

CARBON NANOTUBES FOR THE SYNTHESIS OF CERAMIC MATRIX COMPOSITES (CLEANING, DISPERSION, SURFACE MODIFICATION) (REVIEW)

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In light of the continuing decrease in the cost of carbon nanotubes (CNT) and the promising properties of ceramic matrix composites (CMC) reinforced with CNTs, their wide application in industry is on the agenda. For this, inexpensive technologies for the production of CNTs are necessary. Technological stages of the industrial production of complex-shaped products from carbon nanotube-reinforced ceramic matrix composites (CNT-CMC) are reviewed: the cleaning of raw materials after their production, the dispersion of aggregates and some methods for modifying their surface.

Keywords: ceramic matrix composites (CMC), ceramic matrix nanocomposites (CMNC), carbon nanotubes (CNT), cleaning, disaggregation, surface modification.

BASIC TECHNOLOGICAL STAGES FOR PRODUCING CARBON NANOTUBE REINFORCED CERAMIC MATRIX COMPOSITES

Ceramic matrix composites (CMC) are composites consisting of a ceramic dispersion medium (matrix) with the dispersed (reinforcing) phase distributed throughout. Nanomaterials include materials for which the most important operational property is determined by structural elements having dimensions of less than 100 nm. If the matrix or reinforcing phase consists of nanostructures or contains nanostructures that provide the most important operational properties of the material, then it can be called a nanocomposite. Therefore, ceramic composites reinforced with CNTs with a diameter of less than 100 nm are ceramic matrix nanocomposites (CMNC). The technology for producing carbon nanotube (CNT) reinforced CMNC differs little from the traditional ceramics technology. The diameter and size of CNTs are usually smaller than or commensurate with the size of ceramic powder particles, regardless of the use of nanopowders in the matrix.

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Ceramics technology includes the preparation of molding masses, molding of billets from the masses, removal of binder, and firing. During firing, a billet consisting of individual particles acquires strength through mass transfer processes, called sintering. In this case, the structure of the material changes significantly: the shape, size and number of pores and original particles of the solid phase change [1].

Preparation of the ceramic molding mass includes the preparation of powders, their mixing, the introduction of a temporary technological binder. If a liquid binder is added to the powder (or mixture of powders) and its volume content is increased, then at first up to about 10 – 40 vol% the mixture will behave like a powder; as the amount of binder is increased to 35 – 50 vol%, the mixture acquires the consistency of playdoh (ductile mass); with increase up to 50 – 70 vol%, the mixture becomes fluid (ceramic slip). These boundaries are arbitrary and depend on the surface properties of the particles of the solid phase, their size and shape, the properties of the binder. Specific methods of billet molding correspond to particular types of masses: dry or semi-dry pressing of powders, powder injection molding of ductile powder masses, and ceramic mold casting of ceramic slips.

The main task in the preparation of the molding mixture is uniform distribution of its components. The mixing of

powder particles is hampered by friction forces between the particles, as well as between the particles and the walls of the container in which they are mixed. Therefore, all methods of reducing friction will facilitate mixing. Such methods, for example, would be the use of liquids and vibrations. Powders can be mixed by passing air through them to form a fluidized bed. However, after mixing, the friction forces become necessary to prevent the difference in particle mass from violating uniformity of the mixture. Therefore, mixing of powders is easier in the liquid state, but their storage is easier in the form of powder mixtures. Another phenomenon that impedes uniform mixing is the aggregation of particles of the mixed components. With decreasing particle size, this process intensifies, and this also applies to CNTs.

To obtain a molding mixture for CNT-CMNC, it is necessary to first prepare the components, and first of all, CNTs. Consider the following stages.

1. Cleaning CNTs after they are obtained.

Newly grown CNTs usually contain carbon-containing impurities (carbon black, graphite, fullerenes, etc.) and (if catalysts were used) metal catalysts (Fe, Co, Ni, Cu), as well as catalyst carriers (silicates and other oxides). Cleaning methods are categorized as physical, chemical, and combination [2]. Physical methods are based on the difference in the physical properties of CNTs: particle size, particle size distribution, density, magnetic properties, etc. These methods are implemented, for example, by centrifugation, filtration, flotation, etc. Their advantage is that they do not change the properties of CNTs. Chemical cleaning methods depend on the environment in which they are carried out (liquid phase, gas phase). Since graphite can form intercalates, these methods are isolated separately. In order to remove impurities from CNTs, they must first be converted into a solution or a gas phase. In a liquid medium, washing is required to remove dissolved impurities; in the gas phase, the impurity evaporates. A combination of physical and chemical purification methods is implemented with multistage purification, which provides the highest quality cleaning of CNTs [3 – 5].

By combining various methods, it is possible to separate CNTs by length and electrical conductivity or maintain the intact structure of the material, for example, by cutting off the ends of the CNTs, or add functional groups to the side walls, selectively opening the ends of the CNTs. Carbon-containing impurities can be removed by oxidation to carbon oxides or reduction to methane and other gaseous or liquid compounds. For oxidation, various gaseous (ozone, oxygen, air, peroxides, vapors of oxygen-containing acids) and liquid (oxygen-containing acids, peroxides, salts containing anion-oxidizing agents) media are used. The use of basic media is effective. They facilitate the oxidation of carbon-containing impurities with the formation of CO_2 , which immediately binds to produce carbonate. Hydrogen and other reducing agents can be used to reduce carbon. Silicates and oxides can be dissolved in HF and alkali metal bifluorides (for example, in NaHF_2).

Metals are removed by dissolving in acids, most often in liquid media. They can be converted to gaseous compounds. Metal catalysts (Fe, Co, Ni) can react with carbon monoxide (CO) to form volatile carbonyl compounds [6]. In this case, it is possible to remove 60% Ni (from 1 to 0.4 wt%). In inorganic and organic chemistry, many similar reactions have been developed for metals used as catalysts in the preparation of CNTs.

The main purpose of cleaning is to prevent undesirable reactions with CNT during reactions with impurities. However, sometimes, when the functionalization of CNT is required, such reactions may be useful. The high bond strength between the carbon atoms in a CNT contributes to the preservation of its structure. For a chemical reaction, the chemical bond in the starting materials must be broken. In most carbon-containing impurities (with the exception of fullerenes) and in nanoparticles of metal-catalysts, chemical bonds are much weaker than in CNTs. The presence of defects in CNTs (impurity atoms instead of carbon, dislocations, etc.) weakens the strength of chemical bonds at the defect sites. This is used to remove defective CNTs and produce high quality CNT in the remainder. Using differences in the strength of chemical bonds, it is possible to select conditions that lead not only to purification to remove impurities, but also to obtaining pure single-walled CNTs (SWCNT) with a narrow size distribution of diameters [7].

To break chemical bonds, it is necessary to expend energy, and the more energy is expended, the stronger the chemical bond. Any methods of adding energy to chemical bonds facilitate their rupture. Heating is the most common, but other methods can be used also, such as microwave heating. It is shown that microwave heating increases the rate of purification, especially at elevated pressure [8]. At the same time, the removal of metal catalysts (regardless of the type) is reduced from 24 hours to 15 minutes using acid washing.

Often, when cleaning in a liquid medium, large particles of graphite are removed by filtration first, then fullerenes are removed in organic solutions, metal particles – metal catalysts are removed in acid solutions, then centrifugal washing is carried out, followed by microfiltration and chromatography. Centrifugal washing before microfiltration allows the separation of CNTs from unwanted nanoparticles and amorphous carbon, which quickly clog the membrane filter. Various methods of cleaning CNTs are presented in [9].

The authors of [2] studied the acid purification of SWCNTs with various reagents (HNO_3 , H_2SO_4 , HCl , H_2O_2) to remove metal catalysts, which were synthesized using the catalytic method of chemical precipitation (CMCP). In this case, HNO_3 , H_2SO_4 and H_2O_2 are oxidizing agents and are capable of oxidizing carbon-containing impurities. The effect of their concentrations (3 M and 6 M), the purification temperature (75 and 120°C), and the duration of the purification (6.8 and 15 hr) were studied. The purified CNTs were washed with distilled water to pH 7, and then dried at 105°C for 48 hrs. The results of the experiments are presented in Table 2 using gravimetric analysis (TG) data. The purification

yield (PY), %, was determined by the formula $PY = [(w_0 - w_t)/w_0] \times 100$, where w_0 is the content of metal in the newly obtained SWCNT, %; w_t is the metal content in the purified SWCNT, %. The purification yield increased with increasing temperature and duration of the process. Best results are obtained using HNO_3 . Without microwave heating, the process requires a long time of exposure.

In [39], acid purification of multi-walled CNT (MWCNT) is described. The best result was obtained after cleaning in a mixture of sulfuric and nitric acids within 24 hrs. The results of purification of double walled CNTs (DWCNTs) in various media (3 M or 15 M nitric acid, mixture of concentrated HNO_3 and H_2SO_4 , solutions of $KMnO_4$ or $K_2Cr_2O_7$ in sulfuric acid) are described in [40]. All methods turned out to be quite effective, but secondary reactions

TABLE 1. Characteristics of Various Methods of Cleaning CNT [9]

Process	Description	References
Gas phase oxidation	<ol style="list-style-type: none"> 1. In general, chemical oxidation includes oxidation in the gas phase (using air, O_2, Cl_2, H_2O, etc.), liquid phase oxidation (treatment with acid and refluxing, etc.) and electrochemical. 2. CNTs are heated at a controlled rate, either in humid air, or in a vacuum, or in other oxidizing agents for a long time at a temperature of about $330^\circ C$. This is a good way to remove carbon impurities. 3. The disadvantages of this method are that it often opens the ends of a CNT, cuts the CNT, damages the surface structure, and introduces oxygenated functional groups ($-OH$, $-C=O$ and $-COOH$) to the surface of the CNT. Metal particles cannot be directly removed, additional acid treatment is necessary. 	[10 – 21]
Oxidation in the liquid phase (acid cleaning)	<ol style="list-style-type: none"> 1. Typically, acid treatment removes metal catalysts and some fullerenes. 2. Dissolution in HNO_3, HCl or other acid within 4 to 48 hrs. 3. HNO_3 is the only acid that does not destroy CNTs (unless CNTs are left in HNO_3 for extended periods of time, typically >16 hrs). 4. The metal catalyst is solvated, while the CNT remains in the form of a suspension. 	[11, 16, 22, 23]
Electrochemical oxidation	<ol style="list-style-type: none"> 1. CNTs with fewer defects show greater electrochemical resistance to oxidation than CNTs with a larger number of defects. Suitable for cleaning CNTs without destroying their relative position. 2. Electrodes from CNT are immersed in a 0.2 M HNO_3 solution or 0.2 M HCl (N_2 purge for 20 min before use), the potential is in the range from +1.00 to +2.00 V at a scanning speed of 50 mV/sec. 3. Increases the specific surface area of CNTs, cutting off their tips and converting the surface from a hydrophobic to a hydrophilic state. 	[24, 25]
Centrifugation	<ol style="list-style-type: none"> 1. Centrifugation with an acceleration of 7000g or more for 30 min to 3 hrs. Often the supernatant is removed after one pass and centrifuged again. 2. Removes nanospheres, metal nanoparticles, carbon particles, but some methods produce low nanotube yield, especially when centrifuging is repeated many times. 	[26 – 28]
Filtration	<ol style="list-style-type: none"> 1. This method is often used in combination with oxidation. Products of acid treatment of CNTs (as opposed to unprocessed CNTs) are well soluble in the main solution. They are easily separated using a basic solution with $pH = 11$ when filtering using a filter (3 – 5 μm), often under vacuum. 2. The method allows to remove nanospheres, metallic nanoparticles, polyatomic carbon-containing particles and fullerenes without any noticeable negative effects. 	[29]
Ultrasound treatment	<ol style="list-style-type: none"> 1. CNTs are distributed in distilled water, toluene, or acid solution and sonicated for 5 – 30 min. 2. This separates the tubes from the attached particles, creating a dispersion of CNTs and other particles for better centrifugation. 3. Particle separation is highly dependent on the surfactant, solvent and reagent used. The solvent affects the stability of dispersed CNTs in the system. 	[19, 20, 26, 30 – 32]
Magnetic properties	<ol style="list-style-type: none"> 1. CNTs are distributed in an aqueous solution of soap or in toluene, powder of nanoparticles (ZrO_2, NH_4Cl, $CaCO_3$, diamond) is added. These particles will attach to the CNT and make them magnetic. 2. The suspension is treated with ultrasound for 2 hrs, and then the magnetized particles are captured using constant magnetic fields. 3. This is followed by chemical treatment. 4. This method allows you to remove metal-catalysts and small inorganic particles of other impurities. 	[33 – 35]
Microwave cleaning	<ol style="list-style-type: none"> 1. CNTs are sonicated, then diluted in HNO_3 (or other acid). 2. Microwave radiation is supplied at 100 – 200 W, the microwave energy is increased to $\sim 200^\circ C$ in 30 min 	[36 – 38]

appeared: shortening of CNTs, creation of functionalized amorphous carbon coatings, covalent functionalization of the outer wall. To remove the functionalized carbon coating, it is necessary to apply additional washing with sodium hydroxide solution or heat treatment of CNTs in air.

For the oxidation of carbon coatings to CO_2 , KMnO_4 was used in an acidic medium at 70°C [41]. Oxidation in KMnO_4 occurred at a lower temperature, which led to an up to 40% increase in yield compared with the yield of 27% in case of oxidation in air. For purification of SWCNTs produced in DC plasma, soot produced in large quantities was oxidized by catalytic oxidation with H_2O_2 [42]. Soot removal was carried out in a high-pressure reactor, and metallic iron particles, which acted as a catalyst in the synthesis of SWCNTs, were used as an oxidation catalyst. As the temperature rises, $\text{Fe}/\text{H}_2\text{O}_2$ vapor forms hydroxy radicals, which oxidize soot. Such associations facilitate and reduce the cost of removing impurities.

To clean the SWCNTs obtained using the CMCP, it was proposed to use leaching in NaOH and flotation of the resulting foam [43]. The catalyst (Co–Mo) was applied to a silicate substrate. The carrier was dissolved in a solution of NaOH, and carbon was removed by flotation of the resulting foam. The following are the optimal parameters of the flotation process: duration of ultrasound treatment 3 hrs, amount of surfactant 30 mg/L, pulp density 1.0 g/L, air flow rate 100 mL/min, foam height 22 cm. The treatment of NaOH and the foamy flotation did not change the physicochemical properties SWCNT.

An effective method for single-stage cleaning of carbon nanotubes is described in [44]. The MWCNTs obtained by decomposing acetylene with two types of catalysts were investigated: NaY zeolite-supported Co (2.5% Co) (CNT–NaY samples) [41], and Co particles obtained from a solid solution of CoO in MgO (A/CoMgO samples) [45]. CNT–NaY samples contained a significant amount of metal catalyst par-

ticles and amorphous carbon. The ends of the SWCNTs were mostly closed and surrounded by amorphous carbon. A/CoMgO samples contained only metallic impurities in small amounts, and their ends were always closed.

Samples of MWCNTs were first mechanically mixed with solid NaOH (the NaOH/C ratio was 4/1), then heated to $600 - 800^\circ\text{C}$ in a stream of N_2 (250 mL/min). As a result of redox reactions between NaOH and carbon-containing materials, Na_2CO_3 and metallic Na were formed. KOH cannot be used because metallic potassium forms intercalates that destroy SWCNTs [46]. After that, the samples were washed in dilute HCl and water. Metal-catalyst and Na_2CO_3 particles were removed. After cleaning, all ends of the MWCNT were open.

In order to purify CNTs to remove residues of Fe (catalyst) and carbon-containing impurities, treatment with gaseous CCl_4 at 700°C was proposed [47]. The CCl_4 treatment significantly influenced the surface state of CNT and other carbon nanostructures. The content of iron decreased from about 3 to 1%, but at the same time the content of chlorine increased to 6.8%. The treatment of CNTs with water vapor allowed the controlled removal of carbon materials included in polymers, as well as amorphous and defective CNTs and CNTs of a certain diameter (CNTs of different diameters have different oxidizability when exposed to water vapor) [48]. As a result, CNTs were obtained that are not oxidizable until 900°C under normal conditions. A promising for industrial application method for purifying MWCNTs in ultrapure oxygen was proposed [49]. Optimization of the process allowed removing amorphous carbon at 450°C in 180 sec and reactivating the nickel catalyst. The method makes it possible to preserve the vertical arrangement of the CNTs. The industrial process can be carried out in glass vessels. It has been established [50] that in a two-stage purification, the use of purification in the gas phase before purification in the liq-

TABLE 2. Results of TG Analysis of Purified SWCNTs [2]

Sample number	Concentration, M	Acid	Time, hr	Temperature, $^\circ\text{C}$	Purification yield, %
1	3	HNO_3	8	75	96.54
2	3	HCl	8	75	88.93
3	3	H_2SO_4	8	75	91.24
4	3	HNO_3	15	75	98.13
5	3	HCl	15	75	92.36
6	3	H_2SO_4	15	75	94.44
7	6	HNO_3	6	120	98.29
8	6	HCl	6	120	94.88
9	6	H_2SO_4	6	120	97.70
10	6	$\text{H}_2\text{SO}_4 : \text{HNO}_3$	6	120	97.91
11	3M	$\text{H}_2\text{O}_2 : \text{HCl}$	8	75	96.03
12	3M	$\text{H}_2\text{O}_2 : \text{H}_2\text{SO}_4$	8	75	94.67

uid phase is more effective and less destructive of MWCNT than the reverse sequence.

The method of formation of intercalates with carbon-containing impurities is also used for the purification of CNTs. Thus, copper chloride forms intercalates, which are then reduced to metallic copper, which is an effective catalyst for the oxidation of carbon-containing impurities [51]. A crude cathode sediment consisting of cathode soot and CNT was placed in a molten mixture of copper chloride and potassium chloride at 400°C for one week. Excess copper chloride and potassium chloride were removed by washing in ion exchange water. Cu nanoparticles were obtained by passing a mixture of He and H₂ at 500°C for 1 hr. After oxidation in flow-through air at a heating rate of 10°C/min to 555°C, the material consisted only of CNTs. The disadvantages of the method include the partial oxidation of CNTs and the possibility of intercalate residue entering the product. Intercalates with bromine are used similarly [52]. After bromination, selective oxidation with oxygen was carried out at 530°C for 3 days. The yield of CNTs ranged from 10 to 20 wt% relative to the mass of the original crude cathode sediment. In this case, all the CNTs were open on both sides, but the metal particles remained in the product.

Industrial purification of CNTs should be simple, inexpensive and not lead to deterioration of the properties of CNTs. In reinforcing CMC, the decision to use CNT cleaning and the degree of cleaning is made depending on the purpose of the composite. If CMC is used at relatively low temperatures, then CNTs can be cleaned. Of course, this applies to cases where the method of CNT production does not lead to too much contamination (for example, CMCP). The presence of carbon-containing impurities on the surface of CNTs may even be useful as an interphase. For high-temperature applications, it is desirable to remove the metal-catalysts using, for example, optimized acid treatment. A method of purification with solid NaOH followed by acid washing to remove the metal-catalyst and sodium compounds shows promise [44].

It should be noted that many effective industrial cleaning methods have been developed in chemical technology, primarily for electronics and the nuclear industry. Efficient methods and appropriate equipment have been developed, which can be successfully used to clean CNTs. However, it should be noted that each extra stage will increase the cost of the process.

2. Disaggregation of CNTs

Uniform distribution of CNTs in a ceramic sand is a challenge. CNT nanoparticles are usually bound into rather strong aggregates that must be destroyed without damaging the CNTs themselves. Since polymers are widely used as a binder in ceramic molding materials, the experience of obtaining composites from polymers reinforced with CNTs is quite useful. Moreover, excellent results have already been achieved in this area, confirming that CNTs have a high spe-

cific surface area and tend to reduce it by aggregation. Newly obtained CNTs are combined into aggregates, which are called “bundles” and “clusters”. Thus, SWCNTs aggregate into “ropes” or “bundles” consisting of multiple parallel CNTs [53]. These aggregates have high strength due to the strong Van-der-Waals interactions. To destroy bonds between CNT particles in aggregates, they must be supplied with energy sufficient to break them, but less than is necessary to destroy the CNTs themselves [54, 55].

For the destruction of aggregates, mixing with the implementation of shear stresses is usually used [56 – 62]. After the destruction of the aggregates, it is necessary to take measures to prevent their reaggregation. For this purpose, various surfactants are usually used, which prevent the formation of strong aggregates [61]. Surfactants also contribute to the dispersion by preventing the healing of cracks required for the destruction of aggregates. Table 3 shows the mechanisms of dispersion of various surfactants [54] grouped by the mechanisms of stabilization into those soluble in water or in organic solvents. Surfactants are divided into 6 groups (*A – F*). To separate CNTs in a liquid medium, the surfactant must have two types of functional groups. While one type of functional groups must attach to the CNT wall, the other, due to their lyophilic properties, rotate towards the surrounding liquid medium. These groups, due to either charge and/or steric effect, isolate individual CNTs, preventing them from aggregating. Groups *A – C* combine surfactants that stabilize CNTs due to the available electric charge. The stability of suspensions is ensured by the zeta potential of surfactant/CNT complexes [63, 64]. This mechanism manifests mainly in aqueous solutions that have a high dielectric constant. Large molecules are sorbed in suspensions on the surface of CNT particles and do not allow them to unite into strong aggregates. This stabilization mechanism is called steric, it works not only in aqueous suspensions, but also in non-aqueous ones.

For surfactants of groups *A* [65 – 69] and *D* [70], micelle formation is characteristic, which significantly increases the stability of suspensions. Their molecules contain two parts: hydrophilic (charged) and hydrophobic (uncharged). The best result was obtained when using Triton X-100 as a surfactant, the worst — using sodium dodecyl sulfate [70]. The hydrophobic part of these molecules is relatively small, which makes it possible to attach these blocks to the side surfaces of CNTs. The surfactant *A* groups [70 – 73] have long flexible or semi-flexible hydrophobic parts (biomolecules and some polymeric surfactants). These include polyvinylpyrrolidone, PVP (see Table 3, group *E*) [74, 75]. These pieces can wrap around the CNT. In this case, affine groups of surfactant molecules can join to the surface of CNT with the formation of subsequently rigid p-bonds (see Table 3, group *F*) [76 – 80]. Selecting a surfactant suitable for organic solvents is much more difficult. However, pyrene-siloxanes, which are non-polar organic solvents, have recently been developed as organic solvents [79].

TABLE 3. Dispersion Mechanisms when Using Various Surfactants

Stabilization mechanism	Chemical bonds and compounds		
	hydrophobic	polymerization while keeping the electron pair	polymerization
Electrostatic repulsion	<i>A</i> Sodium dodecyl sulfate and related salts [65 – 68]; phospholipid [69]	<i>B</i> Single-stranded DNA [71, 72]; water-soluble proteins [73]	<i>C</i> Pyrenic acid salts [77, 78]
Steric effect	<i>D</i> Triton X-100, tween 80, tween 20 and sodium dodecyl sulfate [70]	<i>E*</i> Polyvinylpyrrolidone (water, NMP) [74, 75]	<i>F*</i> — Conjugated block copolymers [76]; pyrene-siloxanes (non-polar organic solvent) [79]; Conjugated polymer (polar organic solvent) [80]

* Used for organic solvents, the rest — for dispersion in aqueous solution [54].

Mills widely used in ceramics technology to obtain highly dispersed powders can be used for disaggregation. Thus, when producing the Si₃N₄/MWCNT CMC, the initial components (90% w/w Si₃N₄, 4% w/w Al₂O₃, 6% w/w Y₂O₃ with MWCNT) were placed in distilled water in an attritor and milled at 4000 rpm to 5 hrs (discs with a ZrO₂ stirrer and ZrO₂ grinding balls 1 mm in diameter) [81]. During grinding, the powder in the attritor was contaminated with ZrO₂.

In producing the Al₂O₃/MWCNT composite, the molding mass was also prepared by grinding in a mill [82]. MWCNTs were dispersed for 2 hrs in dimethylformamide (to increase the strength of sonification). Al₂O₃ nanopowder (Sigma-Aldrich, United Kingdom, gamma phase, particle size 2 nm, specific surface area of particles 35 – 43 m²/g) was added to the dispersion. The mixture was placed in a ball mill and milled for 8 hrs, first dried in air at 75°C for 12 hrs, and then in a vacuum oven at 100°C for 3 days.

In ceramics technology, it is generally believed that ultrasonic disaggregation is softer and less disruptive to particles that form aggregates. However, it all depends on the power of the ultrasonic treatment and the duration of the process. Long and powerful ultrasonic treatment can lead to the destruction of CNTs. So, after long-term ultrasound treatment of MWCNTs, their length decreases by about 1/3 of the original length [83], which is consistent with a decrease in the electrical conductivity of polymers reinforced with carbon nanotubes [84].

The effect of surfactants is highly dependent on their type. Thus, the use of such surfactants as Tergitol [85] or sodium dodecyl sulfate [86] for dispersing CNTs led to the destruction of aggregates and the formation of a dense shell surrounding the CNT. This manifested in a decrease in the electrical conductivity of composites with the polymer matrix. At the same time, the use of a silicone resin (siloxanes) as a non-polar organic solvent [79] led to an increase in electrical conductivity, apparently due to the formation of a percolation cluster of CNTs [84].

The correct choice of a surfactant is an effective way to disperse CNTs in various, primarily liquid media and subsequently stabilize suspensions (preventing the reaggregation

of CNTs). These methods are also well developed with the availability of techniques and industrial equipment. It is better to choose the method of producing CNTs, which excludes the formation of durable aggregates. The choice of surfactant is determined by the nature of the surface of the particles forming the aggregates, and the liquid medium in which the disaggregation process takes place.

3. CNT surface modification

Physicochemical processes occurring on the surface of CNTs when they interact with the environment (for example, such as discussed above for surfactants) are often referred to as surface modification of CNTs. The modification is used in the process of dispersing CNT aggregates and for uniform distribution of CNTs throughout polymer matrices. These methods have been optimized, including for composites with carbon nanofibres, and are especially important for molding compounds containing a large amount of binder (ductile molding masses, and especially ceramic slips).

Surface modification is carried out in various media (liquid, gas or plasma). Surface modification improves the interaction between the surface of a CNT and a polymer [87]. The necessary data can be found in the works on obtaining composite materials with a matrix of polymers reinforced with CNTs. It is proposed to distinguish two types of functionalization — non-covalent functionalization and covalent coating of CNT surface [88]. Surfactants, as mentioned above [89], and polymerization techniques (PT) [91] are used for non-covalent functionalization. These methods allow CNTs to preserve their properties, but provide relatively small adhesion to the surrounding polymer. Covalent coating of CNT surface ensures their more efficient interaction with the surrounding polymers [87, 92]. However, chemical interaction with the surface of CNT changes their properties. At the same time, mechanical properties can not only improve, but also deteriorate [93].

Modification of the surface of CNTs by plasma treatment is promising [93]. This method does not create pollution and allows a wide range of different functional groups to be applied to the surface of CNTs, changing the gases used and the parameters of the plasma. Exposure to plasma causes the de-

struction of C–C bonds and the formation of active centers for binding functional groups on the surface of CNTs. Using monomers in plasma, one can create an even stronger coating on the surface of CNT. The creation of such a coating facilitates the subsequent dispersion of CNT aggregates. To preserve CNTs, it has been proposed to prepare active radicals in plasma, and to carry out the interaction with CNTs outside the space occupied by the plasma. Covalent coating of CNT surfaces is used as a polymerization initiator to produce nanohybrid coatings that can be incorporated into polymer matrices.

CONCLUSION

Methods for the preparation of samples from CNTs for the manufacture of molding masses are considered. All obtained billets have contaminants from catalysts and carbon-containing waste, which can be removed by various physicochemical methods. As nanoparticles (and often obtained at high temperatures), CNTs are easily combined into aggregates of different strengths. Surfactants are used to prevent the formation and destruction of the obtained durable aggregates. Technology and equipment are also quite well developed. They are widely used in the use of carbon fibers for the manufacture of various carbon materials with matrices of polymers. Various compounds are used for CNT surface modification. These works are now widely carried out in organic chemistry and in the preparation of composites with polymer matrices.

Thus, many methods of post-firing processing of freshly prepared CNTs (single-wall and multi-walled) have been developed. The cleaning of the original CNT and modification of their surface contribute to the dispersion and uniform distribution of the CNTs in the binder and, accordingly, in the molding mixture and the CMC product. However, with the wrong choice of additives and methods of their application, all this can lead to deterioration of important properties of CNTs. Another problem is that the application of any of the methods described above will undoubtedly increase the overall cost of CMC technology. Therefore, for mass technologies, it is necessary to reduce the volume of these stages by improving CMC production technology, to make the technologies of post-firing treatment of CNTs themselves cheaper in terms of processability and the equipment used.

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