomeration of the final product during EAS in a liquid environment was not considered or was solved by a short synthesis time (30–97 s) and a reduced consumption of reagents for deposit formation [73–60, 76, 95, 100, 101]. Ukrainian researchers went further and created a special plant, with the help of which they solved the issue of CNS agglomeration during electric arc synthesis. The solution is to install a special magnetic vibrator with a power of 50 Hz on the electrode. It allows you to bring and separate the electrodes in a fraction of a second, thereby creating an interrupted electric arc. Synthesis time in the modernized setup began to average  $1 \cdot 10^{-9}$  s, and the temperature of the liquid environment was kept in the range from 4 K to 340 K at a current strength of 200–300 A [67–72, 75, 83, 110]. Upon such conditions, provided by a simple upgrade of the equipment, during the synthesis, CNS nuclei have time to form and quickly quench in a liquid environment.

The problem of all researchers of the electric arc synthesis of CNS is the deposit formed on the cathode. Ukrainian scientists also solved this issue by increasing the gap between the electrodes, which was



*Fig. 5.* Scheme of equipment for obtaining CNP by an arc discharge in water with a forced convective flow [76]

Fig. 6. Scheme of an electric arc plant for the synthesis of CNS, where a liquid hydrocarbon environment is used as a source of carbon (C) in the synthesis zone [59]

>1 mm [67–72, 75, 83, 110]. It led to the absence of a deposit on the cathode electrode. A similar effect is explained by the fact that the charged particles formed in the synthesis zone of the electric arc must now overcome the barrier of the liquid environment, which is extremely problematic. The elimination of deposit formation is an important achievement, since the mass of the synthesis deposit often exceeds the mass of the synthesized nanoproduct.

In a joint work, research scientists from Japan and Thailand attempted to solve the problem of particle agglomeration at EAS in a liquid environment. They focused their attention on the electric arc parameters, which control the CNP synthesis process, and used a forced convective jet in the synthesis process [76]. Electric arc synthesis was carried out in deionized water using graphite electrodes (C/C) with an interelectrode distance of about 1 mm. During the synthesis, deionized water was circulated using a centrifugal pump. Water for the pump was captured near the reactor wall, and then the flow exited through a nozzle 4 mm in diameter at a distance of 15 mm from the arc epicentre (Fig. 5). The authors report that a massive deposit is formed during the synthesis, while very little powder product is obtained.

This method significantly reduces the agglomeration of structures, but increases the number of crystal defects in the walls of MWCNT synthesized at an extremely strong water flow ( $3.2 \text{ dm}^3/\text{min}$ ). In the course of investigations, it was shown that there is an optimal operating mode for electric arc synthesis with a forced convective flow (at a stream flow of  $1.36 \text{ dm}^3/\text{min}$ ), where the obtained CNP have a well-ordered graphitized structure, and their output is of 9.32 g/h. In addition, when using a convective stream, the output of the final nanoproduct increases, and

the process of quenching CNP in the liquid phase is accelerated with significantly less agglomeration than when synthesized by an electric arc in the liquid phase without the use of a convective stream.

Dutch and Japanese scientists proposed an unusual solution to the problem of nanostructure agglomeration [59]. The authors realized a number of experimental studies to determine the effect of the number of carbon atoms and their bonds (C-C and C-H) in a solvent molecule, as well as the influence of the metal electrodes type (Fe/Fe, Ni/Ni) on the formation of ordered carbon nanostructures (Fig. 6) under conditions of thirty-second synthesis. The synthesis was carried out in two solvents: cyclohexane ( $C_6H_{12}$ ) and toluene ( $C_7H_8$ ), having only a single bond and a benzene ring. The experimental plant consists of a pair of electrodes (anode and cathode) immersed in 1000 ml of a hydrocarbon solvent. A pair of iron and nickel rods had purity of 99%, and, during the evaporation of each pair, they maintained an interelectrode gap of less than 1 mm. As a result of the research, it was suggested that the amount of carbon included in the solvent molecule determines the rate of carbon nanostructures formation. Thus, toluene can be converted to CNS more efficiently than cyclohexane. It is also believed that the benzene ring in toluene contributes more to the formation of nanocarbon than the single bond in cyclohexane. The  $\pi$ -electron belongs to the benzene ring and can work efficiently creating nanostructures. In addition, in a number of experiments, it was shown that toluene more efficiently turned into graphite compared to cyclohexane.

In the course of experiments using various pairs of iron and nickel rods, it was found that the synthesis of carbon nanostructures using iron electrodes produces fewer nanoproducts compared to using nickel electrodes [59]. Moreover, no layered structure is formed. In the case of using a nickel electrode, a graphite sheet with a nickel core is obtained in both toluene and cyclohexane.

Thus, steps have been taken to understand that not only the liquid environment influences the final product output, but also the material of the metal electrodes. However, the concluded summaries require study that is more detailed and give rise to even more questions.

Interest in studying the process of CNP synthesis in low-temperature liquids [63, 77, 85, 89, 98, 100] smoothly turned into a hunt for obtaining high-quality CNP with maximum output in various liquid environments. This method made it possible to synthesize MWCNT [77, 85, 89, 98, 100], SWCNT [100], SWCNHs [100], nanoonions [63], metal-filled nanoparticles, CNT [77, 89, 100], and nanocomposites [66–72]. A common feature of the processes covered in these articles is that carbon enters to the synthesis region during the evaporation of graphite electrodes. However, the rate of obtaining CNM is limited by the rate of graphite electrodes evaporation. When an organic liquid is used as a carbon source for synthesis, the process continuity time and the rate of nanomaterial synthesis increase [60, 67–72, 75, 83, 110]. The process of carbon nanoparticles quenching does not differ from the process of nanoparticles quenching in noncarbon containing liquids. However, when considering nanometallic particles synthesized in noncarbon-containing dielectric liquids, the possibility of interaction of metal nanoparticles with oxygen ( $O_2$ ) was revealed, resulting in the oxides formation. In addition, when hydrocarbon liquids containing oxygen atoms are used in the process of CNS synthesis, the oxidation of metals will slow down or stop altogether, since nanometals will be covered with a thin nanostructured film.

Ukrainian scientists showed [67–72, 75, 83, 110] that, in the process of electric arc synthesis in a liquid environment using of metal electrodes (Fe, Co, Ni) (Table 2), metal carbides with nanocomposites formed. To confirm this fact, the authors provided the data of x-ray diffraction analysis, Raman scattering of light and atomic force microscopy, which showed that the synthesized samples contain impurities of various modifications of carbon and metal carbides. As was noted in the works, in the process of synthesis, a powder electrode of a poured nature increases the productivity of the electric arc method for the synthesis of CNS [64, 68].

All over the world, research is underway on the process of plasmachemical synthesis in a liquid environment and the analysis of the resulting products is being carried out. Only a few pay attentions to the spent liquid environment after CNP synthesis. We believe that these

Sample	Phase composition	Content, %	D, nm
Fe powder, initial state	$\alpha$ -Fe	100	270
Fe powder after synthesis	$\alpha$ -Fe Fe <sub>3</sub> C	24 76	_ 24
Fe powder after heating	lpha-Fe Fe $_3 ext{C}$ Fe $_3 ext{O}_4$ FeO	73 11 16	110 40 100
Ni powder, initial state	Ni	100	150
Ni powder after synthesis	Ni Ni–C	96 4	150
Ni powder after heating	Ni	100	130

Table 2. Phase composition and coherent scattering region (CSR) value of iron and nickel powders before and after synthesis [68]



Fig. 7. Equipment for studying the change in the colour of the organic working solution in the electric arc synthesis of CNS [60]

solutions may contain new modifications of soluble organic compounds, which are sought by researchers around the world. Japanese scientists in their studies noting to the change in the colour of the organic working solution of benzene  $(C_6H_6)$  after EAS in a liquid environment using graphite electrodes (C/C) and interelectrode gap of 1 mm

(Fig. 7) [60]. This means that soluble organic compounds were formed in liquid benzene.

The output of the product of one such synthesis was 9.2 mg/s, and that of the deposit was 19.2 mg/s. As noted, the mass of the deposit obtained in liquid benzene is much larger than the mass of the deposit synthesized in a non-hydrocarbon environment. According to the authors of the work, the atomic interaction in organic solvents is more active. In addition, it was confirmed that fullerenes are not formed under these synthesis conditions.

An important question about the studying of the mechanism of formation of deposit for its possible subsequent utilization as a by-product of the electric arc synthesis of CNS was raised in Refs. [102, 103, 109]. As found in the works, in catalytic electric arc synthesis, the deposit



Fig. 8. Nanotubes produced in liquid helium without a catalyst

Fig. 9. Equipment for the continuous production of carbon nanotubes (CNT) from graphite electrodes (C/C) using an underwater ( $H_2O$ ) electric arc of alternating current [90]



Fig. 10. Automated system of electric arc synthesis of CNS [115]

components (core and shell) can be considered as independent products of plasma-chemical synthesis. Physicochemical methods of analysis have shown that the deposit core is filled with CNT, while the shell consists of graphene packets containing a trace amount of the used catalyst [102, 103, 109].

In addition, Ukrainian scientists were able to develop a non-catalytic method for the synthesis of carbon nanotubes by the electric arc plasma-chemical method [111–113]. This is a very valuable achievement, since, in order to obtain pure CNS, they are treated with acids to remove the catalyst. This procedure is relatively expensive, and most importantly, it makes the CNS defective and chemically contaminated. The authors of the technology carried out non-catalytic electric arc synthesis of CNS in an environment of liquid helium during the evaporation of two graphite electrodes [113]. The results of the analysis of the synthesis products showed that the resulting CNS does not require additional purification and contains up to 90% carbon nanotubes (Fig. 8). Such results are difficult to achieve using various methods of nanotube purification.

Based on the foregoing, the electric arc synthesis method is of practical interest for the production of carbon nanostructures on an industrial scale, which was realized by Hungarian researchers in 2003 [90] (Fig. 9). Many researchers have automated systems for the electric arc synthesis of CNS, which facilitated the studying of this method [115] (Fig. 10).



Fig. 12. Dependence of the electrical conductivity of CNS/TiO, (3 wt.%) composites on the type of carbon nanostructures contained in ceramics [117]

gations is being carried out by Chinese and Ukrainian scientists in the field of studving the effect of a magnetic field on carbon nanomaterials obtained by evapora-

Verv interesting investi- $\mathbf{10}^{-5}$  $10^{-6}$ 

ting graphite electrodes (C/C) in liquid nitrogen and distilled water. The products of such synthesis upon application of a transverse magnetic field were MWCNT, carbon onions, metal-encapsulated carbon onions, and single-walled carbon nanohorns [116] (Fig. 11). During the experiment, it was found that, if a transverse alternating magnetic field applied to the arc discharge, this would disrupt the stability of the electric arc column. As was shown in the materials of this literature review, the instability of the electric arc column can catalyse the process of synthesis of defective carbon nanostructures.

Ukrainian scientists affirm that CNS obtained by the electric arc method in a liquid environment, due to their high dispersion, are suitable for use in CJP 3D printing technology [117] and for creation of new materials and composites as consumable raw materials for FDM and SLA 3D printing technologies [21–26, 118, 119].

In investigations on CJP 3D printing technology, work was carried out on the creation of electrically conductive ceramics from various CNS (Fig. 12). Based on this composite, electrodes for fuel cells were created, on which hydrogen  $(H_2)$  is oxidized with the excretion of electric current [117]. This is an important result for hydrogen energy today.

Fig. 11. Scheme of an electric arc plant for synthesis in a liquid environment with a built-in transverse magnetic field [116]



## 3. Conclusions Followed from Analysis of the Main Results

Based on the review of the literature, we can conclude that currently the arc synthesis of carbon nanomaterials in a liquid environment is the least studied method. The analysis of scientific-research works suggests that the electric arc synthesis of nanostructures in the liquid phase allows as follows below:

• the synthesis of a wide range of carbon nanostructures such as carbon nanoclusters [57], carbon nanohorns [57], single-walled carbon nanohorns [100], single-walled carbon nanotubes [100], multi-walled carbon nanotubes [76, 77, 85, 89, 98, 100], nanoonions [63], and nano-composites [66-72];

• to perform experiments in a liquid dielectric environment of various chemical compositions, which takes part in the synthesis process [57, 59, 60, 67-72, 75, 83, 99, 110-113];

Synthesis product	SWCNT, SWCNH (10%)	SWCNT	SWCNH, SWCNT	CNT (85–90%)
Anode	Graphite	Graphite	Graphite	Graphite
Cathode	Graphite with Ni (0.64-4.6 mol.%)	Graphite with Ni (1.8 mol.%)	Graphite with Ni (1.8-4.6 mol.%)	Graphite
Synthesis environment	Nitrogen	Nitrogen	Nitrogen	Helium
Synthesis time, s	45		45	30 min
Volume of liquid envi- ronment, ml	300	_	300	500
Interelect- rode gap, mm	1	1	1	1
Catalyst states after synthesis	f.c.cNi		f.c.cNi	_
Deposit	+	+	+	— (used a mag- netic vibrator)
Ref.	[57]	[100]	[57]	[113]

Table 3. Synthesis of single-walled carbon nanostructures

• to influence the products of electric arc synthesis by varying the chemical composition of the electrodes (anode and cathode) [57, 59] and the liquid environment [60, 67–72, 75, 83, 110–113];

• to solve the issue of bulkiness of equipment for electric arc plasma-chemical synthesis of nanostructures;

• does not require an expensive and bulkiness vacuum system [47-108];

• to perform the synthesis of CNS in cryogenic liquid environments [113];

• to provide a continuous process of synthesis of nanoproducts [90, 114, 115];

• the synthesis of nanostructures by this method makes it possible to create new materials and composites [21-26, 117-136].

The phenomenon of synthesis of defective carbon nanostructures can be considered as a method for increasing the adsorption area of nanoparticles. For this reason, a list of conditions was created that lead to an increase in defective formations in the process of CNS electric arc synthesis:

- convective stream of the working solution with a speed of  $3.2 \text{ dm}^3/\text{min}$  in the synthesis zone [76];

• synthesis of CNS in cryogenic liquid environments [58];

• application of low-quality cheap graphite in the synthesis process [58, 96].

Since one of the most valuable products of the electric arc method is single-walled carbon nanostructures, Table 3 was created. In this table, the conditions for the synthesis of such structures are listed. The analysis of scientific-research works showed that an excessive concentration of catalyst vapours (Me) in the electric arc zone inhibits the synthesis of single-walled carbon nanostructures, such as single-walled carbon nanohorns and single-walled carbon nanotubes. It is also assumed that a relatively inert environment in the electric arc region plays an important role in the synthesis of SWCNS [57, 100, 113].

One of the most important results of the analysis is that, in the case of an electric arc, the chemical composition of the dielectric liquid environment and electrodes can stimulate the growth of various hybrid modifications of CNS [57, 59–61, 67–72, 75, 83, 110–113].

The scientific problem of agglomeration of carbon nanoparticles during their synthesis by the electric arc method in a liquid environment was solved by installing a special magnetic vibrator on the electrode. It makes it possible to bring the electrodes together and apart it in a fraction of a second, thereby creating an intermittent electric arc [67-72, 75, 83, 110]. This innovation makes it possible to control the high speed of the synthesis process. The problem of nanostructure agglomeration was raised in almost every article of the electric arc synthesis method [57-60, 73, 76, 95, 100-101]. The scientific problem of deposit formation, as a by-product of CNS synthesis by the electric arc method in a liquid environment, is solved by increasing the interelectrode gap (>1 mm) or by installing a special magnetic vibrator, which allows bringing the electrodes together and apart it in a fraction of a second [67–72, 75, 83, 110].

Various modes of industrial synthesis of single-walled carbon nanostructures have been developed (Table 3).

Modes (regimes) for creating defective carbon nanostructures have been developed as a method for increasing the adsorption area of nanoparticles [58, 76].

The developed method improves the productivity of electric arc synthesis of CNS in a liquid environment, where a poured powder electrode is used [68].

At present, the following aspects of the electric arc synthesis of carbon nanostructures still remain poorly understood:

• a model of the process of electric arc evaporation of electrodes and the mechanism of growth of nanostructures during the synthesis of CNS in a liquid environment has not been proposed;

the features of the influence of a liquid environment and types of electrodes on the structure and morphology of CNM formed during synthesis have not been studied; this does not allow considering the effect of the nature of the environment on the kinetics and thermodynamics of the processes of synthesis of CNM;

• the process of separating of metal nanoparticles by size fractions has not been studied;

• the possibility of non-catalytic synthesis of nanotubes by the electric arc plasma-chemical method has not been studied;

• the possibility of obtaining graphenes and graphene packages by an electric arc plasma-chemical synthesis method has not been studied.

• compounds, which are formed and dissolved in hydrocarbon liquid environment after the process of EAS, have not been studied;

• there is no 'road map' for the electric arc synthesis of CNS in a liquid environment, which takes into account various types of electrodes and liquid phases.

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#### ЕЛЕКТРОДУГОВІ МЕТОДИ СИНТЕЗУ КАРБОНОВИХ НАНОСТРУКТУР

Оглядаються (переважно авторські) публікації, присвячені питанням електродугового синтезу (ЕДС) різних карбонових наноструктур (КНС). ЕДС КНС можна здійснювати як у газовому, так і в рідкому середовищі. ЕДС у газовому середовищі має ряд переваг, таких як висока продуктивність і швидкість процесу конденсації, а також легкість у керуванні режимами. Одначе такий метод синтезу має також недоліки: він вимагає наявности складної вакуумної й охолоджувальної систем, які надають обладнанню громіздкости. Крім того, даний метод не вирішує проблему аґломерації синтезованих КНС і має побічний продукт синтезу у вигляді наросту (депозиту) на електроді. ЕДС у рідкому середовищі відрізняється більшою компактністю обладнання, оскільки не потребує систем вакуумування (процес перебігає за атмосферного тиску) та охолодження (рідке середовище відіграє роль тепловідведення). За такого способу синтезу використовуються різні типи діелектричних рідин — від дистильованої води та рідкого азоту до вуглеводневих розчинників, які можуть слугувати джерелом вуглецю в зоні синтезу. Змінюючи склад рідкої фази, можна досягти синтезу різних типів КНС. Також цей метод передбачає використання металевих електродів, які, окрім тривалого терміну експлуатації, можуть відігравати роль каталізаторів. При цьому частинки металу можуть бути інкапсульовані КНС, формуючи композити з різними магнітними властивостями. У деяких роботах було показано, що із застосуванням металевих електродів у процесі ЕДС у рідкому середовищі можуть утворюватися суміші карбідів металів. Рідке середовище після ЕДС ВНС також представляє науковий інтерес. Ймовірно, у рідкому середовищі містяться нові модифікації розчинних органічних сполук, пошуком яких займаються дослідники всього світу. Так, вчені виявили, що після ЕДС у рідкому середовищі з використанням графітових електродів робочий розчин (C<sub>6</sub>H<sub>6</sub>) змінив свій колір. Це свідчить про утворення у ньому розчинних органічних сполук. В огляді на основі літературних даних створено таблицю режимів для промислового синтезу одностінних КНС, а також наведено перелік режимів для створення дефектних КНС як методу збільшення площі адсорбції наночастинок. Зафіксовано вирішення важливих проблем методу ЕДС: аґломерації КНС, проблеми формування депозиту, підвищення продуктивности.

Ключові слова: плазмо-хімічний синтез, електродуговий розряд, карбонові наноструктури, карбонові нанокластери, карбонові нанотрубки, кріогенні середовища, рідкі діелектрики.