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CREATION OF 3D-PRODUCTS USING CARBON NANOSTRUCTURES AND 3D-PRINTING TECHNOLOGIES (FDM, CJP, SLA, SLS)

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The article discusses methods for obtaining carbon nanostructures (CNS), as well as their use to create three-dimensional (3D) products using FDM, CJP, SLA, SLS technologies. The process of manufacturing consumables for 3D printing technologies (FDM, CJP, SLA, SLS) for creating new composite 3D products based on carbon nanostructures is described. The paper contains a detailed description of which methods of CNS synthesis are more productive and how they allow you to guarantee the production of one or another type of CNS.

The paper analyzes the existing 3D printing technologies using CNS, developed a scheme for the full cycle of creating a 3D product containing CNS, taking into account various methods for the synthesis of CNS with the transformation of graphite or other carbon-containing material. It also describes the process of creating composite coils for FDM 3D printing from nanocomposite filaments (rigid polymer-CNS) based on a rigid polymer, which have undergone the process of preparation in a special mixer. The process of preparing consumables and printing a 3D volumetric product using FDM, CJP, SLA, SLS technologies using CNS is described. An overview of consumables for 3D products of FDM technology is presented. The analysis of composite 3D products (ceramic-CNS, rigid polymer-CNS) obtained by FDM and CJP technology was carried out.

The paper also describes the three most productive methods for the synthesis of CNS: plasma-chemical synthesis in gas or liquid and pyrolytic method. These synthesis methods make it possible to guarantee the production of a certain type of CNS and have a high quality of the obtained nanoproducts. Various types of CNS are described, including soluble (fullerenes and fullerene-like structures) and insoluble nanostructures (graphenes, carbon nanotubes, carbon nanofibers, nanocomposites, etc.).

Keywords: *FDM, CJP, SLA, SLS, 3D printing, 3D products, nanocomposites, carbon nanomaterials (CNM), pyrolysis, plasma chemical synthesis, polymer matrix, ceramic matrix.*

Introduction

Each method for the synthesis of carbon nanomaterials (CNM) has its own characteristics and makes it possible to obtain various types of nanoproducts. However, today only three methods of synthesis (plasma-chemical synthesis method in a gaseous medium or in a liquid medium, as well as a pyrolytic synthesis method) [1–9] are the most productive and make it possible to reliably obtain nanoproducts of a certain type CNM (fullerenes [10–13], fullerites [14], endofullerenes [15], graphenes [16-17], carbon nanotubes [18-19], carbon nanofibers, etc.).

Such and similar nanomaterials can play the role of fillers for the creation of modern composites [20–23], which is already being studied for 3D printing technologies [24–27]. Such materials make it possible to create modern and advanced materials in the field of promising sorbents [28–36], biological materials [37–42], fuel cells [43–46], solar panels [47–49], and much more.

An interesting fact is that some of the CNMs have already found application even in the field of hydrogen storage [50–54] and can even compete with existing materials of this class [55–72].

The type of systems of such materials (single-component [73–74] or multicomponent [75–78] systems) plays an important role, as does the preparation [79–84] and processing [85–88] of metals, what is confirmed by experimental [89–96] and theoretical data [97-99].

Methods of carbon nanostructure synthesis

Plasma chemical synthesis in a gas environment (electric arc synthesis in a gas environment) is a method that allows synthesis of CNS in the gas phase at plasma temperatures (12.000 K) [100], where the source of carbon atoms (starting carbon) is a graphite anode that evaporates in an electric arc. Often evaporating graphite anodes have a hole along their axis filled with catalyst. The chemical composition of the gas environment involved in plasma-chemical synthesis of CNS can also be varied.To date, only this method allows the synthesis of cheap fullerenes and fullerene-like products in large quantities. In addition, this method is used to synthesize carbon nanotubes, graphene, and graphene packets (Figs. 1, 2).

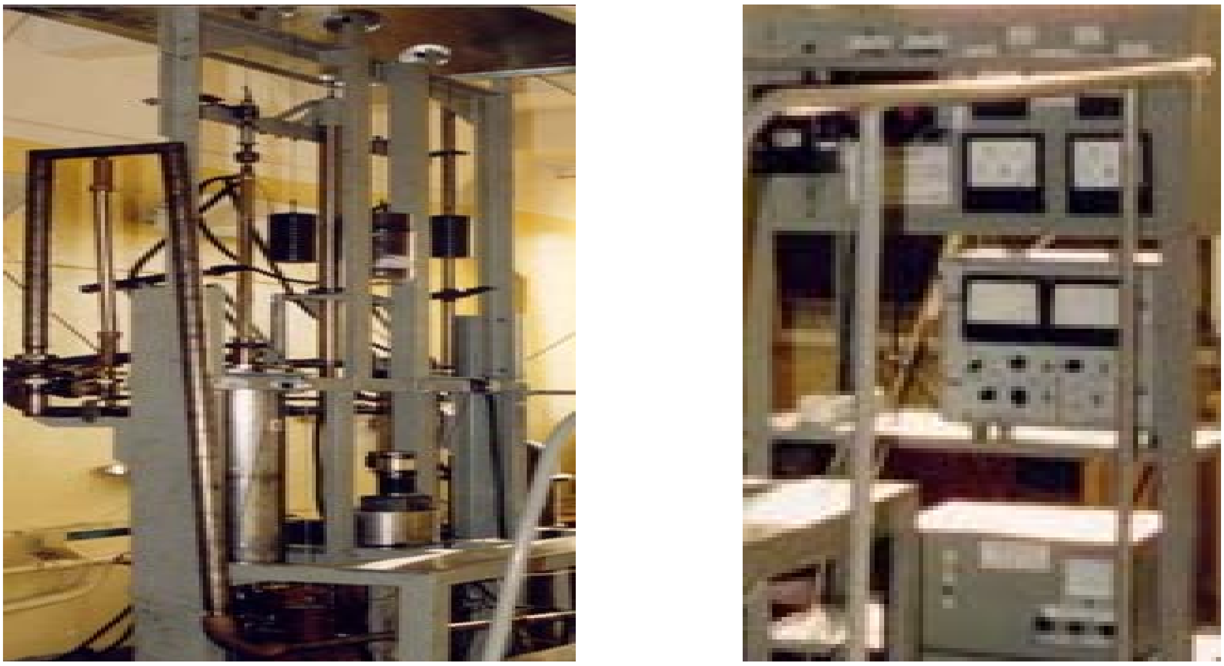

Fig. 1. Photo of the equipment for plasma-chemical synthesis of CNS in a gaseous environment

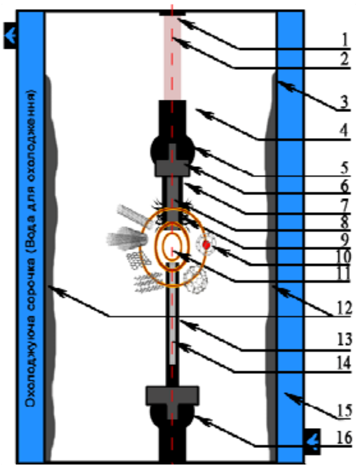

Fig. 2. General view of the process of plasma-chemical synthesis of CNS in a gaseous environment: 1 – cathode rod; 2 – the axis of the CNS synthesis reactor; 3 – reactor wall; 4 – helium-containing environment; 5 – a collet holding a non-consumable cathode electrode; 6 – non-consumable electrode (cathode); 7 –deposit; 8 –deposit core; 9 — depositrind; 10 – synthesized CNS; 11 – plasma; 12 – wall soot; 13 – evaporating anode; 14 – catalyst in the electrode (anode); 15 – cooling jacket (water for cooling); 16 – collet for fixing the anode electrode

Fig. 3. Photo of the equipment for plasma-chemical synthesis of CNS in a liquid environment

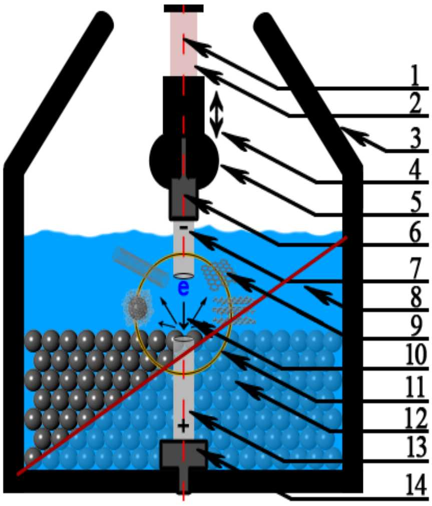

Fig. 4. The principle of operation of the plasma-chemical equipment for the CNS synthesis in a liquid environment: 1 – the axis of the CNS synthesis reactor; 2 –cathode rod; 3 – reactor wall; 4 – movement of the cathode; 5 – magnetic vibrator; 6 – collet holding the cathode electrode; 7 –cathode electrode; 8 – liquid environment; 9 – synthesized CNS; 10 – the direction of the flow of electrons; 11 – plasma; 12 – consumable powder anode electrode; 13 –comsumable anode electrode; 14 — a collet holding the anode electrode

Plasma chemical synthesis in a liquid environment is a method similar to plasma chemical synthesis in a gaseous environment, which differs in the synthesis medium (liquid phase). The liquid environment can be any liquid dielectric that contains or does not contain carbon atoms (distilled water) in the chemical composition of its molecule. The liquid environment takes a direct part in the CNS synthesis, therefore, the source of carbon atoms (starting carbon) in the synthesis zone can be both the evaporating graphite anode and the liquid dielectric environment (gasoline, ethers, alcohols, and other hydrocarbons).Today, this method is the only one that allows synthesizing large quantities of metal particles packed in a dense carbon shell (nanocomposite). Carbon nanotubes, graphene and graphene packets are also synthesized by this method (Figs. 3, 4).

For the first time, the method of plasma chemical synthesis in a liquid environment was made public during a report at the "Carbon" conference in the United States of America (USA) in 2000 by Ukrainian scientists (Shchur D.V. with his team) from Department No. 67 "Hydrogen Materials Science and Chemistry of Carbon Nanostructures" of Institute for Problems of Materials Science named after I.M. Frantsevich of the National Academy of Sciences of Ukraine [101–110].The method of plasma-chemical synthesis in a liquid environment is devoid of the disadvantages of a similar method of synthesis of CNS in a gaseous environment and significantly expands the range of synthesized products.

Fig. 5. Photo of the equipment for pyrolytic synthesis of CNS

The pyrolytic method is a technology for the CNS synthesis, where mixtures of gases are used.They play the role of a source of initial reagents under thermal influence. Under the action of high temperatures (775–1500 K), the gas component undergoes decomposition, after which, in the presence of a catalyst, CNS are formed.The type, structure, and characteristics of the obtained CNS are determined by the type (genus) of the used catalysts and gas mixtures.Gas mixtures may contain gaseous hydrocarbons that will serve as a source of carbon (source carbon) in the synthesis zone. Pyrolytic synthesis (Figs. 5, 6) is recognized as the cheapest method of synthesis of CNS (carbon nanotubes, carbon nanofibers, graphene, and others).

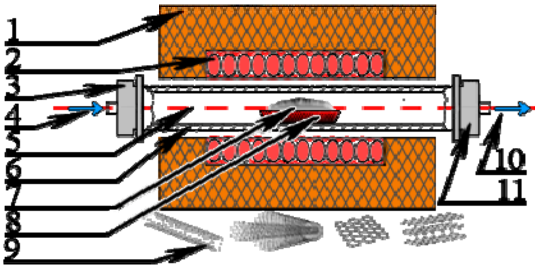

Fig. 6. The principle of operation of the equipment for pyrolytic synthesis of CNS: 1 – thermal insulation of the pyrolysis furnace; 2 – furnace heaters; 3 –1st flange of the reactor with a thermocouple; 4 – directed flow of carbon-containing gases; 5 – axis of the reactor; 6 – quartz reactor; 7 – catalyst layer; 8 – lining; 9 – synthesized CNS; 10 – directed flow of gases for disposal; 11 – the 2nd flange of the reactor

Additive technologies

Additive technologies is the technologies of layer-by-layer build-up and synthesis of objects. The use of 3D technology — a group of technological methods for the production of products and prototypes based on the step-by-step formation of the product by adding material to the base — was widely used.Among the applications of additive technologies, the production of functional products for the needs of the most interested branches of industry is the most in demand: aerospace, automotive and mechanical engineering, the military-industrial complex, medicine, in particular prosthetics, that is, where there is an acute need for the manufacture of high-precision products and their prototypes.It is especially effective to apply similar technologies in material-consuming, energy-intensive industries that use expensive materials.When using 3D printing, it is possible to save up to 90% of energy and materials in some cases. Today, soluble and insoluble CNS are most often used in the creation of modern composites suitable as consumables for 3D printing technologies.

Table 1. Analysis of 3D printing technologies using CNS

Print characteristics	FDM (Fused Deposition Modeling)	CJP (3DP) (Color Jet Printing)	LFS, DLP / SLA (STL) (Laser Stereolithography)	SLS (Selective Laser Sintering)
Minimal cost of a 3D printer, $	~5 000	~15 000	~550	~550
Printer model	CREATBOT F430	PROJET 860 PRO	ANYCUBIC Photon S	SINTERIT LISA
Materials that are used	All types of hard plastic	Gypsum, ceramics	Photopolymer resins	Flexible and durable polymeric powders
Carbon nanostructures (CNS) that are used	Nanocomposites, CNTs, CNFs, graphenes and graphene packages	Nanocomposites, CNTs, CNFs, graphenes and graphene packages	Fullerenes, fullerites, endofullerenes, exofullerenes, nanocomposites, CNTs, CNFs, graphenes and graphene packets	Nanocomposites, CNTs, CNFs, graphenes and graphene packages
Dispersion of consumables, mm	0.005 (5 µm)	0.05 (50 µm)	0.005 (5µm)	0.05 (50 µm)
Layer thickness, mm	0.0127	0.089–0.102	0.01–0.2	0.075
Operating temperature range, °C	до 420	13–40	20–26	180

3D printing is the process of converting a consumable material into a three-dimensional 3D product or 3D product using computer 3D modeling. As a rule, this procedure consists in layer-by-layer application of consumable material with its subsequent fixation.

A 3D printer is a device with software and control for the implementation of additive actions (production) of 3D products.

A 3D product is a 3D printed product or consumable product using 3D computer modeling.

There are different types of 3D printing, which differ from each other in the method of applying layers and the physical and chemical properties of the source material. The types of 3D printing presented in the Table 1 belong to the additive technologies capable of using CNS.From the data in the Table 1 it follows that today SLA 3D printing technology is the only one that has a wide range of possibilities for the CNS using. In addition, it is characterized by a minimum printing step and a minimum 3D printing temperature (~300 K) at a low cost of a 3D printer.

FDM (Fused Deposition Modeling)– this is a 3D printing technology using the method of extrusion of solid polymers or their composites (for example, a solid polymer — insoluble CNS) as a consumable for creating a 3D product. The 3D printing process is carried out by the method of layer-by-layer deposition of a molten filament of a solid polymer or its composite, which is supplied from the bays (Fig. 7, 8).

CJP or 3DP (ColorJet Printing)–this is a 3D printing technology using loose powder materials and binders (adhesives) as consumables (Fig. 9, 10).The 3D printing process is carried out by layer-by-layer application of a loose material (ceramics, plaster, plastic, etc.) or a mixture (for example, ceramics with insoluble CNS), after which each layer is treated with a binder.The binder not only glues, but can also color the particles in the right places, forming a 3D product. Such materials in the form of 2D and 3D products are used in aviation and space engineering, chemical engineering, in the creation of individual armor protection and in other areas.

SLA or STL / LFS, DLP, LCD (Stereolithography) –is a 3D printing technology that uses the method of laser stereolithography — the polymerization of liquid polymer or its suspensions (for example, liquid polymer–CNS) as a consumable when creating a 3D product.The technology is based on the layer-by-layer hardening of a liquid polymer under the influence of a laser beam (Fig. 11, 12). Liquid polymers for SLA technology are photopolymers that change physicochemical properties (such as solidification) when exposed to UV light.In a 3D printer with SLA technology, the source of ultraviolet light is replaced by a laser beam. The laser beam in different models of SLA 3D printers has different wavelength, power and pulse duration per focal point.All the above parameters of the laser beam are calculated depending on the type of liquid polymer used or its suspensions, as well as on the printing step of the 3D printer and environmental conditions (temperature, pressure, etc.). Today, this 3D printing technology is the only one in which all types of CNS (soluble and insoluble) can be used.

Fig. 7. 3D printer of FDM printing technology

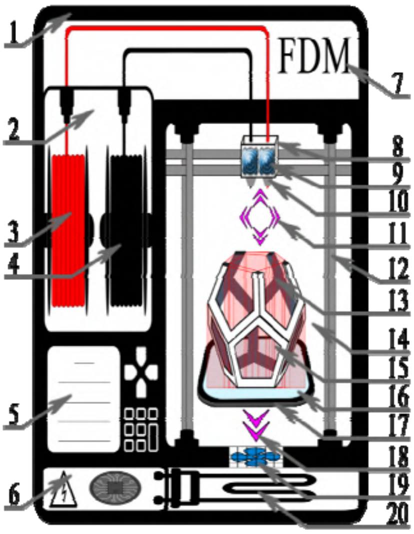

Fig. 8. Scheme of the operation principle of FDM 3D printing technology: 1 – FDM 3D printer body; 2 – hermetic compartment for polymer bays; 3 – a bay used as a support for printing a 3D product; 4 – high-temperature bay with CNS; 5 – 3D printer control panel; 6 – electronic part of the 3D printer; 7 – 3D printer printing type (FDM); 8 – high-temperature 3D printer head for printing; 9 – cooling mechanism of the high-temperature head; 10 – high-temperature head nozzle; 11 – the direction of movement of the high-temperature printing head; 12 – guides for the movement of the construction platform and the print head; 13 – printed 3D product support; 14 – camera for building 3D products; 15 – 3D products with the CNS; 16 – special coating of the working 3D printed table; 17 – a platform for building 3D products; 18 – the direction of movement of the working 3D printed table; 19 – temperature pump in the printing chamber; 20 – a heating element with a thermocouple

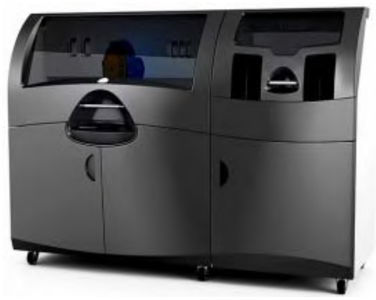

Fig. 9. Appearance of the CJP 3D printer

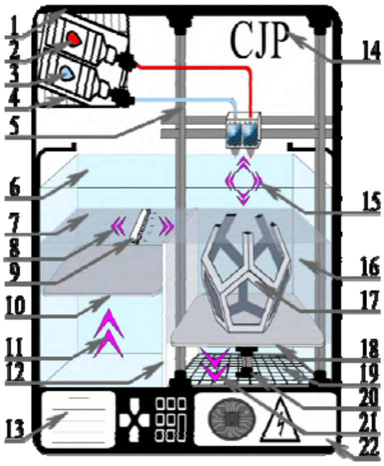

Fig. 10. Scheme of the operation principle of CJP 3D printing technology (color printing): 1 – CJP 3D printer body; 2 – expendable material (catalyst from CNS); 3 – consumable binder; 4 – sealed compartment for consuma-bles; 5 – guide platforms of construction and printing head; 6 – working compartment of the 3D printer; 7 – camera with 3D printer consu-mables (ceramics with carbon nanostructures); 8 – the direction of the layering brush; 9 – a brush for applying layers for construction; 10 – a platform supplying consumables; 11 – plat-form movement direction; 12 – blind partition of theworking compartment; 13 – 3D printer control panel; 14 – printing type of 3D printer; 15 – direction of movement of the printed head of the 3D printer; 16 – camera for building 3D products; 17 – 3D product with carbon nano-structures; 18 – a platform for building 3D products; 19 – ports for cleaning the construc-tion chamber; 20 – construction platform guide; 21 – platform movement direction; 22 – the electronic part of the 3D printer.

Fig. 11. Appearance of the SLA 3D printer

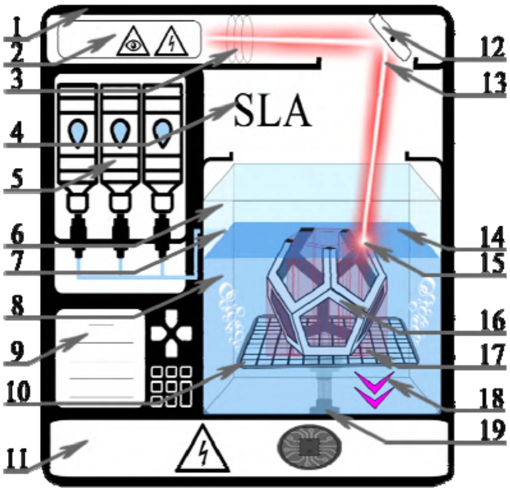

Fig. 12. Scheme of the operation principle of SLA 3D printing technology: 1 – 3D printer body; 2 – laser; 3 – lenses; 4 – printing type of 3D printer; 5 – consumable material (liquid polymer with CNS); 6 – camera for building 3D products; 7 – liquid polymer level control sensor; 8 – liquid polymer with CNS; 9 – 3D printer control panel; 10 – a platform for building 3D products; 11 – electronic part of the 3D printer; 12 – scanning mirror; 13 – laser beam; 14 – polarizable layer of liquid polymer with CNS; 15 – printing of a 3D product; 16 – 3D product from CNS; 17 – 3D product support; 18 – platform movement direction; 19 – construction platform guide

SLS (Selective Laser Sintering)–this is a 3D printing technology, which consists in the layer-by-layer sintering of loose (Fig. 13, 14).The working principle of SLS powder solid polymers or their composites (for example, solid polymer-insoluble VNS) using a laser beam technology 3D printing combines the CJP technology using loose materials and the SLA technology using the method of sintering polymers with a laser beam. Immediately before the 3D printing process, the consumable (shredded solid polymer or its composite) is heated almost to the melting temperature, after which the laser beam is directed to the focal areas of the consumable, sintering them together layer by layer.

SLS technology, unlike other types of 3D printing, provides only a partial melting of the consumable material, which is necessary only to combine it into a single element. The main disadvantage of SLS technology is the high cost of consumables.

This technology has the following advantages: high accuracy of 3D printing, strength and quality of 3D products; the printing consumable has sufficient rigidity to exclude support elements in the process of 3D printing products.

Fig. 13. Appearance of the SLS 3D printer

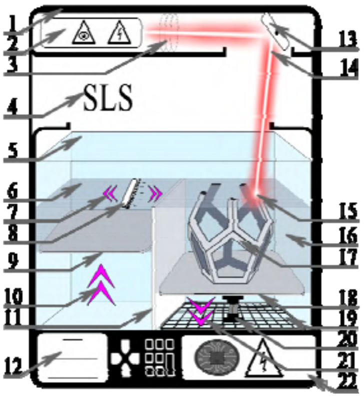

Fig. 14. Diagram of the working principle of SLS 3D printing technology: 1 – 3D printer body; 2 – laser; 3 – lenses; 4 – printing type of 3D printer; 5 – working compartment of the 3D printer; 6 – camera with 3D printer consumables (polymer from CNS); 7 – the direction of the layering brush; 8 – a brush for applying layers for construction; 9 – a platform supplying consumables; 10 – direction of movement of the material feeding platform; 11 – blind partition of the working compartment; 12 – 3D printer control panel; 13 – scanning mirror; 14 – laser beam; 15 – printing of a 3D product; 16 – camera for building 3D products; 17 – 3D-product from CNS; 18 – a platform for building 3D products; 19 – ports for cleaning the construction chamber; 20 – construction platform guide; 21 – platform movement direction; 22 – the electronic part of the 3D printer

Creation of a 3D-product containing a CNS

With an in-depth analysis of the three main methods of synthesis of carbon nanostructures (electroarc plasma chemical method of synthesis in gaseous and liquid environment, pyrolytic method) and all suitable 3D printing technologies that use CNS as raw materials (FDM, CJP, SLA, SLS), it is possible to develop the scheme of the full cycle of creating a 3D product with the content of the CNS.The scheme of the full cycle of manufacturing of such 3D products takes into account the state of the initial carbon for the synthesis of the CNS, and also includes the preparation of the CNS for various 3D printing technologies with post-forming processing of the printed 3D products (Fig. 15).

The cycle of transformation of graphite or other carbon-containing material into a printed functional 3D product on a 3D printer can be divided into three stages (Fig. 15): I — selection of the starting material and selection of the method of the CNS synthesis; II — preparation of CNS — consumable material for 3D printing; III — printing of a 3D product and its post-forming processing.

Stage I — selection of the starting material and selection of the synthesis method of CNS. The transformation cycle includes the production of insoluble carbon nanostructures, such as graphenes, CNTs, and CNFs, as well as nanocomposites (metal particles encapsulated in a carbon matrix), using one of three synthesis methods. The synthesis of soluble carbon nanostructures (fullerenes and fullerene-like structures) is also considered as the main product of the plasma chemical method of synthesis of CNS in a gaseous environment.

Stage II — preparation of CNS and consumables for 3D printing. Unfortunately, today, directly after synthesis, CNS are unsuitable for use in 3D printing technologies (FDM, CJP, SLA, SLS). For each 3D printing technology and for each CNS, there is a pretreatment technique that allows not only to increase the strength of the composite in the 3D product, but also to increase the effect of the interaction of the filler (CNS) with the supporting matrix (ceramic or polymer).

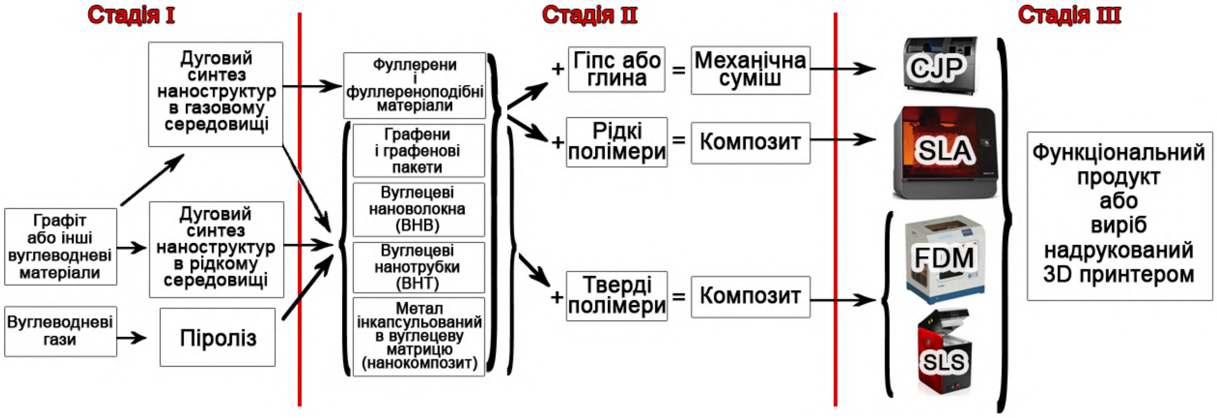

Fig. 15. Scheme of the full cycle of creating a 3D product that contains CNS, taking into account the transformation of graphite or other carbon-containing material into CNS

Usually, the CNS pre-treatment technology includes heat treatment at a temperature of 375–575 K, which allows removing the resinous component of CNS and activating the surface of nanostructures to improve polymer adhesion. Chemical processing of CNS is also possible, but, as a rule, it is used for individual composites with narrowly focused specificity.

After thermal or chemical treatment, the conglomerates of insoluble CNS are crushed on a ball mill (Fig. 16) and divided into different fractions by passing through a sieve of the required dispersion. This process is very important because each printer has its own 3D printing step, and the size of the carbon nanostructures must not exceed it. For this reason, conglomerates of carbon nanoparticles are subject to re-grinding.

Fig. 16. Ball mill

CJP technology. After technological processing of CNS, they can be used to prepare a mechanical mixture (for example, ceramics–CNS) for 3D printers of CJP technology. Such mixtures should have high flowability and dispersion.Mechanical mixtures for the CJP technology are prepared by thoroughly mixing the CNS and the support matrix, which allows the CNS to be evenly distributed in the volume of the composite. The percentage content of CNS can vary depending on the purpose of using the mixture. As practice shows, similar composite materials have increased electrical conductivity and resistance to thermal and mechanical shock.

FDM and SLS technology. FDM, SLS and SLA 3D printing technologies require a stage of composite preparation (Stage II) in special mixers (Fig. 17), where the process of mixing the filler (processed CNS) and the carrier matrix (polymer) takes place.

In the case of FDM and SLS technology, it is necessary to prepare composites based on solid polymers (solid polymer–CNS), after which they are crushed into crumbs to the required dispersion in special shredders. With SLS technology, the composite crumb can be used without pretreatment.For FDM technology, after obtaining the composite crumb, it is necessary to melt the composite thread by the extrusion method. As a rule, such threads are stored in bays (Fig. 18), sealed in hermetic vacuum packages. Such bays are convenient for transportation and storage at the places of their use.

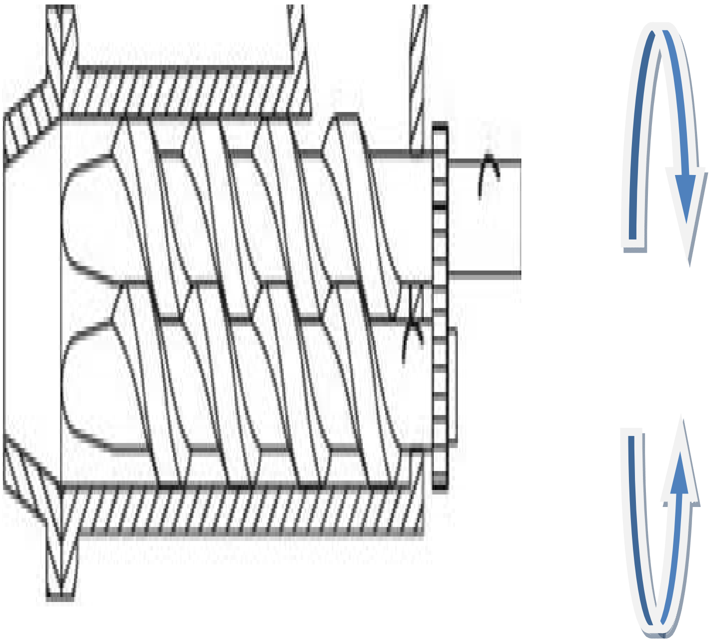

Fig. 17. A mixing device with screws that engage and rotate in the opposite direction

Fig. 18. Composite threads (hard polymer–CNS) in the bays

An important element of the production cycle of the raw material composite (solid polymer – CNS) for FDM and SLS 3D printing technology is the process of uniform mixing of CNS with a solid polymer (supporting matrix of the composite).The main problem of creating a composite is the appearance of pores due to the capture of air bubbles by carbon nanostructures when they enter the polymer matrix. This effect is eliminated by pre-treatment of CNS and solid polymer with the same wetting reagents.To prepare the composite, these reagents are added to the heated mixing device (Fig. 17), which ensures high-quality and uniform mixing of the components due to screws that cling and rotate in the opposite direction.

In the case of improper introduction of CNS and poor mixing of the composite, carbon nanostructures clump together, which further enhances the process of formation of air cavities in the composite near the CNS.Studies of the strength of FDM and SLS 3D printed products show that when an improperly prepared composite is stretched, the rupture occurs exactly at the places of such defects. In addition, conglomerates from CNS are capable of clogging the nozzles of extruders when melting composite thread, and can also disable 3D FDM printers. That is why it is so important to eliminate the coagulation effect of CNS in the process of preparing the composite (solid polymer–CNS).

The SLA 3D printing technology is characterized by the smallest thickness of the print layer (from 0.01 mm) and is the only one capable of creating composites (liquid photopolymer–soluble CNS) based on a liquid photopolymer containing fullerenes and fullerene-like nanostructures in the 3D printing process (Table 1).

Mixtures for SLA 3D printing, prepared from liquid polymer and insoluble CNS, have the form of a pulp (suspension), which must be used in 3D printing as soon as possible, before the processes of sedimentation and coagulation of CNS begin. 3D products made of such a composite can compete in terms of their characteristics with products of FDM 3D printing technology.

In addition, the use of complex composites (liquid polymer–soluble CNS–insoluble CNS) in SLA 3D printing has recently been of particular interest. They are created in two stages: first, soluble CNS are dissolved in a liquid polymer (photopolymer) by the method of long-term mixing with exposure to constant temperatures, and then insoluble CNS are added with the same mixing.The product of such a process is a suspension, which may lose its working characteristics during long-term mixing or settling. Therefore, the complex composite suspension should be used immediately after preparation.Similar materials have increased compression elasticity, high mechanical wear resistance and other improved physical and chemical characteristics. All this allows SLA technology to create 3D products of high complexity (thin walls and small elements) from composites that have no analogues in other 3D printing technologies.

Stage III – printing of the 3D product and its post-forming processing. After preparing the necessary consumable mechanical mixtures or composites, depending on the 3D printing technology (FDM, CJP, SLA, SLS), 3D products are printed (Fig. 19–22). After that, it is recommended to carry out post-molding processing for printed 3D products containing CNS.

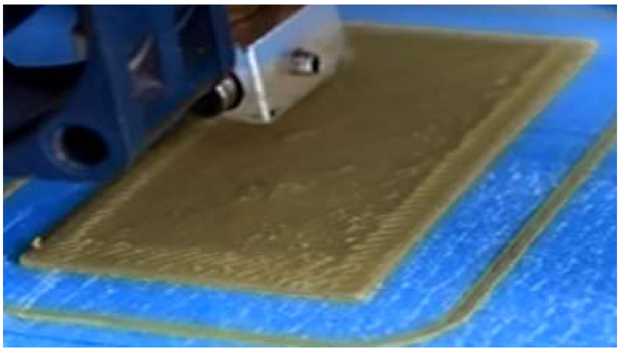

Fig. 19. The process of printing a 3D product from composite bays (solid polymer–CNS) using FDM technology

Fig. 20. 3D product from a mechanical mixture (ceramic–CNS) using CJP technology

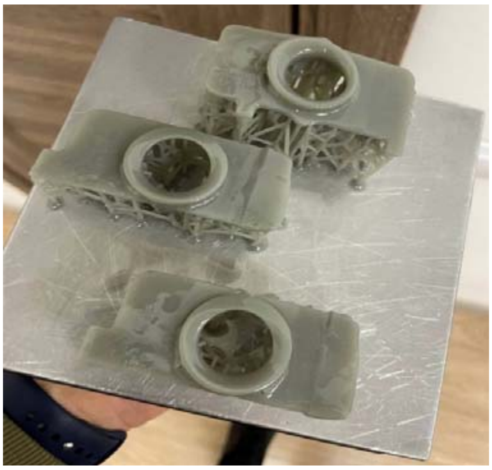

Fig. 21. 3D composite product (liquid polymer–CNS) using SLA technology

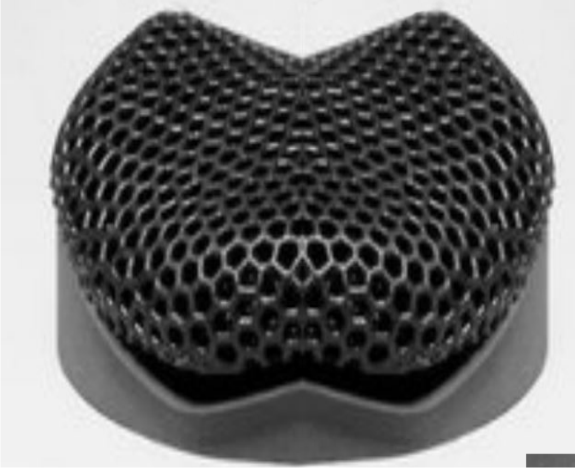

Fig. 22. 3D product made of composite (solid polymer–CNS) finely dispersed crumb using SLS technology

3D printing products

CJP technology 3D printing products. To eliminate surface irregularities, external defects of 3D printing (pits and cracks) and reduce the effect of surface hygroscopicity, post-forming treatment of the surface of 3D products by spraying with a salt solution is recommended. This treatment increases the strength of the 3D product by eliminating defects on its surface.

When using metal oxides as the supporting matrix of the composite (for example, Al_2O_3–CNS), a mandatory condition for post-molding processing is the sintering of the 3D product in the temperature range of ~1000–2100 K, as a result of which a ceramic material is obtained, into which carbon CNS are introduced.

To provide additional strength and improve the appearance, 3D products can be soaked in special fixatives (activator - fixative) or treated with resin coatings (sprays, varnishes, paints, etc.).

Products of 3D printing of FDM technology have a ribbed surface due to the mechanism of horizontal deposition by the extrusion method, and the thicker the thread from the bays used, the more pronounced the ribs of each layer. Adjusting the parameters of the 3D printing printer allows you to reduce the visual ribbing of the 3D product, but cannot eliminate it completely. Therefore, in order to obtain a smooth surface of the 3D product, it is necessary to carry out a special surface post-forming treatment (Table 2).

3D products of FDM technology made of solid polymers and their composites (for example, solid polymer — CNS) are easily subject to post-molding high-quality coating with paint, varnish, enamel, automotive coatings, etc. Such a coating not only increases the durability of the 3D product, but also increases its resistance to various aggressive environments.The high hardness and strength of 3D products allows them to be subjected to various types of post-forming mechanical processing, such as machine tool mechanical (locksmith works), grinding, polishing, cutting, drilling, etc. One of the main advantages of 3D products of this class at the household level is that they are easily restored and glued together with any plastic glue.

SLS technology 3D printing products have the same or maximally similar physical and chemical characteristics as FDM technology 3D printing products. For this reason, SLS 3D products can have the same post-molding treatment as FDM 3D printed products. The only difference between SLS 3D printed products is that they have a particularly smooth surface compared to the ribbed surfaces of FDM 3D products.

Table 2. Overview of materials for 3D products of FDM technology.

№	Type of 3D material	Colour	Polymer strength	Application temperature	Post-forming processing
1	ABS eco, ABS, ABS+, ABS Pro, ABS Flex	Any, there is no clear one	High	from –10 to +90 °C	In ethyl acetate($C_4H_8O_2$)
2	coPET	Clear	Medium	from–40 to +60 °C	Temperature and mechanical
3	PLA, PLA+	Any, there is no clear one	Medium	from–10 to+60 °C	Dichloroethane, dichloromethane, ethyl acetate
4	MBS	High clear	High	from–40 to+ 80 °C	Easily processed
5	PC	High clear	High	to120°C	
6	ELASTAN	Any	High	from–60 °C to+90 °C	
7	PET	Clear	High	from–60 to+220 °C	Hardening is possible
8	Nylon (Нейлон, PA-6)	White	High	from–40 °C to+140 °C	
9	PA (поліамиду-6+)	Any	High	from–20 to+80 °C	
10	PBT (Полібутилен-терефталат)		High	from–40 °C to+120 °C	
11	ASA		High	from–40 to+ 85 °C	
12	PCL (полікапролак-тон)		Low	59–64 °C	

Continued table 2

№	Type of 3D material	Additional Information
1	2	3
1	ABS eco, ABS, ABS+, ABS Pro, ABS Flex	Has: medium print resolution. Print elements of cars.
2	coPET	Has: high transparency and uniform light scattering, glossy surface; inertness to solvents; high adhesion between layers during printing; absence of deformation and deformation during printing. Printing: bottles.
3	PLA, PLA+	Has: no shrinkage, high print resolution (detail). Biodegradable.
4	MBS	It has impact resistance and is a styrene-acrylic copolymer. "Transparent ABS". Headlights, lamps are printed.
5	PC	It has high rigidity and resistance to high temperatures. Printing: headlights, lamps
6	ELASTAN	t has: different hardness, high wear resistance, oil and gasoline resistance, high resistance to bending (repeated deformations). As the temperature rises, it becomes softer. Printing: seals, corrugations.
7	PET	Has: high mechanical strength and impact resistance. Resistant to abrasion and repeated deformations during stretching and bending. Printing: seals, corrugations.

1	2	3
8	Nylon (Нейлон, PA-6)	Has: high tensile strength, rigidity, wear resistance. Quickly absorbs moisture, before printing it needs to be additionally dried. Printing: plastic gears.
9	PA (поліамиду-6+)	Has: impact resistance, wear resistance, weak reaction with moisture. Increased interlayer adhesion.
10	PBT (Полібутилен-терефталат)	Has: properties similar to polyamides, high rigidity and hardness, good dielectric and has anti-friction properties. Printing: bearings, washers, etc.
11	ASA	Has: resistance to ultraviolet radiation, water, salt water. "Similar" to ABS. Printing: external elements of the car.
12	PCL (полікапролак-тон)	It has: biocompatibility, long shelf life (for many weeks) and is a biodegradable polyester plastic. Printing: medicine.

SLA technology 3D printing products have the widest range of modification of applied composites (liquid polymer–CNS), since this technology involves the use of both insoluble and soluble carbon nanostructures (Table 1).

3D products of SLA technology from composites containing soluble CNS (liquid polymer - soluble CNS) have increased flexibility and resistance to fracture, and are also capable of responding to an electromagnetic field or other types of radiation.

Despite the possibilities of using SLA technology in complex composites in 3D products, they are easily amenable to post-molding processing. All 3D products are characterized by high smoothness and flawless surface.

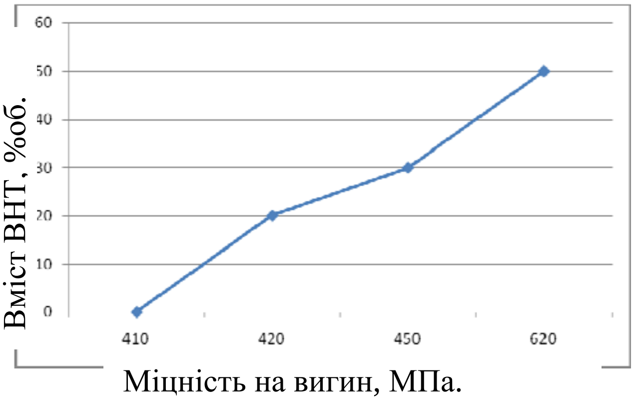

Fig. 23. Dependence of flexural strength on the content of CNTs in a composite product (ceramic–CNS) obtained using the CJP technology

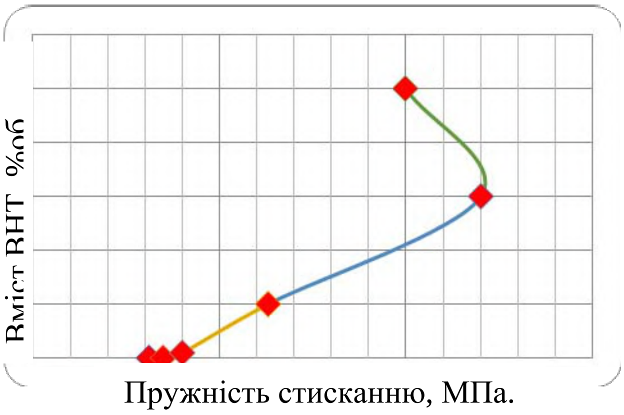

Fig. 24. Dependence of elastic compressive strength on the content of CNTs in a composite product (solid polymer–CNS), obtained using FDM technology

Research results

The strength characteristics of composite 3D products obtained from a mechanical mixture (ceramic–CNS) and polymer composite (solid polymer–CNS) were studied as part of the research work. In the results of the research, a tendency to increase the strength characteristics of 3D-products can be observed when using CNS as a filler of the supporting matrix (Figs. 23, 24).

Conclusions

It has been established that there are different types of 3D printing, which differ from each other in the method of applying layers and the materials used, in particular CNS.

The following 3D printing technologies include FDM, CJP, SLA, SLS. A comparative analysis of the proposed 3D printing technologies showed that, to date, the SLA technology is the only one with a wide range of CNS applications, and also has a minimum step and minimum temperature (~300 K) of 3D printing at a low cost of a 3D printer. This is an important advantage, because in other 3D printing technologies, the operating temperature reaches 700 K.

It is established that each 3D printer has its own printing step, and the size of carbon nanostructures should not exceed it. For this reason, large agglomerates of carbon nanoparticles must be subjected to re-grinding after processing. Mechanical mixtures (ceramics-insoluble CNS) for CJP 3D printing technology must have high flowability and dispersion.

It has been established that FDM, SLS, and SLA 3D printing technologies have a composite preparation stage (Stage II) in special mixers, where the filler (treated CNS) and the carrier matrix (polymer) are mixed.

An important step in the raw composite production cycle (solid polymer–insoluble CNs) for FDM and SLS technologies is the process of uniform mixing of CNS with the solid polymer–supporting matrix of the composite.

It was established that the main problem of creating a composite for FDM and SLS 3D printing technologies is the appearance of pores, which are formed due to the entrapment of air bubbles by carbon nanostructures when they enter the polymer matrix. This effect is eliminated by pre-treatment of CNS and solid polymer with the same wetting reagents.

It was established that the SLA technology is the only one capable of creating composites (liquid polymer–soluble CNS) using fullerenes and fullerene-like nanostructures.

It was established that the mixtures prepared for 3D printing using SLA technology from liquid polymer and insoluble CNS have the appearance of a pulp (suspension), which must be used in 3D printing as soon as possible, before the beginning of the process of sedimentation and coagulation of CNS.

In SLA 3D printing technology, complex composites can be used (liquid polymer–soluble CNS–insoluble CNS). This technology allows you to create 3D products of high complexity (thin walls and small elements) from composites that have no analogues in other 3D printing technologies.

It has been established that post-forming processing is recommended for printed 3D products containing CNS. CJP technology 3D printing products require post-forming surface treatment by spraying with a salt solution to remove surface irregularities, external 3D printing defects (pits and cracks) and reduce the effect of surface hygroscopicity.This treatment eliminates surface defects, thereby increasing the strength of the 3D product. 3D products of FDM technology from solid polymers and their composites (for example, solid polymer-insoluble CNS) are easily subject to post-molding high-quality coating with paint, varnish, enamel, automotive coatings, etc. The products of FDM technology can be subjected to various post-forming mechanical treatments, such as machine tooling (locksmithing), grinding, polishing, cutting, drilling, etc. It is indicated that 3D products of SLS technology can have the same post-molding processing as products of FDM technology.

It was established that the 3D printing products of the SLA technology have the widest range of modification of the applied composites (liquid polymer–CNS), since both insoluble and soluble carbon nanostructures can be used. SLA technology 3D printing products can easily be post-formed.

An overview Table of materials for 3D products of FDM technology has been created.

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СТВОРЕННЯ 3D-ПРОДУКЦІЇ З ВИКОРИСТАННЯМ ВУГЛЕЦЕВИХ НАНОСТРУКТУР І ТЕХНОЛОГІЙ 3D-ДРУКУ (FDM, CJP, SLA, SLS)

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Розглядаються методи одержання вуглецевих наноструктур (ВНС), а також їх використання для створення 3D-продуктів за допомогою технологій 3D-друку (FDM, *CJP, SLA, SLS). Розроблений процес виготовлення витратних матеріалів технологій 3D-друку (FDM, CJP, SLA, SLS) для створення нових композитних 3D-виробів на основі вуглецевих наноструктур. Детально проаналізовані методи синтезу ВНС, які є найбільш продуктивними та гарантують отримання цільових ВНС.*

Проведено аналіз існуючих технологій 3D-друку з використанням ВНС, розроблено схему повного циклу, від перетворення графіту або іншого вуглецевмісного матеріалу при синтезі (різними методами) ВНС до створення 3D-виробів, які містять ВНС. Також розробленний процес створення композитних бухт для 3D-друку (FDM) з нанокомпозитних ниток на основі твердого полімеру, що готується у спеціальному змішувачі. Охарактеризовано процес підготовки витратного матеріалу для друку об'ємних 3D-виробів за технологіями 3D-друку (FDM, CJP, SLA, SLS) з використанням ВНС. Розглянуті витратні матеріали для 3D-виробів за технологією FDM. Проведено аналіз композитних 3D-виробів, отриманих технологіями 3D-друку FDM та CJP.

Розглянуто також три найбільш продуктивні методи синтезу ВНС: плазмохімічні у газових та рідких фазах, а також піролітичний метод. Методи синтезу гарантують отримання ВНС, та забезпечують якість цільових нанопродуктів. Розглянуті різні типи ВНС, включаючи розчинні (фуллерени та фуллереноподібні структури) та нерозчинні наноструктури (графени, вуглецеві нанотрубки та нановолокна, нанокомпозити тощо.).

Ключові слова: *FDM, CJP, SLA, SLS, 3D друк, 3D-вироби, нанокомпозити, вуглецеві наноматеріали (ВНМ), піроліз, плазмохімічний синтез, полімери, кераміка.*