

Chapter 2

Materials Containing Carbon Nanoparticles for Hydrogen Power Engineering

E.M. Shpilevsky, S.A. Zhdanok, and D.V. Schur

Abstract Nanostructural state of the materials alters quantitatively and qualitatively their properties in comparison with traditional materials. The nanostructured materials often exhibit unusual combination of properties, which attracts more and more researchers and provides an intensive development of this direction. The materials containing carbon nanoparticles (fullerenes, carbon nanotubes and wires, nanodiamonds, thermally expanded graphite, graphenes, etc.) occupy the prominent place among the nanostructured materials. Despite its still high cost, the nanostructured materials have already found the practical applications. It may be the most effective in hydrogen energy, biomedicine, and as the active elements of sensors. The report are based on the analysis of published data of last 10 years, the prospects of the use of materials with carbon nanoparticles in hydrogen energy as: sorbents (hydrogen storage), membranes, catalysts, constructional, electrical and decorating materials, materials for friction, sensor elements, seals and coatings are considered.

Keywords Carbon nanoparticles · Cluster · Nanotube · Hydrogen storage · Lubricant · Electron microscopy · Grain size

2.1 Introduction

Nanostructural state of the materials alters their properties quantitatively and qualitatively in comparison with traditional materials. The values of the melting temperature, the solubility limit of components (chemical elements), the kinetic

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parameters of charge transfer processes in nanostructured materials are substantially different from the bulk samples. In nanostructures the uncharacteristic of traditional materials the structural states (metastable phases) are realized. For nanostructures the band theory of solid state is not acceptable. The properties of nanostructures are being actively studied and already it is known much. A number of reviews and monographs [1–4] is devoted to the exploration of nanomaterials and to the development of nanotechnology. It is shown that with the grain decreasing the electrical, mechanical, optical and magnetic properties of materials and also the phase transition temperature, elastic module are changed. Nanostructured materials often exhibit unusual combination of properties that attracts more and more researchers and provides an intensive development of this direction. The materials containing carbon nanoparticles (fullerenes, carbon nanotubes and wires, nanodiamonds, thermally expanded graphite, graphenes, etc.) occupy the prominent place among nanostructural materials. Despite its still high cost, the nanostructured materials have already found the practical applications. They may be the most effective in hydrogen energy, biomedicine, and as the active elements of sensors.

In this paper, on the base of an analysis of published data during last 10 years, the prospects of the use of materials containing carbon nanoparticles in hydrogen energy are submitted, such as: sorbents (hydrogen storage) and catalysts, constructional and electrical materials and also the materials for internal friction, seals, sensors.

2.2 Nanoparticles and Nanostructures

The fullerenes – carbon clusters with an even, more than 20, the number of carbon atoms, forming three bonds with each other. The atoms in molecules of fullerene are located on the surface of the spheroid at the tops of hexagons and pentagons.

The fullerene molecule C_{60} has the highest symmetry and the highest stability among all fullerenes. The carbon atoms in C_{60} molecule are placed on a spherical surface at the tops of 20 irregular hexagons and 12 regular pentagons and are linked by a covalent bond. The length of the C–C in the pentagon is 1.43 Å, the same length has the side of the hexagon, which is common to both figures, but the side which is common to two hexagons has a length of about 1.39 Å. The radius of the molecule C_{60} is 0.357 nm. Fullerenes have a high chemical inertness to the process of molecular decay: molecule C_{60} , for example, is stable in an inert atmosphere up to 1,700 K. At the oxidation, one molecule of C_{60} can attach 12 atoms of oxygen. Fullerene molecules can form crystalline phases – fullerites as endohedral and exohedral structure.

Fullerenes and fullerene-like particles – are the special large and diverse type of nanoscale clusters with a stable electronic bond between the atoms, they are much more stable compared to usual clusters (conglomerates of atoms). For fullerene-like particles are carbon nanotubes, aggregates of ultrafine carbon (“onion”

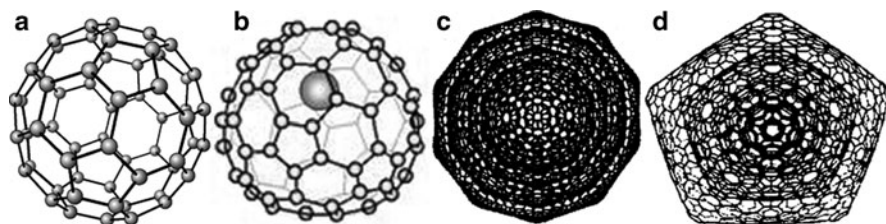


Fig. 2.1 Models of fullerenes and multilayer carbon clusters: **a** – fullerene C_{60} ; **b** – endofullerene; **c, d** – ultrafine carbon aggregates of multilayer type

structures, thermally expanded graphite, graphene, nanodiamonds). Ultrafine carbon aggregates (UFCA) are the association of carbon clusters.

Clusters can have a different structure: the chainlike, singlelayer, multilayer (“onion”), etc. Figure 2.1 shows the models of fullerenes and multilayer carbon clusters.

Although fullerenes are the weak acceptors (E for $C_{60} = -0.44$ v, E for $C_{70} = -0.41$ v) they form a series of molecular complexes with organic molecules of different classes. In which fullerene C_{60} acts as acceptor and organic molecule acts as donor. In these compounds the donor molecules and C_{60} are connected by Van-der-Waals bonds or π - π interactions. In crystals C_{60} molecules are packed in chains, layers or three-dimensional structures. The charge transfer from the organic molecule on the C_{60} is virtually absent. Photoexcitation of molecular complexes leads to a state with charge separation, the mechanisms of carrier generation are different.

The organization of associates from nanoclusters occurs on the same mechanisms as the formation of crystals from atoms. However, clusters have a real surface and the intercluster boundaries. Therefore, the formation of associates of the nanoclusters is accompanied by the emergence of a large number of defects and significant mechanical stresses. Defects and mechanical stresses lead to a significant change in the properties of UFCA.

Carbon nanotubes (CNT) are the graphite planes which are rolled into a cylinder, i.e. they form the surfaces from the regular hexagons with the carbon atoms in the tops. There are single- and multiwall nanotubes. The last differ from single-walled carbon nanotubes that they consist of several layers. The distance between the layers is 0.34 nm, which corresponds to the distance between the layers in crystalline graphite. In addition, the properties of individual nanotube are determined by its chirality, i.e. by angle of orientation of the graphite plane relative to the tube axis. Figure 2.2 shows the electron microscopic images of multiwalled CNT obtained by the method of [5] and used by us to modify various materials [6].

Thermally expanded graphite (TEG) can be considered as a polymer layered graphite crystal with thickness of several atomic layers, which is characterized by the presence of active chemically “dangling” bonds. Figure 2.3a shows the structure

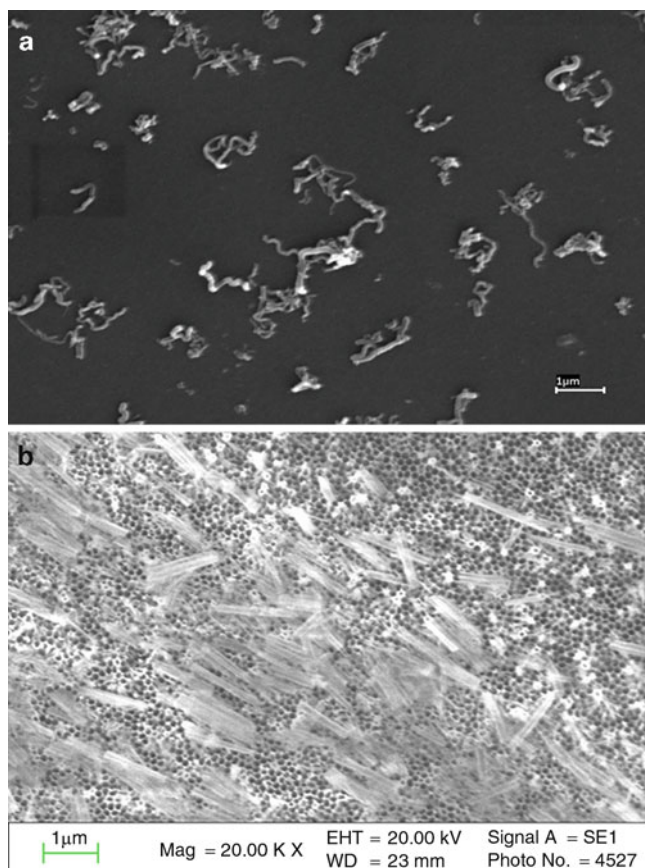


Fig. 2.2 Electron microscopy image of multiwalled CNTs used for the modification of metals

of TEG, which was received with a scanning electron microscope. TEG in our papers was used for modification of polymers [7].

In recent years the possibility of obtaining a single layer of graphite was revealed [8]. Such layers one atom thick, were called graphene. Graphene model are presented in Fig. 2.3b. The adsorption of the atoms of other elements on graphene surface can get new two-dimensional nanostructures. The authors of [9] managed to attach the hydrogen atoms to the graphen. This structure was called grafan. Figure 2.3c illustrates the graphan structure.

Nanostructures can be formed exposing the known materials by thermo-mechanical treatment, electrochemical treatment, by the condensation of evaporated substances in vacuum into the place of the condensation of nanoparticles, and by using other methods of action. Figure 2.4 shows the nanostructure of Al_2O_3 , obtained by multistage anodization.

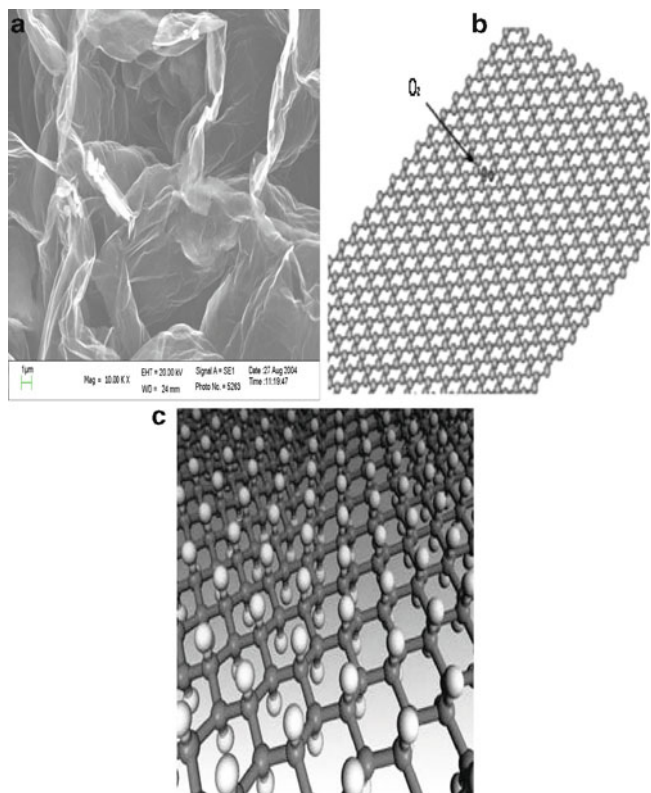


Fig. 2.3 Electron microscopy image of thermally expanded graphite (a) and the graphene (b) and grafan (c) models

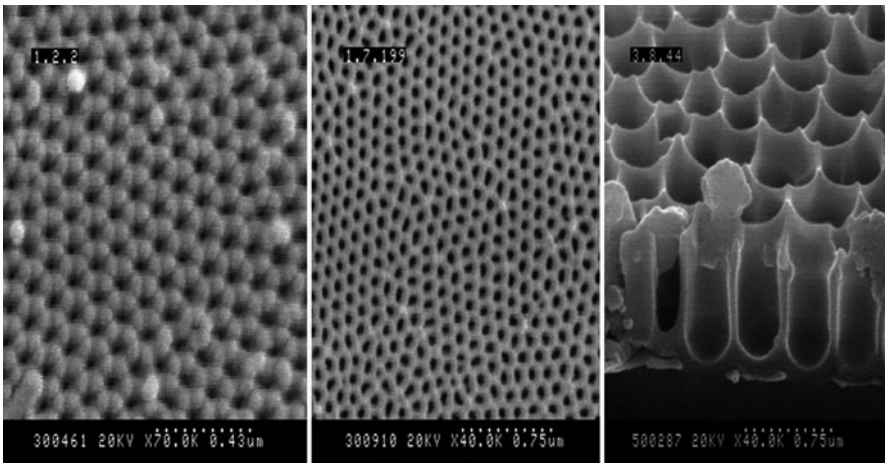


Fig. 2.4 SEM images of nanostructures Al_2O_3 , obtained by multistage anodization

The presented types of nanoparticles and nanostructures are the convenient and effective modifiers of materials (metals, semiconductors, dielectrics, polymers, ceramics).

2.3 Key Achievements in the Study of Nanomaterials

To date, many methods for obtaining of nanomaterials and nanostructures are developed [10, 11]. We say only the most common: from the combined atomic-molecular beams, in electric arc, by the electrochemical deposition, with the help of powder metallurgy and conventional (vacuum) metallurgy, by the diffusion annealing, shock wave and dynamic loading, ion implantation, mechanical action, by the use of self-organized natural matrices, by the use of Langmuir-Blodgett method, multi-stage anodizing of aluminum, silicon and other substances, by the formation of nanoscale objects through solid mask. Most of them are tested with the participation of the author of this work [12, 13]. The various methods to ensure the introduction of nanoparticles into the matrix of various substances are tested.

It is shown that nanomaterials possess several unique properties: (a) low coefficient of friction, (b) high wear resistance, (c) increased corrosion resistance, and (d) high strength, and (e) increased the elastic properties; (f) non-linear optical properties [14].

The new effects observable only in nanostructures are found. For example, the effect of giant magnetoresistance, which differs from the Gause effect by size, sign and mechanism of carriers dispersion; the effect of the plasmon resonance absorption observed on the metal nanoparticles; the quantum Hall effect, and other dimensional effects [14–16]. The features of displaying of known physical effects in nanostructures (Hall, Gause, Seebeck, other galvanomagnetic, tenzoelectric, thermoelectric effects) are shown [17–19].

It is shown that fullerenes as a special type of carbon molecules can enter into chemical interaction with metals, even those that do not form carbides (Cu, Sn) [20]. Scientific instrumentation provided an opportunity for observation of nanoscale objects by creating a high-resolution electron microscopes, atomic force and tunneling microscopes. The technologies of industrial production of fullerene C₆₀, carbon nanotubes, TEG are developed [21, 22].

The ability of fullerite to polymerize at high temperatures and pressures, as well as the impact of radiation is established [23, 24]. Ferromagnetism of rhombohedral phase of C₆₀ is discovered [25].

It is shown that the introduction of fullerenes in material even in small proportions (up to 1.0 wt.%) significantly (in some cases in several times) changes their physical and physico-chemical properties [26].

Experimentally proved that the diffusion processes in metal-fullerene structures have several features: (a) high partial diffusion coefficients of metal atoms, and (b) change in concentration of components in the surface layer during annealing,

(c) the formation of conglomerates of metal on the structure of fullerite defects, including vacancies (d) high rates of migration of fullerene molecules of C60 on metal surfaces ($10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$) [27].

2.4 Materials Containing Carbon Nanoparticles for Hydrogen Power Engineering

To create new materials, fuel elements, environmentally harmless engines and power plants which are running on hydrogen fuel, the great scientific potential and significant financial investment are already exploited. In the search of new materials the materials containing carbon nanoparticles occupy a special place [28, 29].

2.4.1 Sorbents, Accumulates, Catalysts, Membranes

Carbon nanoparticles and structures since the discovery of ways to get them have attracted the attention of scientists as potential sorbents, batteries, catalysts, membranes. The particular interest have been shown to the fullerenes C60 and carbon nanotubes [30–34].

The process of adsorption is significantly affected by the electronic structure of surface atoms, which, in turn, depends on the size of the nanoparticles. Figure 2.5 shows the dependence of the rate constants of adsorption of nitrogen molecules (molecules/second) on the number of niobium atoms within the cluster. As can be seen from the figure, the rate of adsorption has a complex dependence on cluster size. This is due to the fact that the union of atoms in the nanoparticle is accompanied by a decrease in the interaction energy of the electrons and nuclei. The minimum energy of interaction is possible with a certain arrangement of atoms.

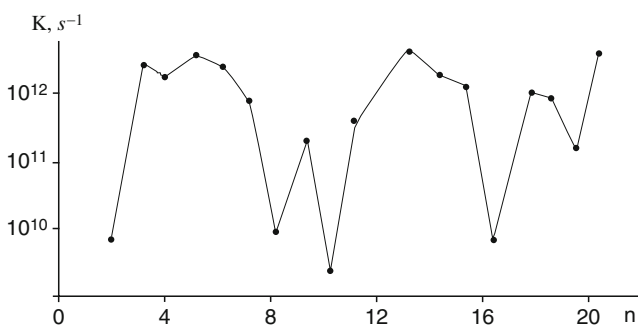


Fig. 2.5 The dependence of the rate constant of N2 adsorption (molecules/second) from the number of niobium atoms in the cluster

For this the size of the cluster is not important, but the redistribution of electrons at the changing of the number of atoms in the cluster and the surface area of the cluster.

Due to the high specific surface area and good sorption characteristics the carbon nanostructures can adsorb on their surface and enough strongly retain the metal nanoparticles, which are highly efficient catalysts. In [32] the methods of applying Pt clusters on the surface of carbon nanofibers have been developed. According to the data of transmission microscopy the size of Pt clusters, deposited on carbon nanofibers, are at an average of 5 nm. The obtained Pt/CNF catalysts were investigated in the membrane-electrode units of the hydrogen-air fuel elements. The measurements showed that the maximum power at the anode is 105 mW/cm^2 , that indicates the prospects of using of these electrocatalysts.

The carrier for the electrocatalysts must satisfy the following requirements: to provide the high electrical conductivity and the availability of the reagents to the catalyst surface, to have the high corrosion resistance. At last time, the nanostructured forms of carbon are actively studied as a carrier of catalytic particles [32, 33].

The membrane properties of nanoporous materials are determined by both adsorption and diffusion processes. The study of these characteristics is especially important for creating a new generation of membranes in which the selective layer contains carbon nanotubes, nanostructured graphite and other carbon nanostructures. The contradictory of few published data related to the behavior of gases and liquids inside carbon nanotubes (CNT) and other nanostructures, are apparently conditioned by the fact that it does not take into account the important questions about the nature and mechanisms of adsorption and diffusion kinetics. The analysis for hydrogen, conducted in [34–37], shows that the unusual properties of membranes based on carbon nanotubes and other carbon nanostructures (the enhanced diffusion compared with the normal in the regime of Knudsen and the selectivity of 10 ... 20 for a pair of methane – hydrogen which does not conform to this regime) which have been found by some researchers, it seems, can be explained by the diffusion models and characteristics, taking into account the possible chemisorption processes for hydrogen in graphite and related carbon nanomaterials with sp^2 -hybridization [34]. “Anomalous” Knudsen regime can be attributed to monolayer chemisorption of hydrogen (for example from methane in the case of a mixture of methane, hydrogen) on the chemisorption carbon centers. In this case there is an amplification of the elastic repulsion of the hydrogen molecules (or, even more, methane) from carbon “walls”, “decorated” by the chemisorbed hydrogen atoms.

By treatment of the mixture of carbon nanotubes and MgH_2 powders in a planetary ball mill the composites have been prepared, which are perspective for hydrogen generation and storage. It was found that the pressure of hydrogen, which is separated by composite MgH_2 -CNT at temperatures of 150°C , 250°C and 335°C , are higher than that of activated magnesium hydride. The process of hydrogenation of the composites after desorption proceeds more fast than for high dispersive

magnesium. MgH_2 -CNT composites have high activity in the reaction with water and acid solutions, which allows to use this reaction to create hydrogen accumulators.

Thus, the activity of the catalyst depends on the size of the cluster. A carbon nanostructures can be used as a carrier of metal catalysts and membranes, as components of hydrogen storage.

2.4.2 Construction Materials

At the joint condensation of metal and fullerene, the size and the shape of the alloy grains depend on the type of metal, its concentration and the temperature of the substrate. Thus, for the system Al- C_{60} the grains mainly take the form of pyramids, for the system Cu- C_{60} – elongated domes, and for the system Ti- C_{60} – hemispheres. Their linear dimensions are 30 ... 3,000 nm [13]. Homogeneous metal films depending on technological conditions may have a grain size of 80–3,000 nm. With the increasing of concentration of C_{60} molecules in the atomic-molecular flow the grain size initially decreases. By exceeding the volume concentration of fullerene 50%, the grain size of the alloy increases with the concentration of molecules of C_{60} . The structure of the films is determined by the conditions of their formation (composition, substrate temperature, the density of an atomic cluster flow).

At the changing of the share of the components in the films the grain size decreases with increasing heterogeneity. Figure 2.6 shows the size dependence of the structural particles on the number of fullerene molecules per one metal atom.

The nanomaterials are characterized by the dependence of the mechanical properties on the grain size [38]. For example, the microhardness is proportional to the limit of the fluidity σ_y , whose dependence on the grain size (d) is determined

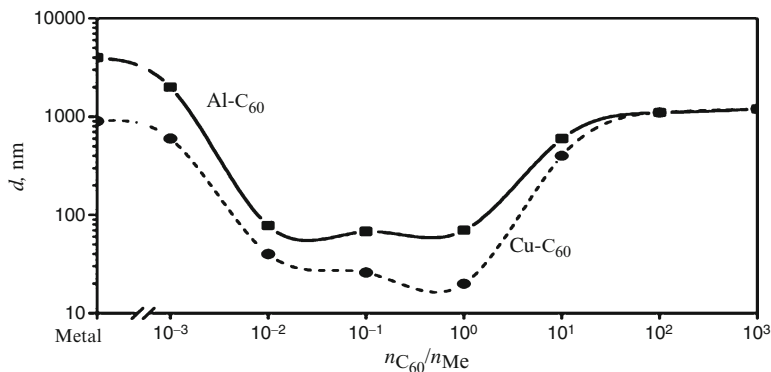


Fig. 2.6 The dependence of the average grain size on the number of fullerene molecules per 1 atom of metal

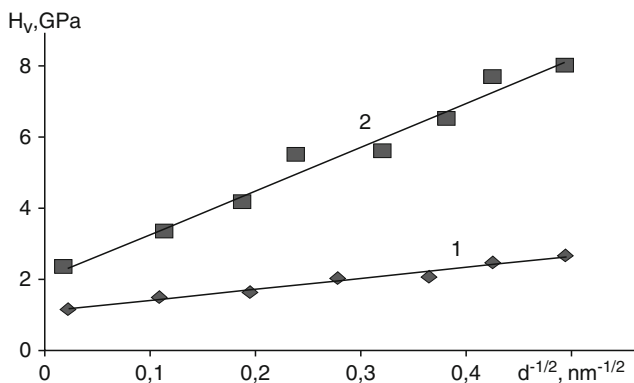


Fig. 2.7 The influence of grain size on the microhardness of metals: 1 – for copper, 2 – for Armco-iron

by the law of the Hall–Petch: $\sigma_y = \sigma_0 + k_y d^{-1/2}$. Figure 2.7 shows the dependence of microhardness of copper and Armco-iron on grain size.

The significant increase in Young's modulus and strength of polymer material can be achieved by the introduction of nanoparticles (eg, fullerenes or CNTs) into polymer matrix. For example, the addition of 1% wt. CNTs in polystyrene composite leads to an increase in Young's modulus by 40%, and in the rupture strength – at 25% [39, 40].

2.4.3 Electrotechnical Materials

Any modern power plant, including running on hydrogen fuel, requires the equipment with electrotechnical devices, and consequently, the materials with different electrical characteristics. Metal-fullerene materials have the widest range of electrical properties: from insulator to metal [6, 14, 41]

The titanium-fullerene material is obtained which shows the properties R–C–L – chains at alternating current. On the basis of this material the filter of high frequencies is designed, for which the position of the minimum of electric resistance on the frequency dependence is determined by equity ratio of titanium and fullerite [41, 42] (Fig. 2.8).

2.4.4 Materials for Units of Friction

Modification of oxide ceramics by fullerenes is accompanied by a significant increase in its wear durability. The ceramics, containing 0.1–0.6 wt.% of fullerenes has the best anti-wear properties. In this case, the wear rate of oxide ceramics is reduced to about 15 times in comparing with the original unmodified state.

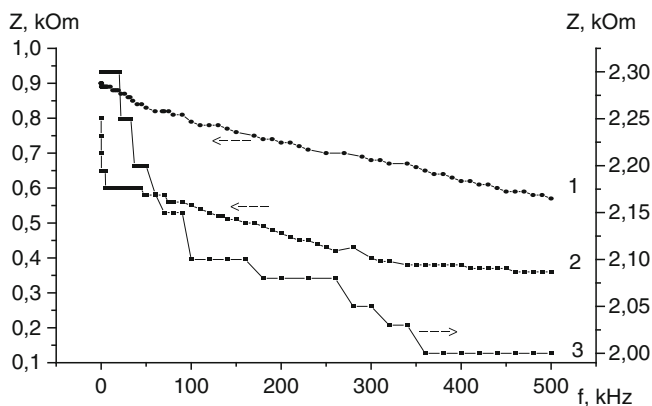


Fig. 2.8 Dependence of the changes in electrical resistance of the films on the frequency at different concentrations Ti/C_{60} : 1 – $\text{nTi}/\text{nC}_{60} = 680$, 2 – $\text{nTi}/\text{nC}_{60} = 270$, 3 – $\text{nTi}/\text{nC}_{60} = 140$

The increase of fullerene concentration in the ceramics up to 1.2 wt.% does not lead to such significant increase in its durability. Mass wear rate of the modified oxide ceramics in this case is $0.8 \cdot 10^{-5}$ mg/m, that is only 3 times lower in comparison to the unmodified state. Thus, the modification of ceramics by fullerenes at the concentration 0.1–0.6 wt.% provides the marked improvement in wear resistance of oxide-ceramics coating. The reduction of tribological properties of oxide ceramics at content exceeding 0.6 wt.%, may be associated with the possibility of the formation in this case of the sufficiently large crystals of fullerite. Coming out the pores of the oxide ceramics and getting into the zone of frictional contact, such particles may have (under certain conditions) the properties inherent in abrasives [43], and, consequently, may increase the rate of the wear of the surface of triboconjugation.

The studies of elemental composition on the base of the intensity of characteristic X-rays have discovered in thin layers, formed on the surface friction of ceramic coating, carbon, iron and oxygen, and, surprisingly, the absence of aluminum. It turns out that the iron atoms not only actively diffuse into the modified oxide ceramics, but at the same time replace aluminum. The atomic ratio of elements in the formed layers is $\text{Fe}:\text{O}:\text{C} = 1:2:3$, or one molecule of C_{60} per 20 iron atoms and 40 oxygen atoms.

The appearance of these layers coincides with the sharp decrease in the coefficient of friction from 0.13 to 0.08 at the friction distance $L = 300$ m (see Fig. 2.9).

The stopping of the motion and the holding out the friction units under the pressure changes the friction coefficient, that indicates on diffusion processes and phase formation. The filling of the ceramic coating by fullerenes has also a significant influence on his wear strength.

Figure 2.10 shows a diagram of changes in the wear rate of modified and unmodified ceramics depending on pressure on the unit of friction.

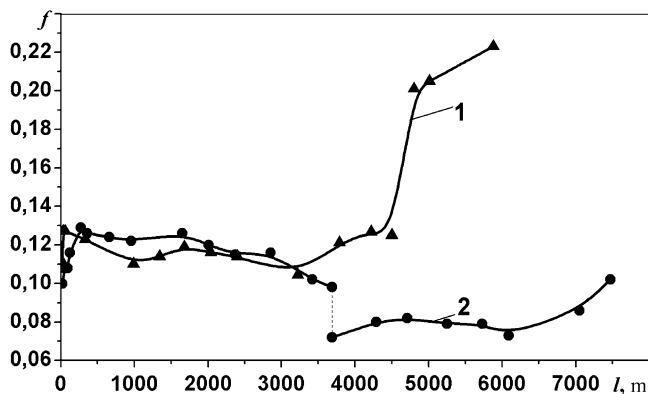


Fig. 2.9 Changes in the coefficient of friction from duration of a test at a pressure of 45 MPa

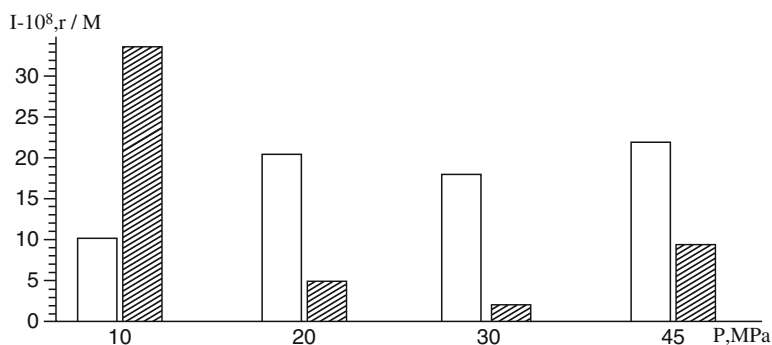


Fig. 2.10 The wear rate of the modified and unmodified ceramics depending on pressure on the unit of friction: $P = 10, 20, 30, 45$ MPa

The dependence of the wear for the coatings which were modified with C60 fullerenes on the contact pressure has the “extremum” character.

For the investigated pressure the minimum wear rate ($2.05 \cdot 10^{-8}$ g/m) is recorded at a pressure $P = 30$ MPa, which should be associated with the formation of iron-oxide fullerene surface layers (Fig. 2.2). The excess or reduction of this pressure is accompanied by the increasing wear, the most value of which equal to $33.6 \cdot 10^{-8}$ g/m and was recorded at a pressure of 10 MPa, which is associated with mechanical destruction of the layers and abrasive wear.

2.4.5 Materials for the Sensitive Elements of Sensors

On the base of materials which have been modified by carbon nanoparticles and metal carbon complexes the variety of sensors to determine the pressure, the flow

rate of liquid or gas, temperature, optical properties, mass, pressure, strength, and also devices for determining various chemical substances can be created [44–46].

Sorption sensors. Metal-fullerene films are the good sorbents. Our studies of the electrical properties of thin films of Cu – C60 with different composition (the ratio of copper atoms per fullerene molecule NCu: NC60 have been changed) showed a high sensitivity of their electrical resistance to the adsorption of oxygen [45].

These changes in electrical resistance (in the tens of percentages) point out the good prospects for the use of such structures as sorption detectors.

Using piezoelectrical effect the tensor sensors can be built on the base of metal-fullerene films. Metal-fullerene films have a high coefficient of tensor sensitivity, it is more than 10, while the highest for metals (platinum) is 1.6.

Fullerenes possess photoconductivity in the range of wavelengths from 280 to 680 nm. The probability of formation of electron-ion pair at the absorption of one photon is 0.9. On the basis of fullerene and metal particles structures of two types can be created: islet (i.e., with isolated inclusions of metal) and network (i.e., with interconnected metal inclusions). Such structures with periodicity much less than the wavelength of electromagnetic radiation behave as photonic crystals with forbidden photonic band. There is a significant change in plasmon frequencies in such structures.

At the study of the transmission spectra of nanostructures fullerite C60, copper and C60 – Cu in the visible and near infrared spectrum it is revealed that the spectral position and the intensity of the resonance plasmon absorption depend on the parameters of nanostructures C60–Cu, the conditions of their production and storage period on the air.

The formation of phases in the metal-fullerene structures [46] allows to achieve their desired characteristics and high selectivity of adsorption by technological methods. On these parameters it can be seen that the fullerene materials are perspective for the photoelectric sensor devices.

The external electric and magnetic fields change the electrical properties of the metal-fullerene films thanks to the interaction with electrons. This allows the use such films as sensors not only to determine the values of external influence, but to fixate the positions, deformation values and others. Fullerenes interspersed into the metal matrix, may serve as sensors of weak electronic and electromagnetic flows, deformations, force fields, in addition to other used materials. That expands the range of possible approaches and solutions.

Sensors for the determination of small external influences play an increasing role in various areas, which require precision, low cost, speed and efficiency of obtaining information. The use of nanoparticles as a specific electrochemical label is the new platform to enhance the effectiveness of sensors for determination of the small external influences.

Using different properties of nanostructures (electrical, piezoelectrical, galvanomagnetic, thermoelectrical, photovoltaic, optical, adsorption, diffusion, chemical, biochemical) the sensitive elements of the sensors of new generation can be developed. The typical features of such sensors will be: the high localisation (from several to tens of nm), fast response time (at least an order of magnitude faster

than the classical solid-state sensors), the highest sensitivity to virtually all physical, physicochemical, chemical and biochemical parameters, the reducing of the influence of it's presence on the object of the control (on the orders).

Nanostructures, particularly carbon nanotubes and metal nanoparticles have the excellent catalytic properties. Their introduction to electrochemical sensors reduces the strain of many important for the analysis electrochemical reactions, and even allows to carry out some redox reactions in the opposite direction, that it is impossible for classical non-modified electrodes [45]. Such properties of metal-carbon complexes at their use in sensors increase the sensitivity and selectivity, and also reduce the response time [46, 47].

2.4.6 Lubricants

To modify the lubricants the carbon nanoparticles represent the considerable interest, thanks to their unique complex of physical and mechanical properties [6, 48]. The use of lubricants, modified with carbon nanoparticles, reduces the wear rate of the test material in 1.4–1.8 times. At using lubricants modified with carbon nanoparticles the wear resistance of materials increases with increasing of specific load in the friction zone. The modification of oils by carbon nanoparticles allows to stabilize the friction coefficient with increasing temperature and raise to 20–30% upper the limit of working temperatures for modified oils [49, 50].

2.5 Conclusions

The research area related to the obtaining of new substances and materials in the base of fullerenes and other carbon nanostructures is successfully developing. The effective methods to obtain nanostructured materials containing carbon nanoparticles and nanostructures are developed. The structure, optical, magnetic properties, photoconductivity, processes of photoseparation of charges, the possibility of practical use of these materials are investigated. The introduction of carbon nanoparticles or nanostructures into the materials, even in small proportions (up to 1.0 wt.%) significantly (in some cases in several times) changes their physical and physico-chemical properties.

The use of carbon nanoparticles and nanostructures in multifunctional materials in engineering (including the hydrogen power engineering) often requires the chemical modification of their surface. To improve the interaction and compatibility of nanoparticles and nanostructures with the matrix material it is efficiently to apply the fluoridation.

Various methods for modification of carbon nanoparticles and nanostructures – oxidation, fluorination, hydrogenation, and the addition of free radicals and other highly reactive molecules are developed.

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Systems - II

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Veziroğlu, A.; İbrahimoglu, B. (Eds.)

2011, XXXIV, 540 p. 278 illus., Hardcover

ISBN: 978-94-007-0898-3