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NANOMATERIALS

Lecture Notes

Lectures 1–16

COURSE OF LECTURES

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Lecture 1. Nanomaterials: General Characteristics

Outline

1. Nanomaterials and nanotechnologies: history, present state and prospects.
2. Basic terms and definitions.
3. Sizes of objects in the surrounding world.
4. General characteristics of atoms and substances.
5. Special properties of nanomaterials.
6. Nanosystems and their main characteristics.

1. Nanomaterials and Nanotechnologies: History, Present State and Prospects

The term "**nanotechnology**" was first proposed by the Japanese scientist N. Taniguchi in 1974. In 1981, the German scientist H. Gleiter pointed out the possibility of creating materials with grain sizes below 100 nm that would meet stringent requirements and possess better properties than conventional microstructured materials. Gleiter and, independently of him, I. D. Morokhov introduced the concept of *nanocrystals* into the scientific literature. Later, H. Gleiter also introduced the terms *nanocrystalline*, *nanostructured*, *nanophase* and *nanocomposite* materials.



Figure 1. Founders of the science of nanomaterials: N. Taniguchi (left), H. Gleiter (centre) and I. D. Morokhov (right)

Today, interest in this new class of materials is growing steadily both in fundamental and applied science and in industry. This is due to the following reasons:

1. the drive to reduce the dimensions of products;
2. the unique properties of materials in the nanostructured state;
3. the need to develop and introduce new materials with qualitatively and quantitatively new properties;
4. the development of new technological techniques and methods based on the principles of self-assembly and self-organisation;

5. the practical introduction of modern instruments for the study and inspection of nanomaterials (for example, scanning probe microscopy, X-ray methods and nanoindentation);
6. the development and introduction of new technologies (ion-plasma technologies for surface treatment and the deposition of thin layers and films; LIGA technologies, which comprise a sequence of lithography, electroplating and moulding processes; technologies for the production and consolidation of nanopowders, etc.).

2. Basic Terms and Definitions

One of the most widely used terms of the nanoworld is "**nanomaterials**". The concept of a "material" is closely related to that of a "substance". *Materials* are substances that are used to solve practical problems.

Substances are one of the forms of matter. The main characteristics of substances are their structure and properties. *Structure* is the totality of the constituent elements of a substance that have stable interrelations ensuring its integrity and the preservation of its properties. *Properties* are the qualitative or quantitative attributes of a substance that reflect its individuality or, conversely, its commonality with other substances and that manifest themselves when different substances are compared.

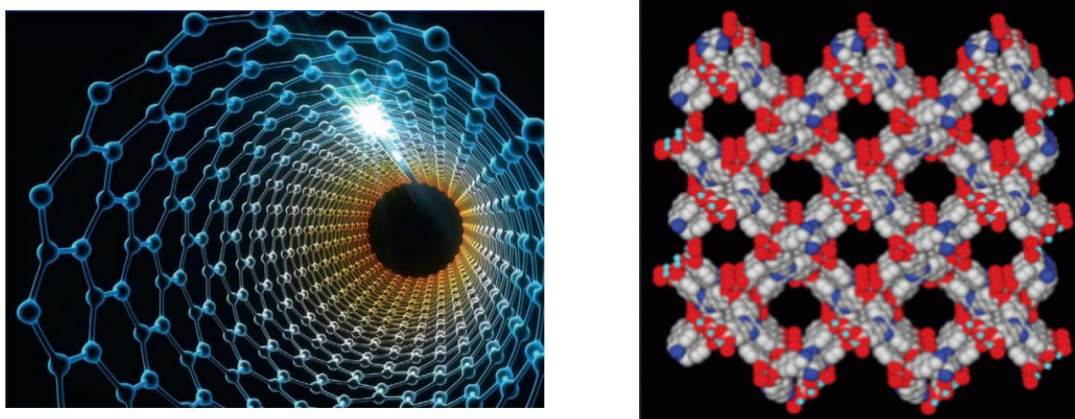


Figure 2. Examples of the nanoscale structure of substances: a carbon nanotube (left) and a molecular crystal framework (right)

The prefix "**nano**" in the terms of the nanoworld denotes a change of scale by a factor of 10^9 : 1 nm (one nanometre) = 10^{-9} m, i.e. one millionth of a millimetre. Table 1 gives the sizes of some objects in the range from 10 m to 1 Å (1 Å = 10^{-10} m; thus 1 Å is ten times smaller than a nanometre and corresponds to the diameter of a hydrogen atom).

It is generally accepted that objects of the nanoworld are objects whose characteristic dimensions lie in the range from **1 to 100 nm**.

The main feature of nano-objects is their distinctive properties, which in many cases can also manifest themselves when the dimensions of the nano-objects exceed the established limit of 100 nm; such materials, with particle sizes up to 1 µm, are then called *nanodispersed materials* (Figure 3).

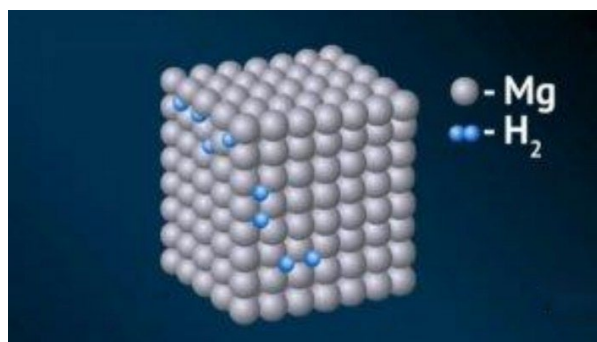


Figure 3. Nanodispersed magnesium powder: model of hydrogen (H_2) uptake in the magnesium lattice

Thus, the prefix "nano" is a generalised reflection of the objects of research, the predicted phenomena and effects and the ways of describing them, rather than simply a characteristic of the extent of a structural object.

3. Sizes of Objects in the Surrounding World

In accordance with the above size limitation of nano-objects, the upper boundary of the nanoscale region corresponds to the components of integrated circuits widely used today in electronic engineering. On the other hand, the size of many viruses is ~ 10 nm, and that of protein molecules is ~ 1 nm (for example, the radius of the DNA double helix is exactly 1 nm).

Table 1. Characteristic sizes of objects in the macro-, micro- and nanoworld

Size region	Characteristic size	Object
Macroworld	5...10 m	Shark
	1.5...2 m	Human being
	10 cm = 10^{-1} m	Bird
	1 mm = 10^{-3} m	Grain of sand
Microworld	100 μm = 10^{-4} m	Thickness of a sheet of paper
	10 μm = 10^{-5} m	Thickness of a human hair
	1 μm = 10^{-6} m	Red blood cell
Nanoworld	100 nm = 10^{-7} m	Component of integrated circuits
	10 nm = 10^{-8} m	Virus
	1 nm = 10^{-9} m	Protein molecule; diameter of the DNA helix
	0.1 nm = 10^{-10} m	Hydrogen atom

4. General Characteristics of Atoms and Substances

All substances ultimately consist of elementary particles (protons, neutrons, electrons, etc.). An **atom** is an electrically neutral system consisting of a positively charged nucleus formed by nucleons (protons and neutrons) and a negatively charged shell formed by electrons (Figure 4).

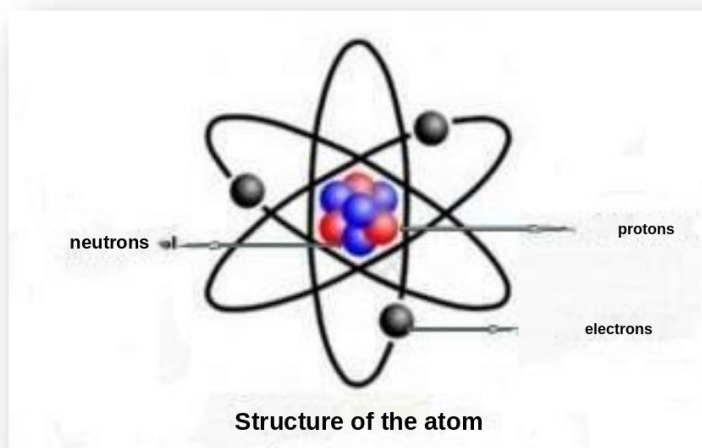


Figure 4. *Structure of the atom*

An *atom* is the smallest particle of a chemical element, an assembly of nucleons and electrons characterised by a definite atomic number, which is numerically equal to the magnitude of the nuclear charge and uniquely determines the chemical identity of the element and its place in the Periodic Table of chemical elements.

The whole diversity of substances is due to the various combinations of atoms with one another. By bonding with one another, atoms of one or of different chemical elements form more complex particles, namely **molecules**. The number of atoms in a molecule varies within very wide limits: from two (for example, the hydrogen molecule) to several hundreds and thousands (for example, polymer molecules).

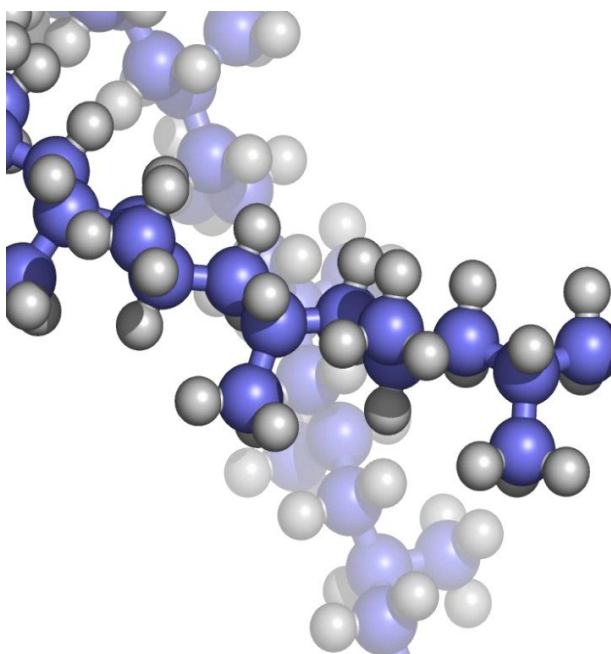


Figure 5. *Model of a polymer molecule*

Substances can exist in different states of aggregation: plasma, gaseous, liquid and solid (Figure 6). By origin, they may be natural or synthetic. They may have various physical, chemical or biological properties that depend on their structure.

The main difference between materials and substances is that the former are characterised by *functional properties* that determine the fields of their practical application. Materials serve for production activities or for solving problems of health care or environmental protection.

5. Special Properties of Nanomaterials

Nanomaterials include materials that have a nanometre scale of dimensions in at least one of the three dimensions. The nanometre scale may refer either to the material specimen as a whole or to its structural elements.

Like conventional materials, nanomaterials can exist in different states of aggregation. In practice, solid-state nanomaterials are the most widespread.

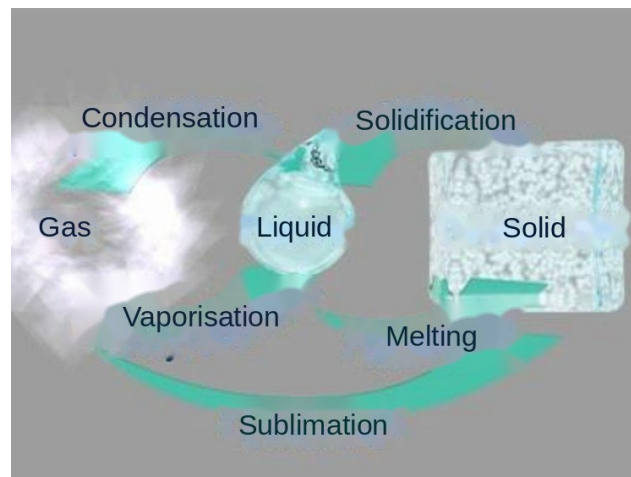


Figure 6. *Transitions between the states of aggregation of a substance*

Their most characteristic features are:

- the appearance of unconventional types of structural symmetry and special types of interphase boundaries;
- the leading role of self-organisation processes in structure formation;
- the high catalytic activity of the surface of nanoparticles and their ensembles;
- the special character of energy and charge transfer processes, which are distinguished by low energy consumption, high speed and synergetic features.

6. Nanosystems and Their Main Characteristics

The concept of nanomaterials is closely related to that of **nanosystems**. In general, systems are understood as elements arranged in a certain order, which may be either material or non-material objects. For example, the Periodic Table is a set of symbols of chemical elements arranged in a certain order according to their atomic numbers.

In practical activities, *functional systems* play a particularly important role. They are manufactured from various materials, which are subdivided into raw materials (materials that have not been processed previously) and semi-finished products (materials after preliminary processing).

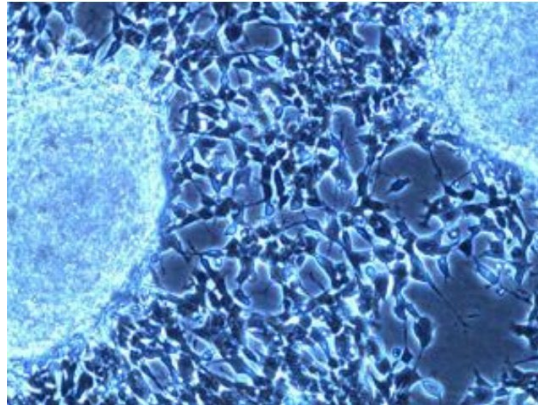


Figure 7. *Microstructure of a functional material*

Functional systems also have design features and differ in their structural complexity. As a rule, they are devices whose design is determined by the configuration, dimensions, spatial arrangement and interrelation of their constituent components.

Functional nanosystems, like nanomaterials, are characterised by a nanometre scale of dimensions in at least one of the three dimensions. Their properties, like those of nanomaterials, may manifest themselves in a highly unusual way owing to their inherent nanometre scale of dimensions. In practice, solid-state functional nanosystems are used most frequently.

Nanomaterials develop in close interrelation with **nanotechnologies**, which are a set of methods and means that make it possible to create nanomaterials in a controlled manner and to manipulate them.

Thus, nanotechnologies provide solutions to the following three interrelated tasks:

- the production of nanomaterials with a specified structure and properties;
- the investigation of the structure and properties of nanomaterials;
- the application of nanomaterials for specific purposes.



Figure 8. *Nanotechnologies in the service of humankind*

In practice, solid-state nanomaterials are the most widespread; therefore, the most important scientific basis for their development is **solid-state physics**.

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Lecture 2. Structural Features and Classification of Nanomaterials

Outline

1. Structural features of nanomaterials.
2. Classification of nanostructured materials.
3. Classification of nanomaterials by category.
4. Classification of nanomaterials by type of structure.

1. Structural Features of Nanomaterials

Nanomaterials have a number of structural features determined by parameters that may relate both to the structure as a whole and to its individual elements. There are various types of nanomaterials, each of which has a specific structure and specific properties.

According to their structure, nanomaterials are subdivided into **nanoparticles** and **nanostructured materials** (Figure 1). Nanostructured materials are ensembles of nanoparticles, in which the nanoparticles play the role of structural elements.

Accordingly, depending on the nature of the interconnection between the nanoparticles, nanostructured materials are subdivided into **consolidated** and **nanodispersed** materials.

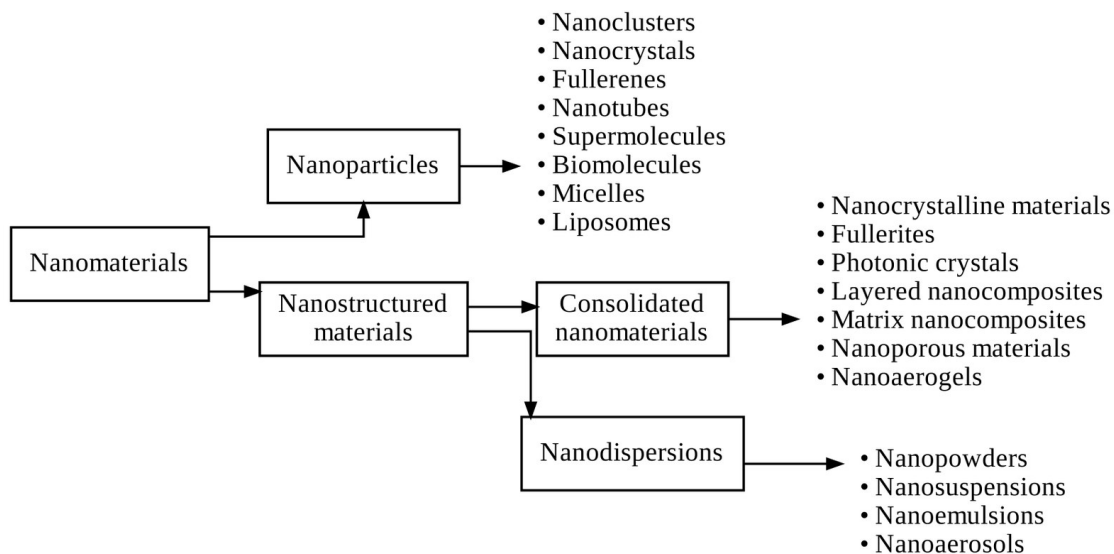


Figure 1. Classification of nanomaterials by structure

2. Classification of Nanostructured Materials

Nanoparticles include:

- *nanoclusters*, among which a distinction is made between ordered nanoclusters, characterised by a definite arrangement of atoms (molecules) and strong chemical bonds, and disordered nanoclusters, in which there is no order in the arrangement of atoms (molecules) and the chemical bonds are weak;

- *nanocrystals*, characterised by an ordered arrangement of atoms (molecules) and strong chemical bonds, similar to bulk crystals;
- *fullerenes*, consisting of carbon atoms (or atoms of other elements) and forming a structure in the form of a sphere-like cage;
- *nanotubes*, consisting of carbon atoms (or atoms of other elements) and forming a structure in the form of a cylindrical cage;
- *supermolecules*, consisting of a host molecule with a three-dimensional structure whose cavity contains a guest molecule;
- *biomolecules*, i.e. complex molecules of biological origin with a polymeric structure (DNA, proteins);
- *micelles*, consisting of molecules of surface-active substances (surfactants) and forming a sphere-like structure.

Consolidated nanomaterials are compact solid-phase materials consisting of nanoparticles that have a fixed spatial position in the volume of the material and are rigidly bonded directly to one another.

Consolidated nanomaterials include:

- materials consisting of nanocrystals, which are usually called *nanocrystallites*;
- *fullerites*, consisting of fullerenes;
- *photonic crystals*, consisting of spatially ordered elements comparable in size to half the wavelength of light;
- *layered nanocomposites* (superlattices), consisting of layers of different materials of nanoscale thickness;
- *matrix nanocomposites*, consisting of a solid-phase base, the matrix, in whose volume nanoparticles are distributed;
- *nanoporous materials*;
- *nanoaerogels*, which contain interlayers of nanoscale thickness separating the pores.

3. Classification of Nanomaterials by Category

Nanomaterials can be divided into four main categories (Figure 2). The **first category** comprises materials in the form of solids whose dimensions in one, two or three dimensions do not exceed 100 nm. Such materials include nanosized particles (nanopowders), nanowires and nanofibres, very thin films (less than 100 nm thick), nanotubes, etc. Such materials may contain from one structural element or crystallite (for powder particles) to several layers of them (for a film).

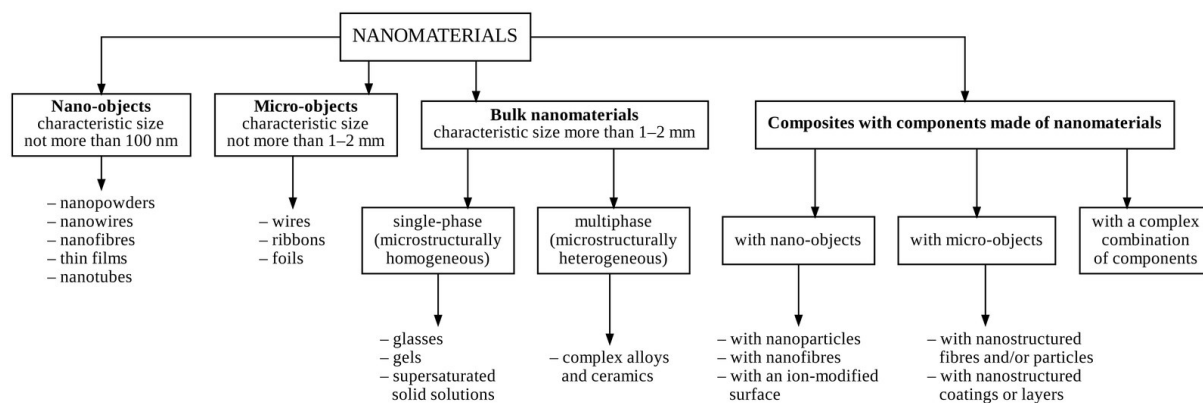


Figure 2. Classification of nanomaterials by category

In this connection, the first category can be classified as nanomaterials with a small number of structural elements, or nanomaterials in the form of nano-objects (nanoproducts).

The **second category** comprises materials in the form of small-sized products with a characteristic size in the range of 1 μm ...1 mm (wire, ribbon, foil). Such materials already contain many structural elements, and they can be classified as nanomaterials with a large number of structural elements (crystallites) or nanomaterials in the form of micro-objects (Figure 3).

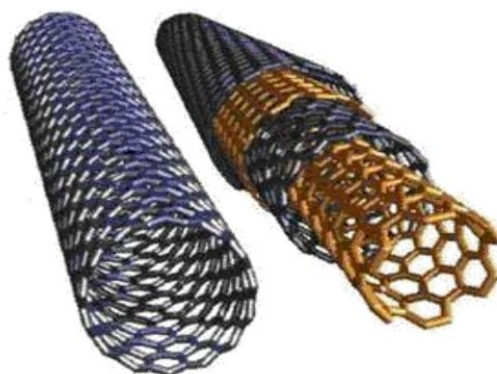


Figure 3. Carbon nanotubes

The **third category** comprises massive (in other words, bulk) nanomaterials, the products made of which have dimensions in the macroscopic range (more than several millimetres). They consist of a very large number of nanosized elements (crystallites) and are in fact polycrystalline materials with a grain size of up to 100 nm (Figure 4).

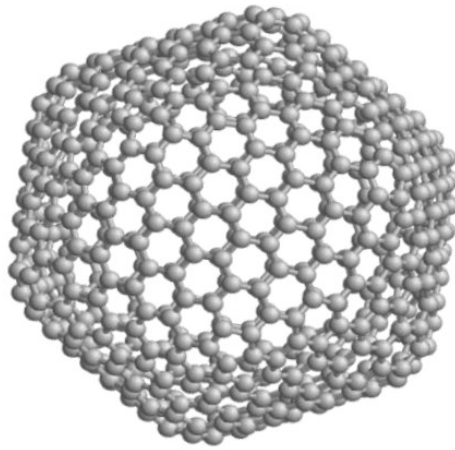


Figure 4. Model of a nanosized carbon cage structure

In turn, the third category of nanomaterials can be divided into two classes.

The *first class* includes single-phase materials (in accordance with the terminology, microstructurally homogeneous materials) whose structure and/or chemical composition varies over the volume of the material only at the atomic level. Their structure is, as a rule, in a non-equilibrium state. Such materials include, for example, glasses, gels and supersaturated solid solutions.

The *second class* includes microstructurally heterogeneous materials consisting of nanosized elements (crystallites, blocks) with different structures and/or compositions. These are multiphase materials, for example, those based on complex metallic alloys. The second and third categories of nanomaterials fall under the narrower definition of *nanocrystalline* or *nanophase* materials.

The **fourth category** includes composite materials containing components made of nanomaterials.

Nanomaterials assigned to the first category (composites with nanoparticles and/or nanofibres, products with a surface layer or thin film modified by ion implantation) and to the second category (for example, composites reinforced with fibres and/or particles having a nanostructure, materials with a modified nanostructured surface layer or coating) may act as such components (Figure 5).



Figure 5. Composite panel with a honeycomb core

Composite materials with a combined use of nanocomponents can also be distinguished.

4. Classification of Nanomaterials by Type of Structure

The properties of nanomaterials depend substantially on the nature of the distribution, the shape and the chemical composition of the crystallites (nanosized elements) of which they consist. It is therefore expedient to classify the structures of nanomaterials according to these features (Figure 6).

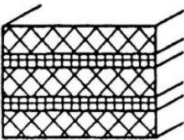
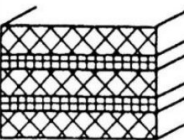
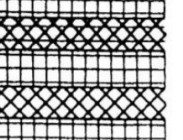
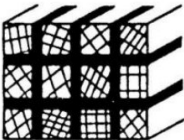
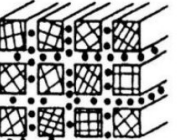
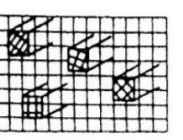
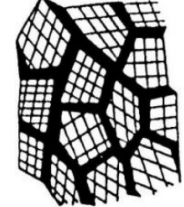
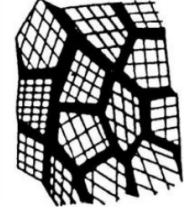
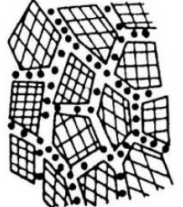
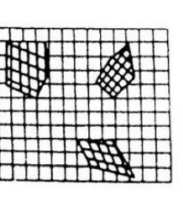
Distribution type	Crystalline			Matrix
Chemical composition	same composition of crystallites and boundaries	different composition of crystallites, same composition of boundaries	different composition of crystallites and boundaries	crystallites dispersed in a matrix of different composition
Crystallite shape:				
layered				
fibrous				
equiaxed				

Figure 6. Classification of nanomaterials by chemical composition, shape and distribution of crystallites

According to the shape of the crystallites, nanomaterials can be divided into **layered** (lamellar), **fibrous** (columnar) and **equiaxed** materials. Naturally, the layer thickness, the fibre diameter and the grain size in this case take values of about 100 nm or less.

Four groups of nanomaterials are usually distinguished:

1. The chemical composition of the crystallites and of the interfaces is the same. Such materials are also called single-phase materials. Examples are pure metals with a nanocrystalline equiaxed structure and layered polycrystalline polymers.
2. Materials in which the composition of the crystallites differs, but the boundaries are identical in chemical composition.
3. Nanomaterials in which both the crystallites and the boundaries have different chemical compositions.

4. Nanomaterials in which nanosized precipitates (particles, fibres, layers) are distributed in a matrix of a different chemical composition. This group includes, in particular, dispersion-strengthened materials.

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Lecture 3. Methods for Producing Nanomaterials

Outline

1. Plasma-chemical synthesis.
2. Gas-phase synthesis using laser heating.
3. Application of synthesis in other fields.
4. Thermal decomposition.
5. Production of nanopowders by mechanical action.
6. Mechanical attrition.
7. Self-propagating high-temperature synthesis.
8. Other methods for producing nanomaterials.

1. Plasma-Chemical Synthesis

Plasma-chemical synthesis comprises several stages. In the *first* stage, active particles are generated in arc, high-frequency (radio-frequency) and microwave plasma reactors. *Arc plasma reactors* have the highest power and efficiency; however, the materials produced in them are contaminated with electrode erosion products. Electrodeless high-frequency and microwave plasma reactors are free of this drawback.

Next, the interaction products are separated as a result of quenching. By selecting the location and rate of quenching, powders with a specified composition, shape and particle size can be obtained. Such powders have a regular shape and particle sizes from 10 to 100 nm and more.

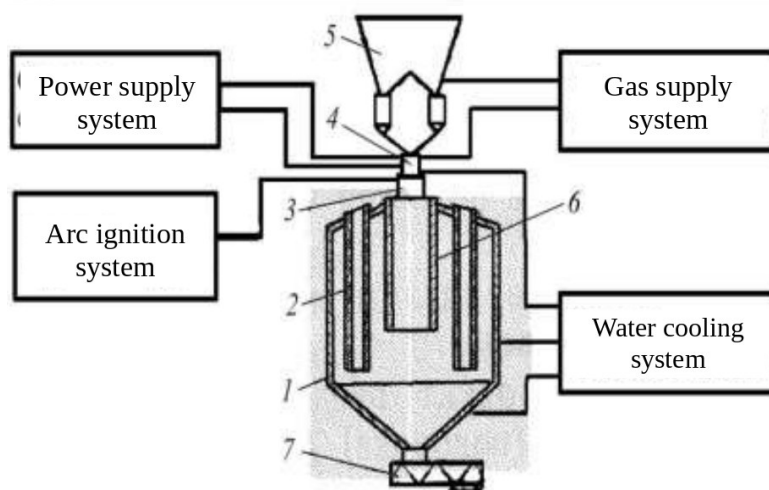


Figure 1. Schematic of a unit for producing refractory metal powders by plasma-chemical synthesis (reduction of oxides): 1 – unit housing; 2 – bag filters; 3 – reaction chamber; 4 – plasmatron; 5 – device for feeding the product to be reduced into the plasma jet; 6 – powder annealing tube; 7 – discharge device

Plasma-chemical synthesis can also be used to produce multicomponent submicrocrystalline powders that are mixtures of carbides and nitrides, of a nitride and borides, of nitrides of various elements, etc.

Plasma-chemical powders of metal, boron and silicon carbides are usually obtained by reacting the chlorides of the corresponding elements with hydrogen and methane or other hydrocarbons in an argon high-frequency or arc plasma; nitrides are obtained by reacting chlorides with ammonia or a mixture of nitrogen and hydrogen in a low-temperature microwave plasma.

Oxides are synthesised in the plasma of an electric arc discharge by evaporating a metal and subsequently oxidising the metal particles in an oxygen-containing plasma. One study described the plasma-chemical synthesis of aluminium oxide and silicon carbide nanoparticles with an average size of 10...30 nm.

It was found that nanopowders with the minimum particle size are formed when the metal vapour interacts with atmospheric oxygen under conditions of intensive air injection, as a result of which the temperature decreases rapidly.

Intensive cooling not only inhibits particle growth but also increases the nucleation rate of the condensed phase. Plasma-chemical synthesis involving the oxidation of aluminium particles in a flow of oxygen-containing plasma leads to the formation of larger oxide particles than the oxidation of previously produced metal vapour.

2. Gas-Phase Synthesis Using Laser Heating

Gas-phase synthesis using **laser heating** of the reacting gas mixture is close to plasma-chemical synthesis. Laser heating ensures controlled homogeneous nucleation and rules out contamination.

Its advantages are the absence of surfaces that cause heterogeneous nucleation, and uniform and precise control of the process. As an energy source, the laser provides monochromatic radiation of high brightness, owing to which a high degree of conversion of light into heat is achieved.

Laser synthesis of nanocrystalline Si, Si₃N₄ and SiC powders:

1. Silicon powders were obtained by pyrolysis of gaseous silane SiH₄ using a CO₂ laser (the spherical Si powder grains had a diameter of 50 ± 20 nm).
2. Silicon nitride Si₃N₄ powders were synthesised from a gas mixture of silane SiH₄ and ammonia NH₃ (the grains were spherical, with an average size of 17 ± 4 nm).
3. Gas mixtures of silane with methane or ethylene were used to synthesise silicon carbide SiC (the grain size ranged from 18 to 26 nm, with an average of 21 nm).

The grains of nanopowders synthesised using laser heating are distinguished by their spherical shape and narrow size distribution.

3. Application of Synthesis in Other Fields

The *plasma-chemical method* is also used to produce metal powders. For example, submicrocrystalline copper powders with a particle size below 100 nm and a relatively narrow particle size distribution are obtained by reducing copper chloride with hydrogen in an argon arc plasma at temperatures up to 1800 K.

Gas-phase synthesis using laser radiation, in which the radiation is used to create and sustain a plasma where a chemical reaction takes place, has proved effective for the formation of molecular clusters, a new structural modification of matter.

Molecular clusters occupy a special place among nanostructured substances. The best known of them are **fullerenes**, a new allotropic modification of carbon alongside graphite and diamond.

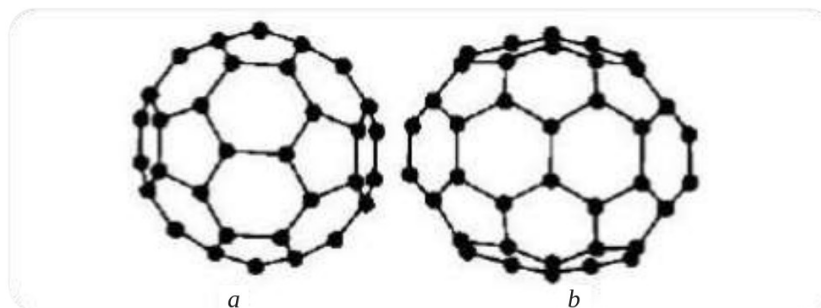


Figure 2. Structure of fullerenes (molecular carbon clusters): *a* – C_{60} ; *b* – C_{70}

4. Thermal Decomposition

Thermal decomposition usually employs complex organoelement and organometallic compounds, hydroxides, carbonyls, nitrates and oxalates of metals, which decompose at a certain temperature to form the synthesised substance and release a gas phase.

A variant of pyrolysis is the decomposition of organometallic compounds in a *shock tube*, after which free metal atoms condense from supersaturated vapour. A long steel tube closed at both ends is divided into two unequal parts by a thin aluminium-foil diaphragm.

The longer part of the tube is filled with argon at a pressure of 1000...2500 Pa containing 0.1...2.0 mol.% of organometallic compounds. The other part is filled with helium or a mixture of helium and nitrogen until the membrane ruptures. When it ruptures, a shock wave arises, at the front of which the temperature can reach 1000...2000 K.



Figure 3. Deformation of pipeline transition branch pipes caused by water hammer

Shock heating of the gas causes the organometallic compound to decompose within a few microseconds after the passage of the wave front, and the free metal atoms form a highly supersaturated vapour capable of rapid condensation. Fine powders of iron, bismuth and lead have been obtained in this way.

A combination of thermal decomposition and condensation is the supersonic outflow of gases from a chamber, in which elevated constant pressure and temperature are maintained, through a nozzle into vacuum. In this case, the thermal energy of the gas molecules is transformed into the kinetic energy of the supersonic flow, and the gas cools on expansion and turns into a supersaturated vapour in which clusters containing from two to a million atoms can form.

Highly dispersed powders of silicon carbide and silicon nitride are obtained by pyrolysis of polycarbosilanes. Initial heating is carried out by means of a low-temperature plasma or laser radiation; the pyrolysis products are then additionally annealed at ~ 1600 K to stabilise their structure and composition.

Polyvinylpentaborane is used to produce nanocrystalline boron carbide; boron-containing polymers of the polyborazine, polyborazole and polyvinylborazine type are used to form highly dispersed boron nitride powders and can also be applied as an additive to titanium powder for the synthesis of nanocrystalline $\text{TiN} + \text{TiB}_2$ compositions.

Powders obtained by thermal decomposition of monomeric and polymeric compounds must be additionally annealed to stabilise their composition and structure; the annealing temperature is 900–1300 K for nitrides and borides and 1200–1800 K for oxides and carbides.

The main drawback of thermal decomposition is the relatively low selectivity of the process, since the reaction product is usually a mixture of the target product and other compounds.

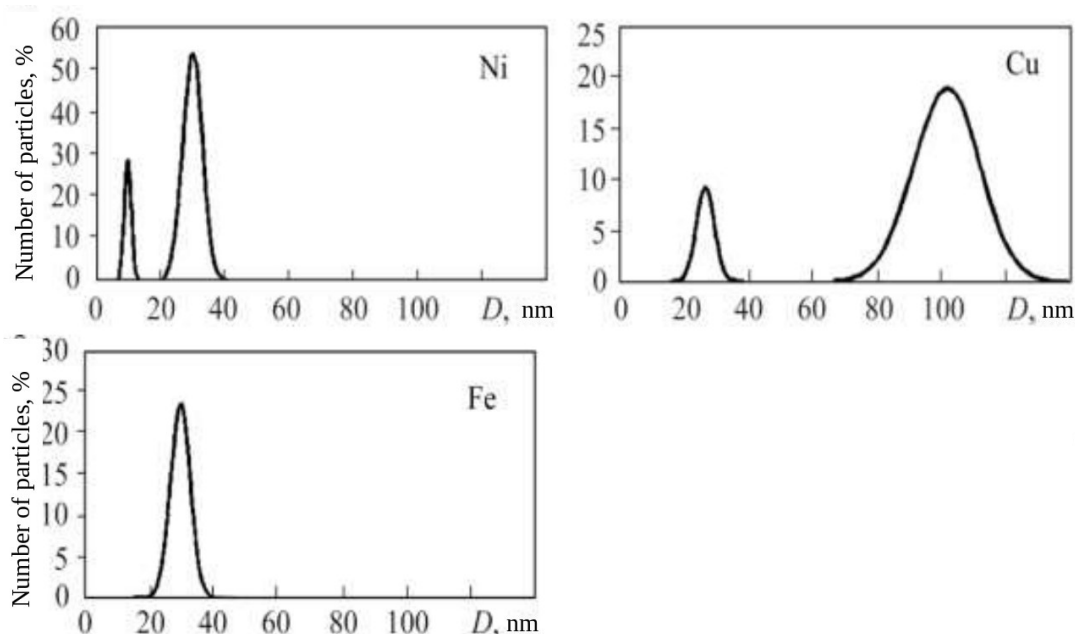


Figure 4. Typical size distributions of metal nanoparticles. The particles were obtained by reducing the metals from their compounds in a hydrogen stream

A common method of producing highly dispersed metal powders is the reduction of metal compounds (hydroxides, chlorides, nitrates, carbonates) in a hydrogen stream at temperatures below 500 K. Its advantages are a low impurity content and a narrow particle size distribution of the powders (Figure 4).

5. Production of Nanopowders by Mechanical Action

Mechanosynthesis is based on the mechanical treatment of solid mixtures, which results in comminution and plastic deformation of the substances, accelerates mass transfer, mixes the components of the mixture at the atomic level and activates the chemical interaction of the solid reactants.

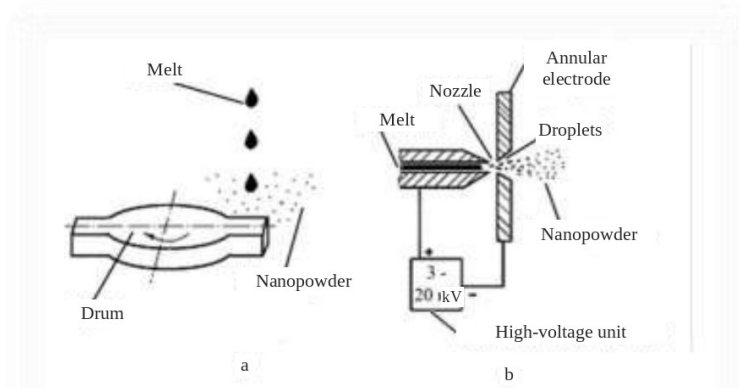


Figure 5. Schematic of nanopowder production from a melt: *a* – impact atomisation; *b* – electrohydrodynamic atomisation of the material

Mechanical milling can reduce the size of microcrystalline blocks to 10 nm or less, which is equivalent to shortening the diffusion paths, and can accelerate the interaction of nanocrystalline particles. This is especially important for multicomponent systems, in which not only mechanical but also chemical forces act in the contact zone of particles of different substances.

Mechanosynthesis, as a method of high-energy mechanical action on a solid to obtain nanopowders, can be divided into two main categories: mechanical milling and mechanical alloying.

Mechanical milling is used both for comminution of the starting material and for its amorphisation: for example, the amorphous state of crystalline intermetallic compounds is achieved by mechanical milling.

Mechanical alloying provides comminution, mixing, mass transfer and chemical interaction of powders of several pure elements, compounds or alloys. It can be used to obtain substances both in the crystalline and in the amorphous state.

As an example, let us consider the mechanosynthesis of titanium carbide (TiC) nanocrystals:

1. Metallic titanium powder and graphite were milled in a ball mill.
2. The ball-to-powder mass ratio was 10:1.
3. Milling was performed at room temperature in an argon atmosphere.

The powder obtained by milling was sintered in an activated plasma for eight minutes. As a result of sintering, compact high-density TiC specimens with an average grain size of ~ 70 nm were obtained.

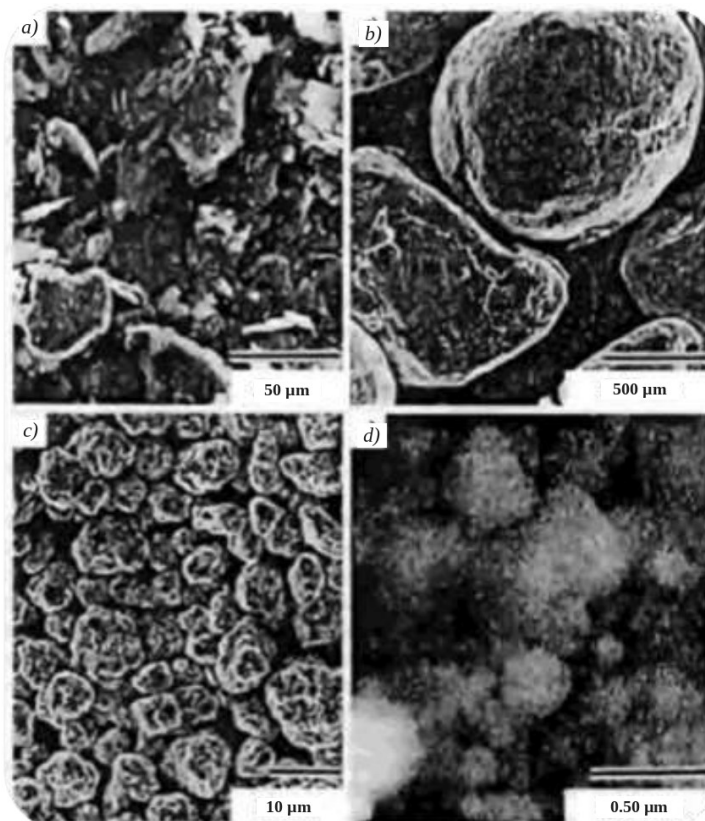


Figure 6. Micrographs of the particles of the starting powder mixture

As a result of mechanical action, a stress field is created in the contact regions of the solid. Its relaxation can occur through the release of heat, the formation of a new surface, the formation of various defects in the crystals and the initiation of chemical reactions in the solid phase.

The predominant direction of relaxation depends on the properties of the substance, the loading conditions and the size and shape of the particles. As the power of the mechanical pulse and the duration of action increase, there is a gradual transition from relaxation through heat release to relaxation associated with fracture, dispersion and plastic deformation of the material and the appearance of amorphous structures of various natures.

Mechanical action during the comminution of materials is pulsed; therefore, the stress field arises and subsequently relaxes not during the entire residence time of the particles in the reactor, but only at the moment of their collision and for a short period thereafter. Consequently, in mechanochemical synthesis it is necessary to take into account the time-dependent character of stress field formation and the kinetics of the subsequent relaxation processes.

Mechanical action is not only pulsed but also local, since it manifests itself not in the entire mass of the solid but only where the stress field arises and then relaxes.

6. Mechanical Attrition

Mechanical attrition is the most productive method of producing large quantities of nanocrystalline powders of various materials: metals, alloys, intermetallics, ceramics and composites. Mechanical attrition and mechanical alloying make it possible to achieve complete solid solubility of elements whose mutual solubility under equilibrium conditions is so small that it can be neglected.

High-energy planetary, ball and vibration mills are used for milling and mechanochemical synthesis (Figure 7); the average size of the powders obtained can range from 200 to 5...10 nm. In particular, ball milling of the boride FeB yielded a powder with an average crystallite size of ~8 nm, and mechanical treatment of barium titanate BaTiO₃ in a planetary mill gave a nanocrystalline powder with an average particle size of 5...25 nm.

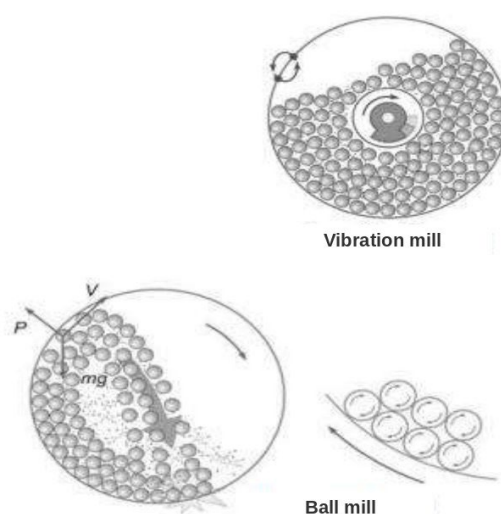


Figure 7. Schematics of a vibration mill and a ball mill

Mechanochemical synthesis of powders of borides, carbides, silicides, oxides and sulphides of transition metals has been carried out by the "explosive" method in a vibration mill.

A study of boron, titanium, zirconium, vanadium and tungsten carbide powders obtained by mechanochemical synthesis in mills showed that the average particle size is 6...20 nm.

7. Self-Propagating High-Temperature Synthesis

Self-propagating high-temperature synthesis (SHS) is a rapidly propagating process of solid-state combustion of reactants: a metal with carbon, boron or silicon to form carbides, borides or silicides, or a metal in a nitrogen atmosphere to form nitrides, at temperatures ranging from 2500 to 3000 K.

SHS relies on the exothermic nature of the reactions between most metals and boron, carbon, silicon and nitrogen. The combustion reaction proceeds in a narrow zone that travels through the compacted specimen owing to heat conduction. Carbides are usually synthesised in vacuum or in an inert atmosphere.

The average grain size of the products after synthesis is 10–20 μm ; the grain size of nitrides is usually smaller, 5–10 μm . Carbides and nitrides of the Group IV and V transition metals synthesised by this method are, as a rule, compositionally inhomogeneous, and additional milling and annealing are required to homogenise them.

To reduce the grain size of the carbide or nitride, the starting mixture is diluted with the final product (for instance, up to 20 wt.% of TiC is added to the Ti + C mixture). For the same purpose, in the synthesis of carbides part of the carbon in the mixture is replaced with organic polymers (polystyrene). As a result, carbides and nitrides with an average grain size of 1–5 μm can be obtained.

One study proposed the SHS of nanosized titanium carbide powders using an inert diluent, namely NaCl, which is chemically inert towards the starting powders of metallic titanium and carbon and towards the titanium carbide TiC product.

During the combustion of titanium and carbon, NaCl, whose melting point is $T_{\text{melt}} = 1074 \text{ K}$, forms a melt that prevents the growth of the synthesised carbide particles. In addition, NaCl is readily soluble in water and is easily separated from the synthesised carbide. The particle sizes of the starting Ti, C and NaCl powders did not exceed 50, 0.1 and 150 μm , respectively. Specimens 30 mm in diameter and 40 mm in height were pressed from the powder mixture.

Synthesis was performed in a standard reactor under argon at a pressure of 0.5 MPa. Combustion was initiated by a current pulse (voltage $U = 15\text{--}20 \text{ V}$, pulse duration 1.0–1.5 s) delivered to the specimen through a tungsten wire. As the amount of sodium chloride added increased, the combustion temperature decreased from 2500 to 1950 K.

During combustion, spontaneous homogenisation of the starting mixture occurred owing to the melting of Ti and NaCl. Microscopic examination revealed titanium carbide particles distributed in the NaCl melt and isolated from one another by a thin layer of this melt, which prevents their further growth.

8. Other Methods for Producing Nanomaterials

8.1. Chemical vapour deposition technologies

This group of technologies is based on chemical reactions of metal compounds in the gas phase. In a certain zone of the reaction chamber, these compounds either decompose thermally to form a solid deposit in the form of nanopowders together with gaseous products, or enter into chemical reactions that likewise yield a powder and gaseous products.

Metal halides (mainly chlorides), alkyl compounds, carbonyls and oxychlorides can be used as the starting materials. This technology has been used to obtain nanopowders of silicon, boron, titanium, zirconium and aluminium oxides, and nitrides with particle sizes from 20 to 600 nm.

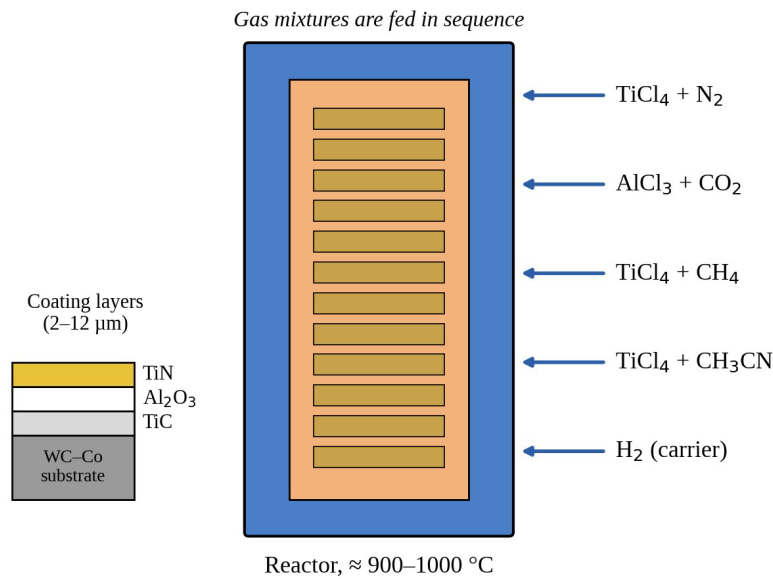


Figure 8. Chemical vapour deposition: inserts on trays or grids are placed in a furnace, and successive gas mixtures are fed into the chamber until a multilayer TiC/Al₂O₃/TiN coating 2–12 μm thick is formed

Two main methods can be distinguished within this group of technologies:

- Transport through the gas phase and reduction with subsequent decomposition.
- A process based on the synthesis and subsequent decomposition of carbonyls.

The recently developed method of *high-temperature hydrolysis* can also be classed among chemical vapour deposition technologies. It is based on the interaction of compounds, mainly chlorides, in a hydrogen–oxygen flame. It enables the production of multicomponent compounds, in particular SiO₂, TiO₂, Al₂O₃ and ZrO₂ nanopowders.



Figure 9. The plasma (violet glow) accelerates the growth of carbon nanotubes in a laboratory PECVD set-up

8.2. Deposition from solutions

This group of technologies is the most thoroughly studied; its distinguishing feature is that chemical reactions take place in aqueous salt solutions. Several different methods are used.

In the *chemical precipitation* method, after the metal salt solutions have been prepared, favourable conditions for precipitation are created, a precipitating agent is added, and the hydroxide precipitate is separated and converted into a metal oxide powder. Ammonia solutions, ammonium carbonate, oxalic acid and ammonium oxalate are most often used as precipitants, and soluble nitrates as the precipitated substances. As a result, oxide nanopowders are obtained.

The method is widely used to produce multicomponent powders, when several compounds are precipitated simultaneously from multicomponent solutions. Its main drawbacks are the large volumes involved, the considerable content of impurities in the powders and the wide particle size distribution.



Figure 10. Hydroxide precipitate formed in a test tube during chemical precipitation

The *sol-gel process* was developed specifically for producing oxide ceramics. It comprises the following stages: preparation of alkoxide solutions, their catalysed interaction followed by hydrolysis, condensation polymerisation and further hydrolysis. The result is an oxide polymer (gel), which is aged, washed, dried and heat-treated.

A *drawback* of the method is the complexity of the equipment, whereas its *advantages* are the high purity and homogeneity of the synthesised compounds and the possibility of obtaining a wide variety of nanopowders.

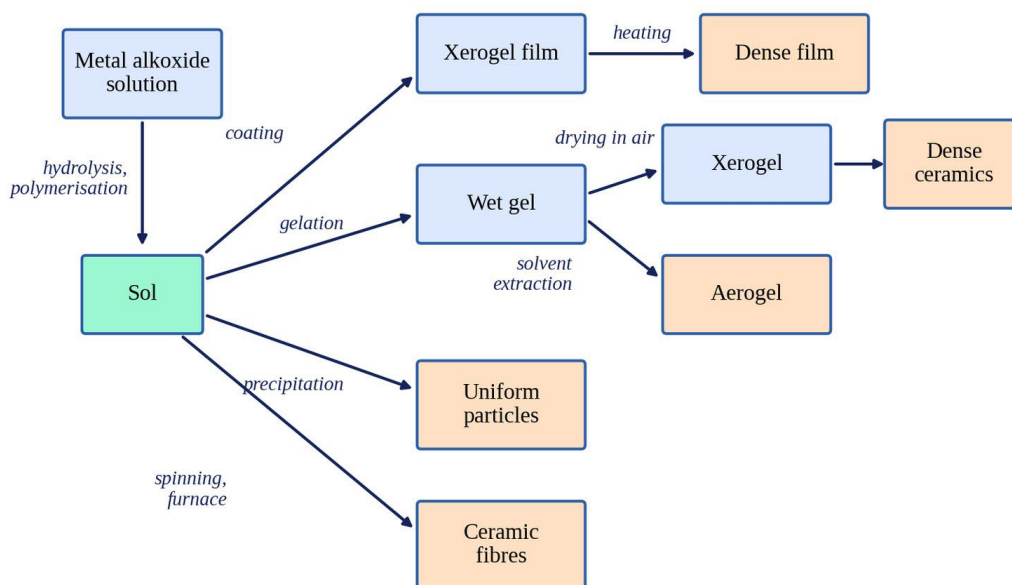


Figure 11. Sol–gel technologies and their products

The method of *liquid-phase reduction from solutions* is used to obtain nanopowders only of metals with low reduction potentials (copper, silver, nickel). For example, copper nanopowders can be obtained in this way from a solution of copper nitrate in 4-methylpentanol. The solutions are mixed to form an emulsion; after it separates, the copper nanopowder is located in the organic phase. To obtain the powder itself, this phase is separated, filtered and dried.

The method of *hydrothermal synthesis* uses hydrothermal decomposition and oxidation reactions that take place in aqueous media at elevated temperatures (100–370 °C) and pressures (up to 100 MPa). The method yields oxide nanopowders with a narrow particle size distribution. Its *drawbacks* are the high cost and complexity of the equipment and the batch nature of the synthesis.

The *microemulsion method* comprises the following stages: preparation of an emulsion of two immiscible liquids, an aqueous solution and an oil; precipitation of the metal hydroxide in the droplets of the aqueous phase by adding an organic precipitant; separation of the components; and drying of the precipitated product. This method was used to obtain a Y_2O_3 powder with spherical particles up to 800–1000 nm in size and a silver powder with a particle size of 2–2.5 nm.

The *cryochemical method* of producing metal oxide nanopowders consists in dissolving salts, rapidly freezing the resulting solutions, subliming the solvent and thermally decomposing the residue. This method was used to obtain copper and yttrium oxide powders. Its advantage is the possibility of obtaining multicomponent homogeneous nanopowders.

8.3. Decomposition of unstable compounds

Today this technology is regarded as promising for obtaining nanopowders with particle sizes of 20–300 nm. The process involves three reactions: thermolysis, oxidation and hydrolysis.

The *advantages* of the method are the low process temperature, small reaction volumes, the absence of labour-intensive and inefficient washing and filtration of the final products, controllable dispersity and the high purity of the powders. Its *drawback* is the difficulty of monitoring and controlling particle size, since two competing processes occur simultaneously: decomposition of the starting compound and sintering of the final product particles under the effect of temperature.

For producing metal oxide nanopowders, alkoxides (alcohol derivatives of metals) are promising starting materials.

Another method is the *radiation-induced decomposition* of compounds. Decomposition of silver azide in this way yielded a silver nanopowder containing mainly two groups of particles, 5–30 nm and 170–220 nm in size. Particles up to 100 nm were spherical, whereas the larger ones were faceted.



Figure 12. Silver azide

8.4. Use of reduction processes

The best-known method here is the *hydrogen reduction of metal compounds*. Metal compounds (hydroxides, chlorides, nitrates, carbonates) undergo reduction in a hydrogen stream at a temperature of about 500 K. For a metal chloride, the reaction can be written as follows: $\text{MeCl}_2 + \text{H}_2 \leftrightarrow \text{Me} + 2\text{HCl}$.

This method can be used to obtain powders of iron, tungsten, nickel, rhenium, molybdenum, copper and calcium, as well as powders of alloys and alloy steels, which are distinguished by a low impurity content and a narrow particle size distribution.

The *chemical–metallurgical method* is also known. First, low-water hydroxides are synthesised by gas-phase interaction, and the resulting hydroxides are then heat-treated in a reducing atmosphere, for example in hydrogen. This yields nanopowders of iron, nickel, molybdenum, tungsten and copper. If the heat treatment is carried out in air, oxide nanopowders are obtained, for example Al_2O_3 , TiO_2 , ZrO_2 or their composites.

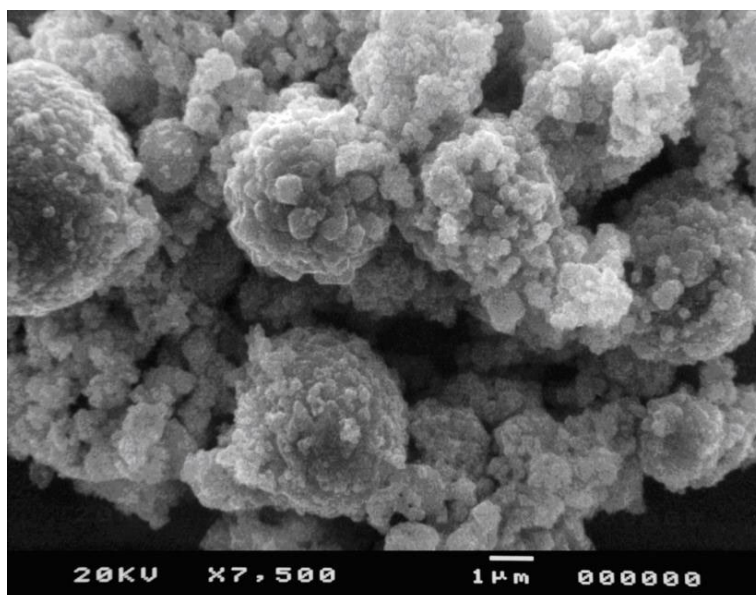


Figure 13. Copper oxide nanopowder (SEM, $\times 7500$)

The *advantages* of the method are the narrow particle size distribution of the nanopowder, low impurity content, relatively inexpensive process equipment and the ease of switching from the production of one powder to another.

8.5. Physical vapour deposition methods

Technologies based on evaporating a substance with various high-intensity energy sources and subsequently depositing it from the vapour phase are well established, easy to control and meet stringent requirements for the purity of the resulting nanopowder, especially when chambers with a controlled atmosphere are used.

Vacuum chambers or chambers filled with inert gases (helium, argon or xenon) are most often used. When metals are evaporated in vacuum or in an inert gas, the metal atoms tend to combine into particles a few nanometres in size, which then settle on a cooled substrate. These methods can produce complex alloyed powders.

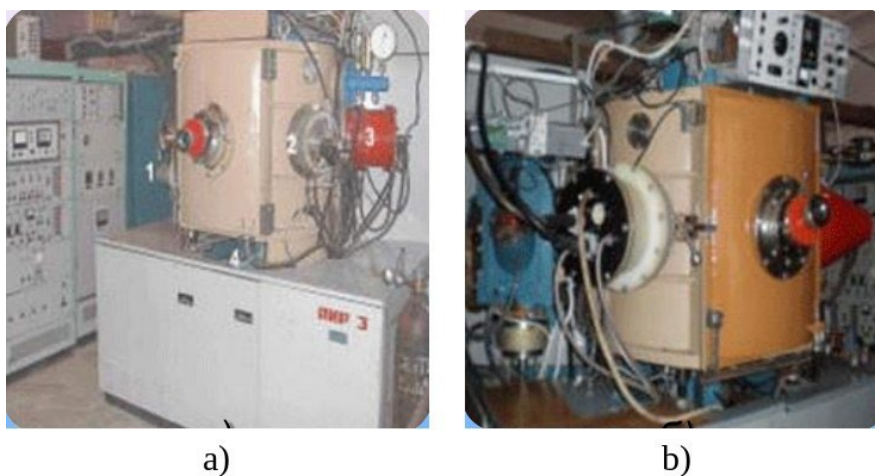


Figure 14. Basic industrial unit AIR-3: a) AIR-3 with arc ionisation of the vapour phase; b) AIR-3M with RF ionisation of the vapour phase

Depending on the method variant and the process parameters, the particle size of the powders can range from 5 to 100 nm.

Depending on the type of evaporation process, the following variants of the method can be distinguished.

Thermal evaporation. Here the material to be evaporated is heated in a crucible. Today various heating methods based on high-intensity energy sources are used: high-frequency induction, electron-beam, electric-arc, plasma and laser heating. A typical schematic of nanopowder production by this method is shown in Figure 8.

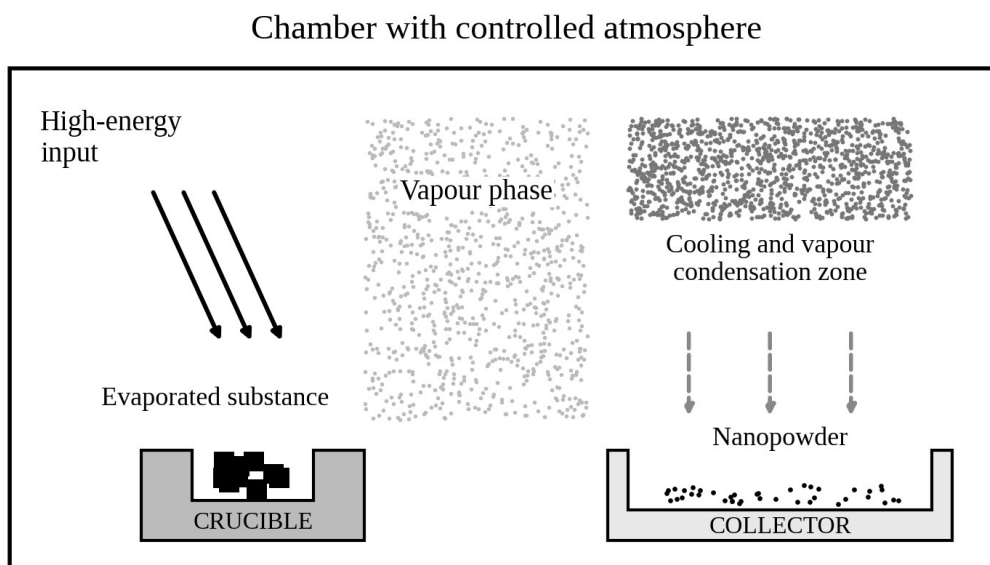


Figure 15. Schematic of nanopowder production by thermal evaporation and condensation of the material from the vapour phase

The powders are spherical or faceted and may be metallic, intermetallic or other compounds. The advantages of the method are pure powders with a narrow particle size distribution; its drawback is low productivity. This drawback is temporary: it results not from the process technology but from the lack of large-scale units for the industrial production of nanopowders.

Explosive evaporation. This rapidly developing method is based on the release of a very large amount of energy within a short period of time. The material evaporates and then, owing to the rapid increase in volume, cools down, and the vapour condenses into small particles.

In some cases, part of the material may not have time to evaporate; it melts and breaks up explosively into liquid droplets. To deliver the required amount of energy, a powerful electric current pulse, an arc discharge or a laser radiation pulse is used.

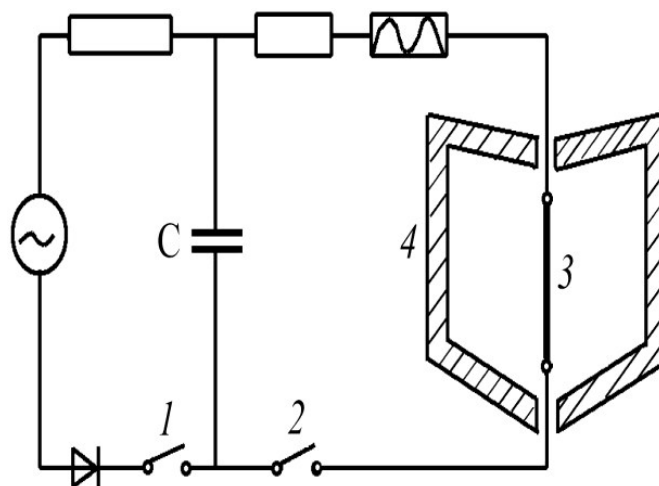


Figure 16. Schematic of powder production from a wire by explosive evaporation: 1 – charging circuit; 2 – discharge circuit; 3 – exploding wire; 4 – inert gas chamber

In this case, the current discharge is generated by a capacitor. The size and structure of the particles are controlled mainly by varying the density and rate of the energy input. The method makes it possible to produce high-purity spherical powders with particle sizes down to 5–10 nm, including powders of metals with high melting points and high chemical activity.

Evaporation in an inert gas flow (levitation-jet method). Here the metal is evaporated in an inert gas flow, for example from a melt droplet at the end of a wire heated by a high-frequency magnetic field.

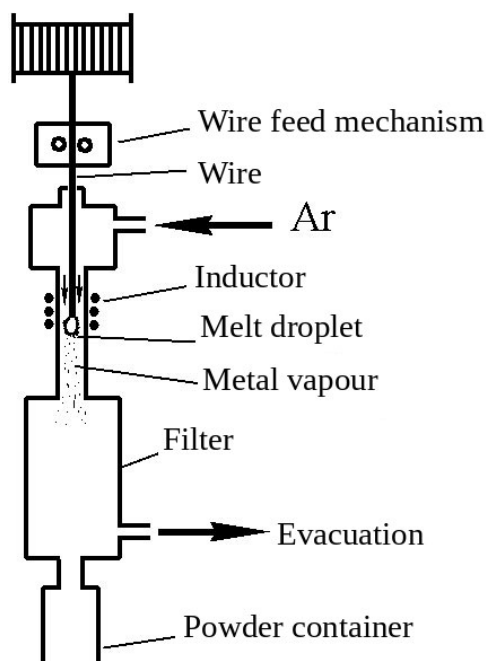


Figure 17. Schematic of a unit for producing nanopowders by evaporation in an inert gas flow

The particle size depends on the gas flow velocity: as the velocity increases, the particle size can decrease from 500 to 10 nm, while the particle size distribution narrows. This method has been used to obtain, in particular, Mn and Sb nanopowders; the latter was amorphous because of the high quenching rate in the gas stream.

A variant of this method is known as *vacuum melting*. In this variant, the wire is melted in a liquid with a very low temperature, for example in liquid nitrogen.

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Lecture 4. Methods for Studying Nanomaterials

Outline

1. Melt atomisation.
2. Deformation methods for producing nanostructured materials.
3. General characteristics.
4. Electron microscopy.
5. Scanning probe microscope.
6. Diffraction analysis.
7. Sedimentation analysis.

1. Melt Atomisation

This group of methods is based on the rapid atomisation and cooling of a melt of the starting material. The technology makes it possible to obtain powders with a particle size of not less than 100 nm. The powder can be produced in a protective atmosphere. Today three variants of this technology are used.

Contact cooling by means of a water-cooled disc or drum. This method is based on feeding the molten material onto a rapidly rotating water-cooled disc or drum made of a material with high thermal conductivity.

Copper is usually used as such a material, providing cooling rates of up to 10^8 K/s. The surface of the drum or disc is made rough (toothed), since a smooth surface yields a foil or wire about 10...50 μm thick with an amorphous or nanocrystalline structure. The finished powder is distinguished by flake-shaped particles. Such a shape can lead to a non-uniform structure and anisotropy of the properties of products. For this reason, the powders are usually additionally comminuted mechanically, which is the main drawback of the method.

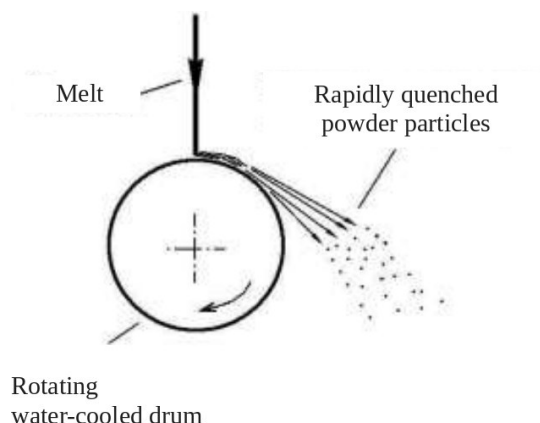


Figure 1. Schematic of powder atomisation from a melt by means of a water-cooled drum

Impact atomisation of the melt. Here a jet or droplets of the melt are mechanically broken up into fine particles on collision with intensively cooled, rapidly rotating metal blades. Cooling rates of up to 10^7 K/s are achieved.

As in the previous method, the powder particles have an irregular shape, and to form high-quality products with a uniform structure the powder must be additionally comminuted.

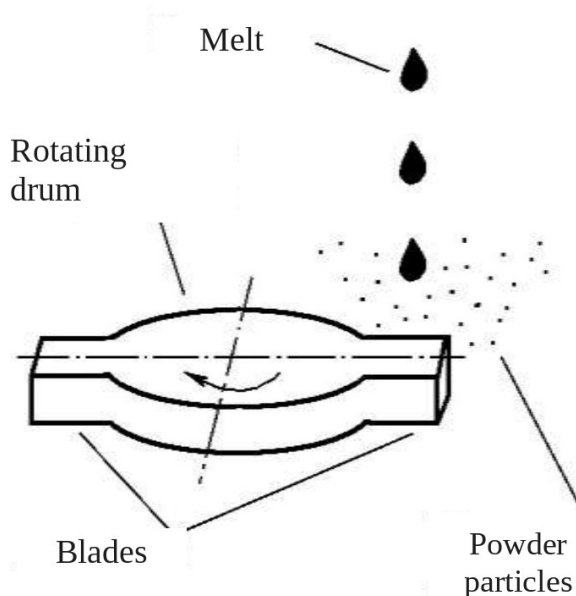


Figure 2. Schematic of impact atomisation of a melt

Electrohydrodynamic atomisation of the melt. In this method, electrostatic forces are used to atomise the melt. The melt jet is fed into a nozzle with an orifice diameter of $\sim 80 \mu\text{m}$, in front of which an annular electrode is located. A constant voltage of 3...20 kV is applied to it. As a result, positively charged fine droplets of the melt fly out of the nozzle, which form powder particles after cooling.

Depending on the material and the process parameters, the particle size can range from 100 nm to 10 μm . The drawback of this method is its very low productivity (2 g/h from one nozzle).

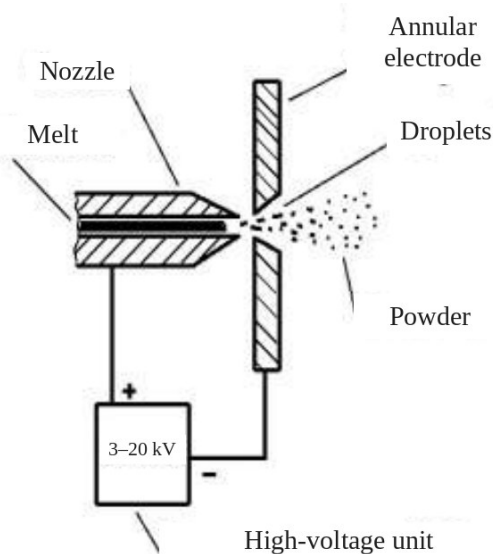


Figure 3. Schematic of electrohydrodynamic atomisation of a melt

Mechanical comminution. This route makes it easier to obtain powders based on brittle materials. The powder obtained by this method meets stringent purity

requirements, is more homogeneous and contains particles of approximately the same size. An intensive gas flow substantially reduces the heating of the particles during milling, which makes it possible to process amorphous and nanocrystalline powders. The main drawback is the complexity and high cost of the process equipment.

Depending on the type of material and the required properties of the nanopowder, mainly planetary, ball and vibration mills are used. The average particle size of the powders can range from 5 to 200 nm. Another variant of the method is the use of high-energy grinding devices (attritors) with a stationary drum body and agitators that transmit motion to the balls in the drum.

The main drawback of the method is contamination of the powder owing to wear of the working parts of the equipment.

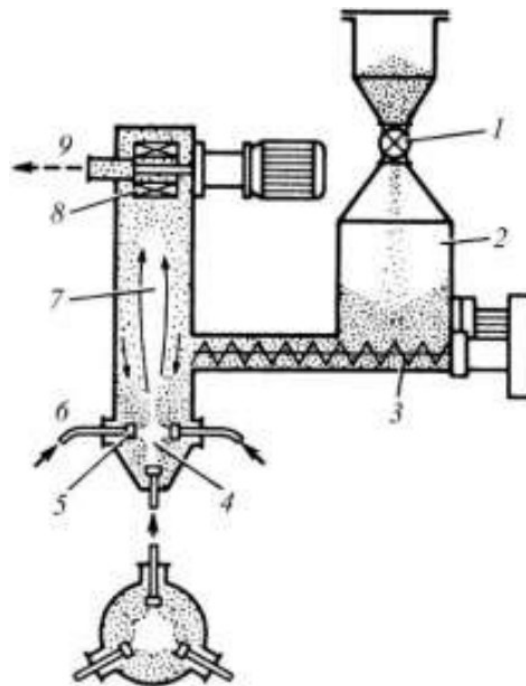


Figure 4. Schematic of a unit for counter-current (jet) milling in a fluidised bed: 1 – feeder; 2 – hopper with the starting particles; 3 – system for feeding the particles into the milling chamber; 4 – fluidised bed; 5 – gas supply nozzles; 6 – high-pressure gas supply pipeline; 7 – milling chamber; 8 – classifier; 9 – gas outlet manifold with fine particles

2. Deformation Methods for Producing Nanostructured Materials

Deformation methods for producing nanostructured materials are based on **severe plastic deformation (SPD)**, which consists in large strains at relatively low temperatures (below $0.3...0.4 T_m$) under high applied pressures, ensuring the production of bulk pore-free nano- and submicrocrystalline metals and alloys.

SPD methods include:

- high-pressure torsion;
- equal-channel angular pressing;
- reversible (alternating) bending;
- twist extrusion;

- accumulative roll bonding;
- multiaxial isothermal forging (MIF).

The following conditions facilitate the achievement of large plastic strains without fracture of the specimen:

- the initial and final cross-sections of the specimen remain unchanged;
- the deformation of the specimen approaches simple shear;
- the deformation is reversed (alternating);
- high pressures.

The requirements for SPD methods that should be taken into account when developing them for the fabrication of nanostructured materials are as follows:

- uniformity throughout the specimen volume to ensure the stability of the properties of the materials obtained;
- the structure must consist of grains and fragments with predominantly high-angle misorientations, since it is in this case that a qualitative change in the properties of the materials occurs;
- the specimens must not contain discontinuities or fractures despite their severe deformation.

SPD schemes are subdivided into two groups:

1. In the first group, high hydrostatic pressures are not possible. It includes multiaxial deformation, reversible bending and accumulative roll bonding. SPD schemes of the first group provide a submicrocrystalline structure ($100 \text{ nm} < D < 1 \text{ }\mu\text{m}$).
2. The second group, which uses high hydrostatic pressure, includes high-pressure torsion, twist extrusion and equal-channel angular pressing. SPD schemes of the second group provide a nanocrystalline structure ($D < 100 \text{ nm}$).

Multiaxial deformation: multiaxial isothermal forging. The MIF scheme is based on multiple repetition of open-die forging operations, upsetting and drawing, with a change in the axis of the applied deforming force.

The billet is deformed stepwise and cyclically. One cycle consists of three passes: the billet is successively deformed along all three coordinate axes. The number of cycles is determined by the attainment of the required degree of accumulated strain.



Figure 5. Billets after multiaxial isothermal forging

The equipment is an open die with heat-resistant nickel-alloy anvils. The temperature of plastic deformation lies in the range $(0.3\text{--}0.6) T_m$ of the alloy.

Advantages of the MIF method:

- it provides the largest dimensions of nanostructured semi-finished products;
- high structural homogeneity and versatility;
- it does not require special equipment or tooling;
- it provides a uniform ultrafine-grained structure down to $D \sim 10\text{--}100$ nm;
- the material is processed over a wide temperature range ($T = 20\text{...}950$ °C) under isothermal conditions, which makes it possible, by combining upsetting–drawing schemes, to achieve uniform deformation and hence a uniform ultrafine-grained structure.

Drawbacks of the MIF method:

- the low productivity of the process of obtaining the specified microstructure in billets;
- the low technological ductility of the deformed material, since during upsetting and drawing the billet experiences tensile stresses along two of its axes and compressive stress along the third axis.

High-pressure torsion is performed in devices in which the specimen is placed between anvils. When the upper anvil rotates, the specimen is deformed in shear by surface friction forces. The lower anvil has a recess to prevent the metal from flowing out.

High-pressure torsion provides a high degree of shear strain, as a result of which the finest structure is formed in the specimen material. The process is usually carried out at a pressure of $4\text{...}6$ GPa.

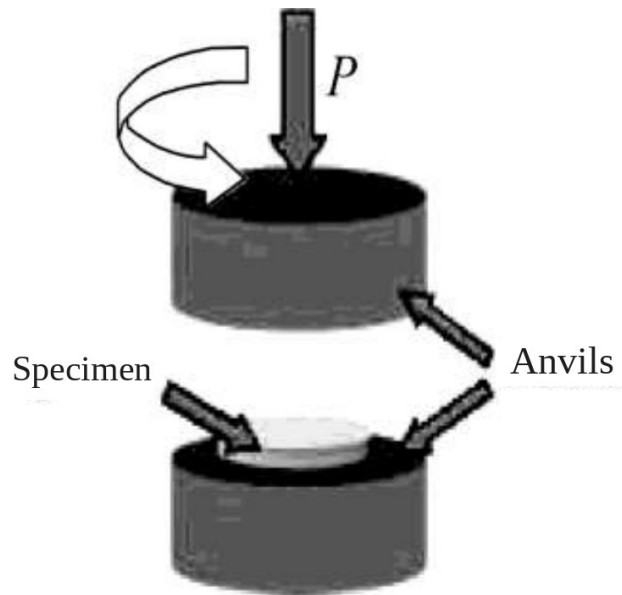


Figure 6. Schematic of severe plastic deformation by high-pressure torsion

Twist extrusion. In this method, a prismatic billet is extruded through a die with a helical channel; therefore, in the literature this method is also called twist (helical) pressing.

The angle β of inclination of the helix to the extrusion axis varies along the height of the die, being zero in its initial and final sections. When the alloy is pressed through the helical channel, the shape of the billet does not change, which makes it possible to perform multiple extrusion passes to accumulate the strain that causes refinement of its structural constituents.

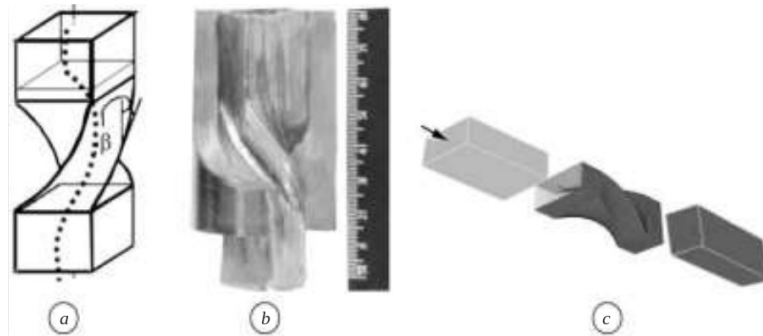


Figure 7. Twist extrusion: a – schematic of the helical channel; b – extrusion of an alloy through the helical channel (longitudinal section); c – schematic of the passage of the billet through the helical channel

The stress state of the metal during twist extrusion is determined by the strain-rate field. As the deformed material moves along the helical channel, the pressure from the active parts and the periphery gradually penetrates into the central zone of the billet. The pressure is distributed more uniformly over the cross-section, although the position of the maximum is retained. Twist extrusion of metals with back pressure makes it possible to increase the strength characteristics of the material while preserving its ductility.

Equal-channel angular pressing (ECAP) was first proposed by Professor V. M. Segal in 1978. During ECAP, the specimen is repeatedly pressed through two channels of equal cross-section that intersect at an angle.

The main parameters of ECAP are the deformation temperature, the channel intersection angle and the pressing route.

The deformation temperature must be below the recrystallisation temperature of the alloy (a smaller diameter of the grains formed, but more non-equilibrium grain boundaries).

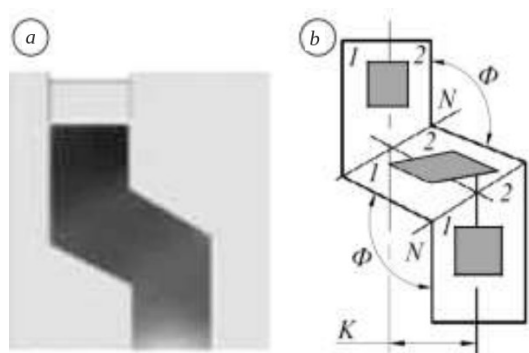


Figure 8. Schematic of ECAP in parallel channels: *a* – longitudinal section of the die with the billet in parallel channels; *b* – schematic of shear deformation of the billet cross-section in different parts of the channels

The principle of the high-productivity process of producing rods of titanium and aluminium alloys with an ultrafine-grained structure is illustrated by the ECAP–Conform scheme (Figure 9).

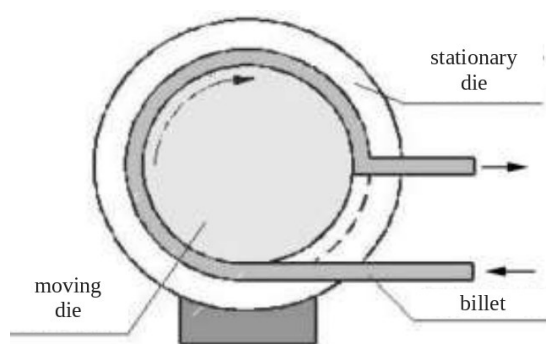


Figure 9. Schematic of the ECAP–Conform process

3. General Characteristics

A decrease in crystallite size below a certain critical value can lead to a substantial change in properties. Size effects appear when the average size of the crystalline grains does not exceed 100 nm and are most pronounced when it is less than 10 nm. Thus, **particle size** is one of the most important parameters determining the specific properties and field of application of a nanomaterial.

A conventional classification of substances by absolute grain size can be adopted. Materials with an average grain size of more than 1 μm are *coarse-crystalline*; polycrystals with an average grain size from 100...150 to 40 nm are

submicrocrystalline; and those with an average grain size of less than 40 nm are *nanocrystalline*.

Physically, the transition to the nanocrystalline state is associated with the appearance of size effects in the properties. If there are no size effects, there is no nanocrystalline state.

To assess the transition to the nanocrystalline state, such physical parameters as the size of magnetic domains in ferromagnets, the electron mean free path and the wavelength of elastic vibrations can be used.

4. Electron Microscopy

Electron microscopy is a visualisation technique. There are two main methods of electron microscopy: *scanning* electron microscopy, which operates with reflected electrons, and *transmission* electron microscopy.

Scanning electron microscopy gives information about the external shape of a particle and its apparent dimensions, but not about its internal structure. Transmission electron microscopy makes it possible to see the structure of particles.

To study the structure of nanoparticles and determine their sizes, the optimal approach is to combine electron microscopy with the diffraction method.

Electron microscopy makes it possible to study objects whose dimensions are substantially smaller than 1 μm . The ability to resolve individual columns of atoms in a crystal led to the emergence of high-resolution transmission electron microscopy.

Electron microscopy can directly determine the sizes of nanoparticles and nanocrystallites; it is therefore widely used both in nanomaterials research and in the nanotechnologies of modern electronics. It is the only direct method for studying the structure of nanoparticles obtained from colloidal solutions.

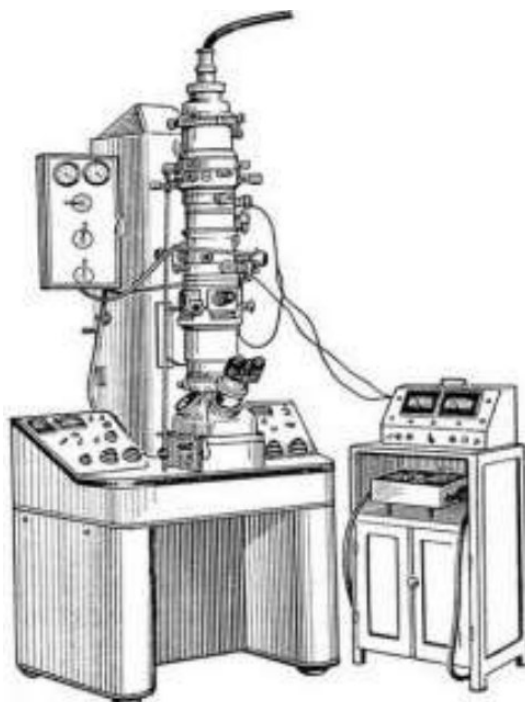


Figure 10. Transmission electron microscope of the 1970s

Electron microscopy has made it possible to observe an unusual nanostructure obtained after ordering of non-stoichiometric vanadium carbide.

Under the microscope at a magnification of about 100 times, only large (up to 20 μm) individual agglomerates of irregular shape are visible in vanadium carbide powder. At a substantially higher magnification, however, it becomes clear that these particles have a complex structure and are an aggregate of a large number of very small particles in the nanometre range.

A micrograph obtained at a magnification of 30 000 times with a DSM 982 Gemini high-resolution scanning electron microscope shows that the vanadium carbide nanocrystallites have the shape of curved petals which, growing together, form a coral-like nanostructure (Figure 11).

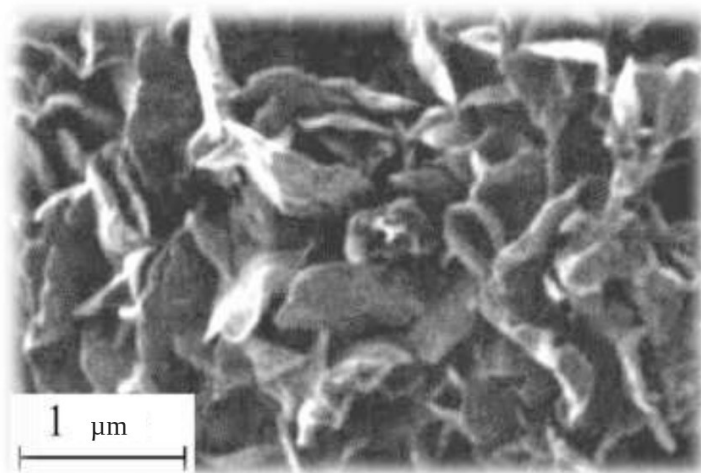


Figure 11. Nanocrystallites of ordered vanadium carbide powder V_8C_7 ($VC_{0.875}$)

For high-resolution transmission electron microscopy, the specimens must be prepared especially carefully.

5. Scanning Probe Microscope

To study the atomic and molecular structure of a surface, **scanning probe microscopy** is often used. Owing to its high resolution, it makes it possible to estimate the sizes of the objects observed, to visualise individual atoms and molecules and to construct three-dimensional images. Its varieties are scanning tunnelling microscopy (STM) and atomic force microscopy (AFM).

In *STM*, the probe is an extremely fine metal (tungsten) needle whose tip may consist of a single atom and have a size of ~ 0.2 nm. Its principle of operation is based on the passage of electrons through the potential barrier formed by a break in the electric circuit, i.e. a small gap between the probing microtip and the specimen surface.

In *AFM*, the force of interaction between the microtip and the specimen surface is monitored, and the instrument is extremely sensitive for measuring the surface profile. The probe is a miniature elastic plate (cantilever) on the free end of which a tip of a hard material is formed by lithographic methods.

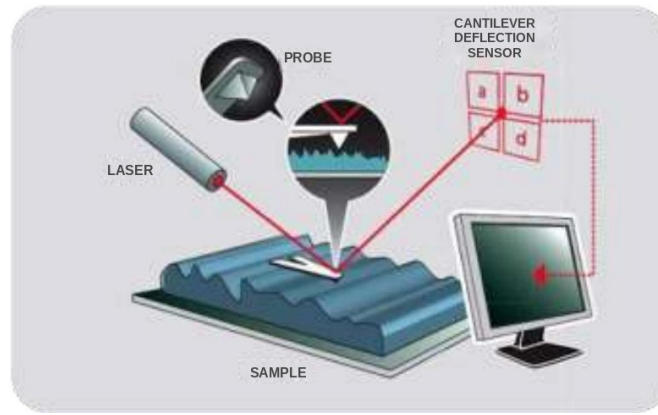


Figure 12. Principle of operation of the AFM

The main drawback of AFM is the lack of simultaneous information about the entire surface, since at any moment information is available only from the area being directly registered by the probe. Modern AFM is used to study any materials.

Scanning probe microscopy is based on the detection of the local interaction that arises between the probe and the surface of the specimen under study when they approach each other to a distance of $\sim \lambda$, where λ is the characteristic decay length of the probe–specimen interaction.

Depending on the nature of this interaction, the following main types of microscope are distinguished:

- the scanning electron microscope (SEM), which measures the current of secondary and reflected electrons;
- the scanning tunnelling microscope (STM), which measures the tunnelling current;
- the scanning force microscope (SFM), which measures the force interaction;
- the scanning near-field optical microscope, which measures electromagnetic radiation.

Scanning force microscopy is subdivided into atomic force, magnetic force microscopy, etc., depending on the type of interaction. The most important methods of scanning probe microscopy are STM and AFM; it is with them that progress in the development of nanostructure research techniques is associated.

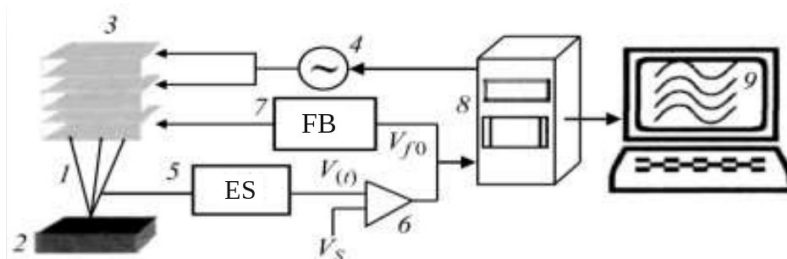


Figure 13. General schematic of a scanning probe microscope: 1 – probe; 2 – specimen; 3 – x, y, z piezoelectric actuators; 4 – scan voltage generator; 5 – electronic sensor (ES); 6 – comparator; 7 – electronic feedback circuit (FB); 8 – computer; 9 – image

When the tunnelling current is measured, a current-to-voltage converter connected into the current path between the probe and the specimen is used in the tunnelling sensor. Two connection options are possible: with a grounded probe (the bias voltage is applied to the specimen relative to the grounded probe) and with a grounded specimen (the bias voltage is applied to the probe relative to the specimen).

The force interaction sensor is usually a silicon cantilever with an optical scheme for registering its bending caused by the force interaction between the specimen and the probe located at the end of the cantilever.

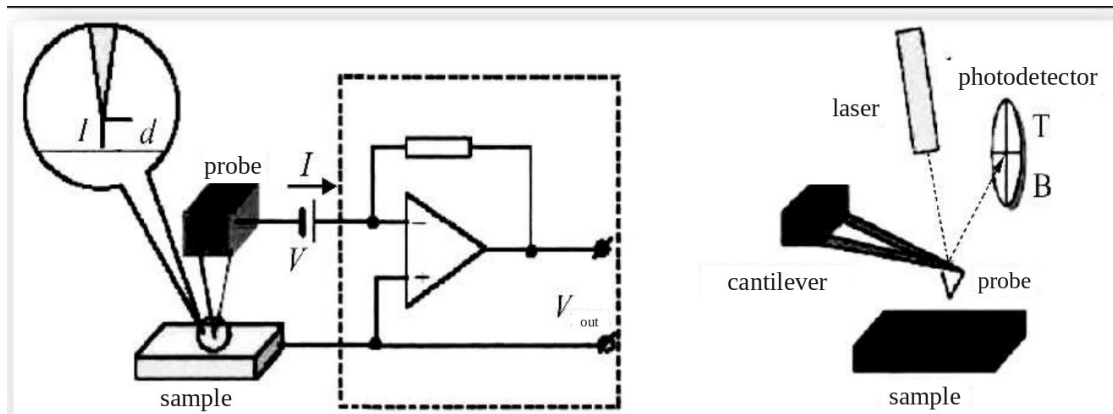


Figure 14. Schematics of sensors: a – tunnelling sensor; b – force sensor

Contact, non-contact and intermittent-contact ("semi-contact") modes of force microscopy are distinguished.

In the *contact mode*, the probe rests against the specimen. In this case, when the cantilever bends under the action of contact forces, the laser beam reflected from it is displaced relative to the centre of a quadrant photodetector, so that the cantilever deflection can be determined from the relative change in the illumination of the upper and lower halves of the photodetector.

In the *non-contact mode*, the probe is removed from the surface and is in the zone of long-range attractive forces. Here the attractive forces and their gradients are weaker than the repulsive contact forces; therefore, a modulation technique is usually used to detect them.

In the *semi-contact mode*, a modulation technique for measuring the force interaction is also used. Here the probe partially touches the surface, being alternately in the region of attraction and in the region of repulsion.

There are simpler methods of measuring the force interaction in which the force interaction is directly converted into an electrical signal, for example, a method based on the direct piezoelectric effect, when bending of a piezoelectric material under the action of the force interaction generates an electrical signal.

For precision mechanical scanning of the specimen under study by the probe, either by moving the probe relative to a stationary specimen or by moving the specimen relative to a stationary probe, *piezoelectric actuators* are used.

The operation of such actuators is usually based on the inverse piezoelectric effect, which consists in a change in the dimensions of a piezoelectric material under the action of an electric field. The piezoelectric material most commonly used is PZT piezoceramics (lead zirconate titanate $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ with various additives).

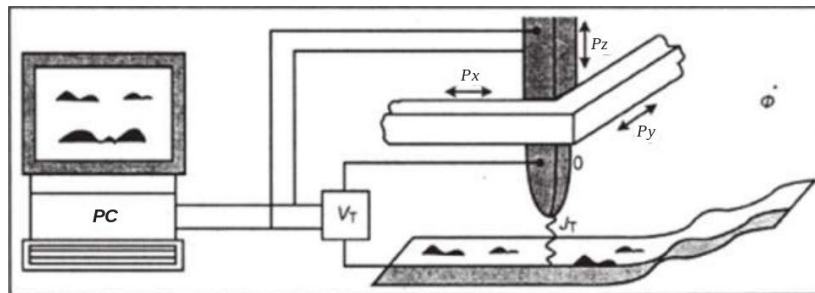


Figure 15. Piezoelectric actuators for linear displacements along the surface (P_x , P_y) and in depth (P_z) and the feedback circuit

Scanning of the surface is similar to the motion of the electron beam across the screen of a cathode-ray tube: the probe moves along a line first in the forward and then in the reverse direction (line scan), and then moves on to the next line (frame scan). The probe is moved by the scanner in small steps under the action of sawtooth voltages supplied by the scan generator.

Scanning electron microscopes are similar in principle of operation to an ordinary television set with a cathode-ray tube.

The idea of SEM is that the specimen surface is scanned by an electron beam produced by an external source at a voltage of the order of several tens of kilovolts. The beam is deflected by a magnetic field produced by an electric current in coils, which is proportional to the voltage applied to the coil.



Scanning electron microscope JEOL JSM-T220A

Figure 16. Scanning electron microscope JEOL JSM-T220A

The surface irradiated during scanning begins to emit either secondary electrons or light quanta, which are registered, amplified, converted in intensity, etc., and then fed to the screen of a cathode-ray tube, creating a visible image of the surface.

The methods of obtaining a magnified image in scanning electron microscopes differ substantially from those used in transmission electron microscopy.

By scanning the surface under study with a fine but sufficiently intense electron beam and feeding the signals from the detector of secondary and reflected electrons to the screen, a magnified image of the surface can be obtained. Naturally, the rate of scanning of the surface and that of the screen must be synchronised. The principle of operation is as follows:

1. The irradiating electron beam emitted by the electron gun passes successively through the condenser lens, the deflection coil and the objective lens and creates a small illuminated "spot" on the specimen surface, whose size can be adjusted by the control system.
2. Secondary and reflected electrons are thereby generated, the number of which depends on the characteristics of the surface: roughness, atomic composition and electric potential of the illuminated area of the crystal.

By measuring and analysing the intensity of these electrons, a magnified picture of a specific area of the surface can be obtained on the screen and converted into a photographic image. In scanning electron microscopes, as in transmission microscopes, a high vacuum must be maintained.

6. Diffraction Analysis

Among the indirect methods of determining particle size, the main place belongs to the **diffraction method**, which is the most widespread and accessible. It can be used to determine not only the phase composition, the crystal lattice parameters, the static and dynamic displacements of atoms from their equilibrium positions and the lattice microstrains, but also the grain size.

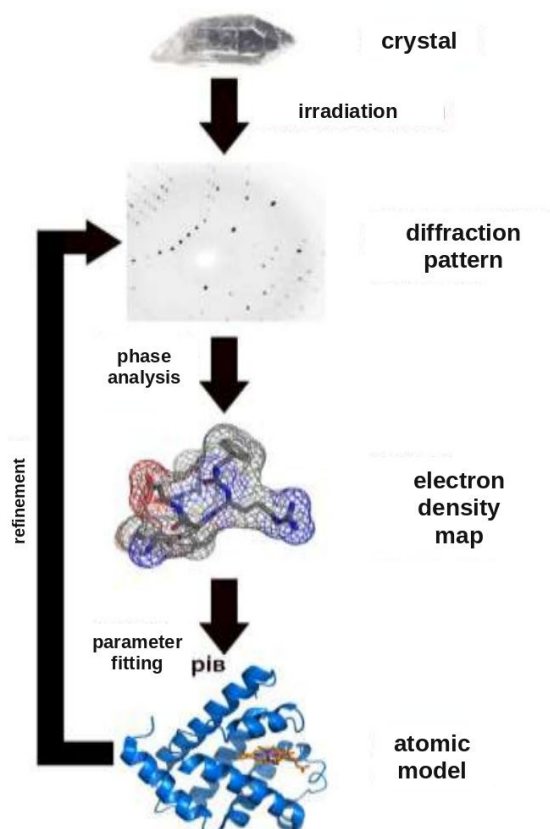


Figure 17. Schematic of the process of determining the structure of a compound by X-ray structural analysis

First, a crystal of the compound is obtained or grown in the laboratory and then irradiated to obtain a diffraction pattern in the form of discrete spots. The crystal is gradually rotated and diffraction patterns are recorded; from these patterns, those corresponding to the clearest crystal orientations are selected.

Using the *Fourier transform*, these arrays of diffraction reflections are converted into a three-dimensional model of the electron density within the crystal lattice. From this electron density, the positions of the atomic nuclei and the distances between them are derived, forming a model of the atoms within the unit cell of the crystal.

Electron microscopy cannot determine the lattice parameters, atomic displacements and microstrains with the high accuracy achieved by X-ray structural analysis.

The determination of the size of grains, particles and coherent scattering regions by the diffraction method is based on the change in the profile of the diffraction reflection with decreasing grain size. The size of an individual grain may not coincide with the size of the coherent scattering region. Indeed, individual grains may consist of several crystallites; moreover, for very small grains ($D \sim 1\text{--}2\text{ nm}$), the coherent scattering region corresponds to the inner region of the grain.

However, the diffraction method gives the grain size averaged over the volume of substance studied, whereas electron microscopy determines the size of objects only within a limited field of view.

Diffraction analysis makes use of the displacement of atoms from lattice sites by defects. All defects can be divided into two groups:

1. Defects of the first group weaken the intensity of diffraction reflections but do not lead to their broadening.
2. Defects of the second group are responsible for the broadening of diffraction reflections. They include microstrains and small particle size.

7. Sedimentation Analysis

The determination of particle size by the **sedimentation method** (settling method) is based on measuring the time during which a particle in a liquid medium of known viscosity η travels a fixed distance H . Another variant of the method is the study of the distribution of particles over height. In gravimetric sedimentation, the mass of the sediment is determined as a function of the settling time.

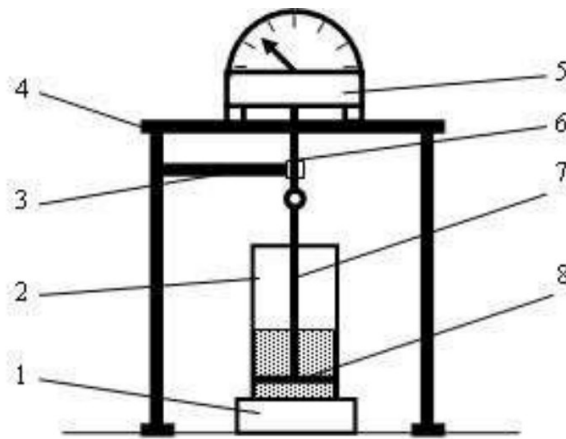


Figure 18. Schematic of an apparatus for sedimentation analysis: 1 – magnetic stirrer; 2 – beaker with the suspension under study; 3 – holder; 4 – balance table; 5 – balance; 6 – balance rod; 7 – disc rod; 8 – round disc for weighing the sediment

Particles of the dispersed phase in a gravitational field settle if their density exceeds that of the liquid medium, or float up if it is lower. Sedimentation results in a concentration gradient of particles over height, which gives rise to diffusion directed towards lower concentration.

By comparing the sedimentation flux I_{sed} and the diffusion flux I_{dif} , it is possible to establish which of the processes predominates in a given system.

The law of particle distribution over height is obtained from the equality of the diffusion and sedimentation fluxes, i.e. from the condition of sedimentation–diffusion equilibrium $I_{\text{sed}} = I_{\text{dif}}$. The sedimentation flux is calculated from the equation:

$$I_{\text{sed}} = u_{\text{sed}} \cdot n,$$

where $u_{\text{sed}} = H / t$ is the linear sedimentation velocity and n is the number of particles per unit volume (particle concentration).

The condition for uniform motion of a particle is the equality of the forces of gravity and friction, i.e. the resistance of the liquid (or gas) to the motion of the body

in it. The friction force is determined by the viscosity of the medium. At a low velocity u_{sed} and small body size, the resistance to the motion of a body with average size R is described by the well-known Stokes formula:

$$F = (4\pi/\alpha) \eta R u_{\text{sed}} = (4\pi/\alpha) \eta R (H/t).$$

The Stokes equation is valid only for solid particles moving uniformly and at low velocity in a medium that can be regarded as infinite in comparison with the falling particle. The distance between particles must be large enough to avoid interaction between them.

Thus, in the sedimentation method, the size of a falling particle is inversely proportional to the time it takes to travel the given path.

In modern sedimentographs, the passage of particles and their number are registered by means of laser radiation. In this way, not only the size of individual particles but also their size distribution, i.e. the dispersity, is determined. The particle concentration in the liquid usually does not exceed 1%. Aqueous solutions of alcohols, organic oils, etc. are generally used for sedimentation.



Figure 19. *Micron Photo Sizer (Seishin) centrifugal sedimentograph*

A drawback of this method is that it cannot measure the sizes of very small particles (less than 50 nm).

In addition, to achieve high accuracy, the particle surface must be well wetted by the liquid; otherwise, the surface tension force will hold small particles on the surface, while larger ones will be surrounded by a gas envelope. It is also necessary to avoid agglomeration of individual particles, which can substantially distort the result.

An effective method of determining the sizes of small particles is based, on the one hand, on the use of Brownian motion and, on the other, on the analysis of the spectral composition of light scattered by a suspension or a colloidal solution. A. Einstein should be regarded as the founder of this method.

The size of small particles can be measured using the well-known Einstein formula describing the Brownian motion of spherical particles in a liquid:

$$R = k_B T / (6\pi\eta D_{\text{dif}}),$$

where η is the viscosity of the liquid and D_{dif} is the diffusion coefficient of the Brownian particles.

If all the particles are assumed to have the same size and shape, a simple relation can be obtained between the specific surface area S_{sp} and the linear size R of the particles. For example, if the mass of a spherical particle is $m = (4\pi/3)R^3\rho$ and its surface area is $s = 4\pi R^2$, its specific surface area is:

$$S_{\text{sp}} = s / m = 3 / (\rho R).$$

Thus, the larger the specific surface area, the smaller the particle size.

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Lecture 5. Methods for Producing Nanomaterials

Outline

1. Plasma-chemical synthesis.
2. Gas-phase synthesis using laser heating.
3. Application of synthesis in other fields.
4. Thermal decomposition.
5. Production of nanopowders by mechanical action.
6. Mechanical attrition.

1. Plasma-Chemical Synthesis

Plasma-chemical synthesis comprises several stages. In the *first* stage, active particles are generated in arc, high-frequency (radio-frequency) and microwave plasma reactors. *Arc plasma reactors* have the highest power and efficiency; however, the materials produced in them are contaminated with electrode erosion products. Electrodeless high-frequency and microwave plasma reactors are free of this drawback.

Next, the interaction products are separated as a result of quenching. By selecting the location and rate of quenching, powders with a specified composition, shape and particle size can be obtained. Such powders have a regular shape and particle sizes from 10 to 100 nm and more.

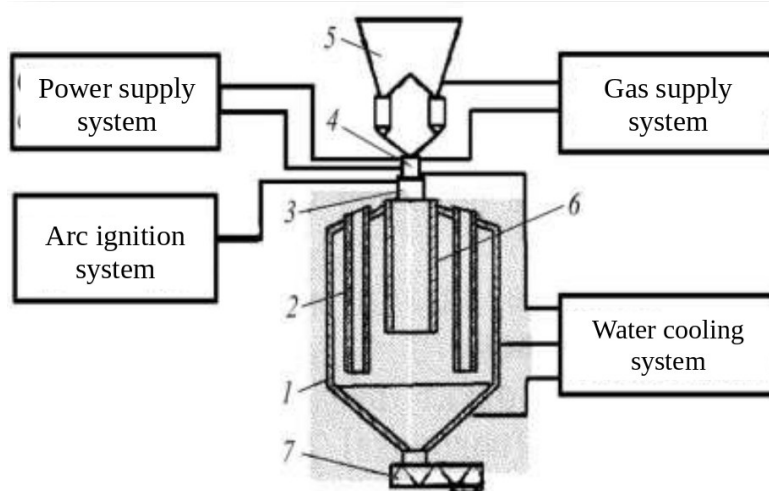


Figure 1. Schematic of a unit for producing refractory metal powders by plasma-chemical synthesis (reduction of oxides): 1 – unit housing; 2 – bag filters; 3 – reaction chamber; 4 – plasmatron; 5 – device for feeding the product to be reduced into the plasma jet; 6 – powder annealing tube; 7 – discharge device

Plasma-chemical synthesis can also be used to produce multicomponent submicrocrystalline powders that are mixtures of carbides and nitrides, of a nitride and borides, of nitrides of various elements, etc.

Plasma-chemical powders of metal, boron and silicon carbides are usually obtained by reacting the chlorides of the corresponding elements with hydrogen and methane or other hydrocarbons in an argon high-frequency or arc plasma; nitrides are

obtained by reacting chlorides with ammonia or a mixture of nitrogen and hydrogen in a low-temperature microwave plasma.

Oxides are synthesised in the plasma of an electric arc discharge by evaporating a metal and subsequently oxidising the metal particles in an oxygen-containing plasma. One study described the plasma-chemical synthesis of aluminium oxide and silicon carbide nanoparticles with an average size of 10...30 nm.

It was found that nanopowders with the minimum particle size are formed when the metal vapour interacts with atmospheric oxygen under conditions of intensive air injection, as a result of which the temperature decreases rapidly.

Intensive cooling not only inhibits particle growth but also increases the nucleation rate of the condensed phase. Plasma-chemical synthesis involving the oxidation of aluminium particles in a flow of oxygen-containing plasma leads to the formation of larger oxide particles than the oxidation of previously produced metal vapour.

2. Gas-Phase Synthesis Using Laser Heating

Gas-phase synthesis using **laser heating** of the reacting gas mixture is close to plasma-chemical synthesis. Laser heating ensures controlled homogeneous nucleation and rules out contamination.

Its advantages are the absence of surfaces that cause heterogeneous nucleation, and uniform and precise control of the process. As an energy source, the laser provides monochromatic radiation of high brightness, owing to which a high degree of conversion of light into heat is achieved.

Laser synthesis of nanocrystalline Si, Si₃N₄ and SiC powders:

1. Silicon powders were obtained by pyrolysis of gaseous silane SiH₄ using a CO₂ laser (the spherical Si powder grains had a diameter of 50 ± 20 nm).
2. Silicon nitride Si₃N₄ powders were synthesised from a gas mixture of silane SiH₄ and ammonia NH₃ (the grains were spherical, with an average size of 17 ± 4 nm).
3. Gas mixtures of silane with methane or ethylene were used to synthesise silicon carbide SiC (the grain size ranged from 18 to 26 nm, with an average of 21 nm).

The grains of nanopowders synthesised using laser heating are distinguished by their spherical shape and narrow size distribution.

3. Application of Synthesis in Other Fields

The *plasma-chemical method* is also used to produce metal powders. For example, submicrocrystalline copper powders with a particle size below 100 nm and a relatively narrow particle size distribution are obtained by reducing copper chloride with hydrogen in an argon arc plasma at temperatures up to 1800 K.

Gas-phase synthesis using laser radiation, in which the radiation is used to create and sustain a plasma where a chemical reaction takes place, has proved effective for the formation of molecular clusters, a new structural modification of matter.

Molecular clusters occupy a special place among nanostructured substances. The best known of them are **fullerenes**, a new allotropic modification of carbon alongside graphite and diamond.

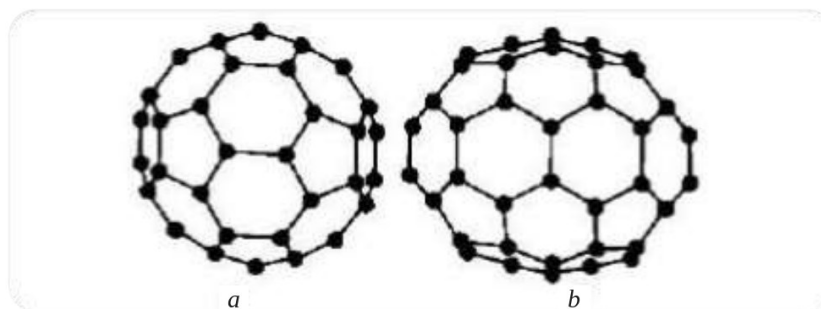


Figure 2. Structure of fullerenes (molecular carbon clusters): a – C_{60} ; b – C_{70}

4. Thermal Decomposition

Thermal decomposition usually employs complex organoelement and organometallic compounds, hydroxides, carbonyls, nitrates and oxalates of metals, which decompose at a certain temperature to form the synthesised substance and release a gas phase.

A variant of pyrolysis is the decomposition of organometallic compounds in a *shock tube*, after which free metal atoms condense from supersaturated vapour. A long steel tube closed at both ends is divided into two unequal parts by a thin aluminium-foil diaphragm.

The longer part of the tube is filled with argon at a pressure of 1000...2500 Pa containing 0.1...2.0 mol.% of organometallic compounds. The other part is filled with helium or a mixture of helium and nitrogen until the membrane ruptures. When it ruptures, a shock wave arises, at the front of which the temperature can reach 1000...2000 K.



Figure 3. Deformation of pipeline transition branch pipes caused by water hammer

Shock heating of the gas causes the organometallic compound to decompose within a few microseconds after the passage of the wave front, and the free metal atoms form a highly supersaturated vapour capable of rapid condensation. Fine powders of iron, bismuth and lead have been obtained in this way.

A combination of thermal decomposition and condensation is the supersonic outflow of gases from a chamber, in which elevated constant pressure and temperature are maintained, through a nozzle into vacuum. In this case, the thermal energy of the gas molecules is transformed into the kinetic energy of the supersonic flow, and the gas cools on expansion and turns into a supersaturated vapour in which clusters containing from two to a million atoms can form.

Highly dispersed powders of silicon carbide and silicon nitride are obtained by pyrolysis of polycarbosilanes. Initial heating is carried out by means of a low-temperature plasma or laser radiation; the pyrolysis products are then additionally annealed at ~ 1600 K to stabilise their structure and composition.

Polyvinylpentaborane is used to produce nanocrystalline boron carbide; boron-containing polymers of the polyborazine, polyborazole and polyvinylborazine type are used to form highly dispersed boron nitride powders and can also be applied as an additive to titanium powder for the synthesis of nanocrystalline $\text{TiN} + \text{TiB}_2$ compositions.

Powders obtained by thermal decomposition of monomeric and polymeric compounds must be additionally annealed to stabilise their composition and structure; the annealing temperature is 900–1300 K for nitrides and borides and 1200–1800 K for oxides and carbides.

The main drawback of thermal decomposition is the relatively low selectivity of the process, since the reaction product is usually a mixture of the target product and other compounds.

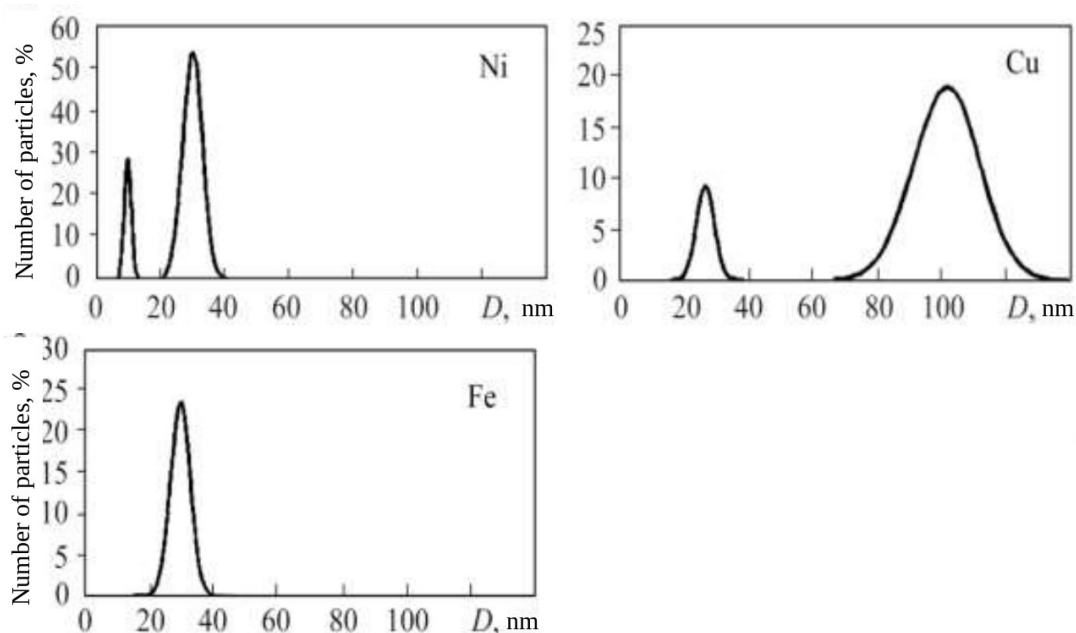


Figure 4. Typical size distributions of metal nanoparticles. The particles were obtained by reducing the metals from their compounds in a hydrogen stream

A common method of producing highly dispersed metal powders is the reduction of metal compounds (hydroxides, chlorides, nitrates, carbonates) in a hydrogen stream at temperatures below 500 K. Its advantages are a low impurity content and a narrow particle size distribution of the powders (Figure 4).

5. Production of Nanopowders by Mechanical Action

Mechanosynthesis is based on the mechanical treatment of solid mixtures, which results in comminution and plastic deformation of the substances, accelerates mass transfer, mixes the components of the mixture at the atomic level and activates the chemical interaction of the solid reactants.

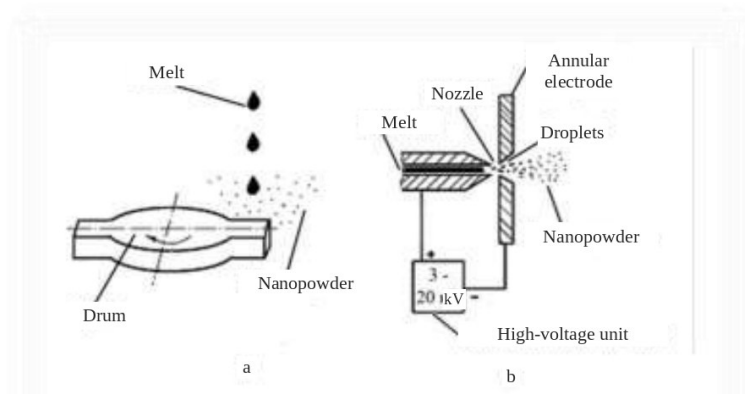


Figure 5. Schematic of nanopowder production from a melt: *a* – impact atomisation; *b* – electrohydrodynamic atomisation of the material

Mechanical milling can reduce the size of microcrystalline blocks to 10 nm or less, which is equivalent to shortening the diffusion paths, and can accelerate the interaction of nanocrystalline particles. This is especially important for multicomponent systems, in which not only mechanical but also chemical forces act in the contact zone of particles of different substances.

Mechanosynthesis, as a method of high-energy mechanical action on a solid to obtain nanopowders, can be divided into two main categories: mechanical milling and mechanical alloying.

Mechanical milling is used both for comminution of the starting material and for its amorphisation: for example, the amorphous state of crystalline intermetallic compounds is achieved by mechanical milling.

Mechanical alloying provides comminution, mixing, mass transfer and chemical interaction of powders of several pure elements, compounds or alloys. It can be used to obtain substances both in the crystalline and in the amorphous state.

As an example, let us consider the mechanosynthesis of titanium carbide (TiC) nanocrystals:

1. Metallic titanium powder and graphite were milled in a ball mill.
2. The ball-to-powder mass ratio was 10:1.
3. Milling was performed at room temperature in an argon atmosphere.

The powder obtained by milling was sintered in an activated plasma for eight minutes. As a result of sintering, compact high-density TiC specimens with an average grain size of ~70 nm were obtained.

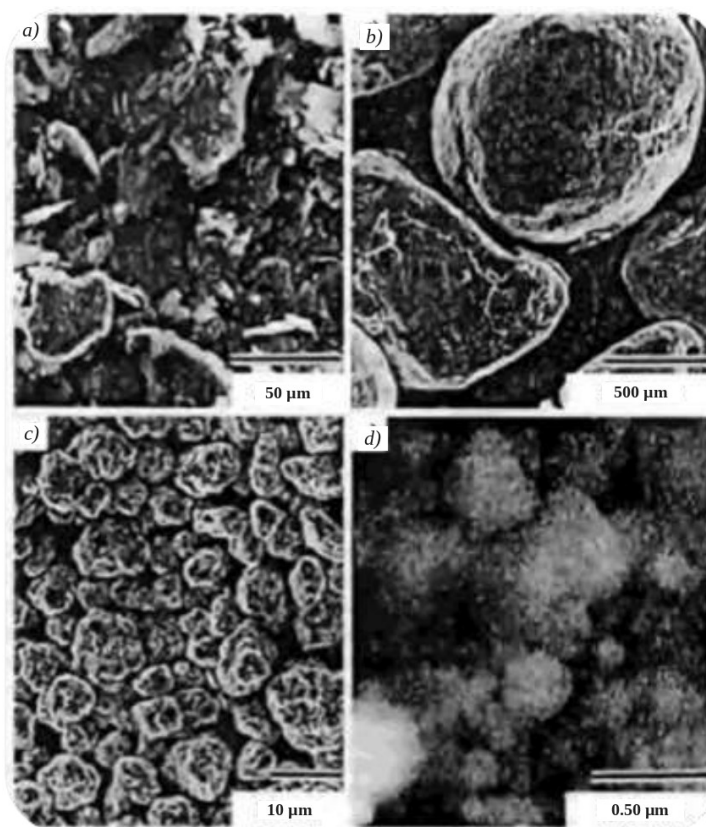


Figure 6. *Micrographs of the particles of the starting powder mixture*

As a result of mechanical action, a stress field is created in the contact regions of the solid. Its relaxation can occur through the release of heat, the formation of a new surface, the formation of various defects in the crystals and the initiation of chemical reactions in the solid phase.

The predominant direction of relaxation depends on the properties of the substance, the loading conditions and the size and shape of the particles. As the power of the mechanical pulse and the duration of action increase, there is a gradual transition from relaxation through heat release to relaxation associated with fracture, dispersion and plastic deformation of the material and the appearance of amorphous structures of various natures.

Mechanical action during the comminution of materials is pulsed; therefore, the stress field arises and subsequently relaxes not during the entire residence time of the particles in the reactor, but only at the moment of their collision and for a short period thereafter. Consequently, in mechanochemical synthesis it is necessary to take into account the time-dependent character of stress field formation and the kinetics of the subsequent relaxation processes.

Mechanical action is not only pulsed but also local, since it manifests itself not in the entire mass of the solid but only where the stress field arises and then relaxes.

6. Mechanical Attrition

Mechanical attrition is the most productive method of producing large quantities of nanocrystalline powders of various materials: metals, alloys, intermetallics,

ceramics and composites. Mechanical attrition and mechanical alloying make it possible to achieve complete solid solubility of elements whose mutual solubility under equilibrium conditions is so small that it can be neglected.

High-energy planetary, ball and vibration mills are used for milling and mechanochemical synthesis (Figure 7); the average size of the powders obtained can range from 200 to 5...10 nm. In particular, ball milling of the boride FeB yielded a powder with an average crystallite size of ~8 nm, and mechanical treatment of barium titanate BaTiO₃ in a planetary mill gave a nanocrystalline powder with an average particle size of 5...25 nm.

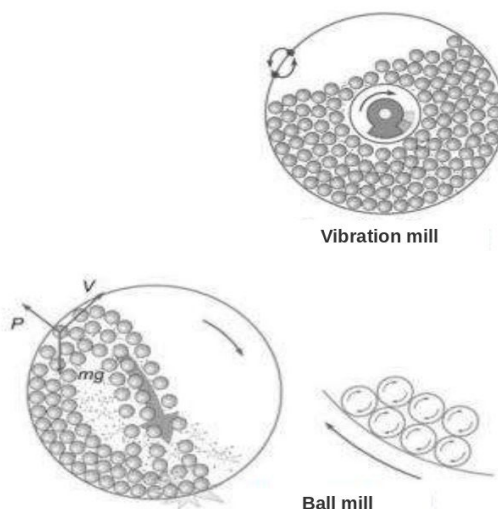


Figure 7. Schematics of a vibration mill and a ball mill

Mechanochemical synthesis of powders of borides, carbides, silicides, oxides and sulphides of transition metals has been carried out by the "explosive" method in a vibration mill.

A study of boron, titanium, zirconium, vanadium and tungsten carbide powders obtained by mechanochemical synthesis in mills showed that the average particle size is 6...20 nm.

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Lecture 6. Methods for Producing Nanomaterials

Outline

1. Self-propagating high-temperature synthesis.
2. Other methods for producing nanomaterials.

1. Self-Propagating High-Temperature Synthesis

Self-propagating high-temperature synthesis (SHS) is a rapidly propagating process of solid-state combustion of reactants: a metal with carbon, boron or silicon to form carbides, borides or silicides, or a metal in a nitrogen atmosphere to form nitrides, at temperatures ranging from 2500 to 3000 K.

SHS relies on the exothermic nature of the reactions between most metals and boron, carbon, silicon and nitrogen. The combustion reaction proceeds in a narrow zone that travels through the compacted specimen owing to heat conduction. Carbides are usually synthesised in vacuum or in an inert atmosphere.

The average grain size of the products after synthesis is 10–20 μm ; the grain size of nitrides is usually smaller, 5–10 μm . Carbides and nitrides of the Group IV and V transition metals synthesised by this method are, as a rule, compositionally inhomogeneous, and additional milling and annealing are required to homogenise them.

To reduce the grain size of the carbide or nitride, the starting mixture is diluted with the final product (for instance, up to 20 wt.% of TiC is added to the Ti + C mixture). For the same purpose, in the synthesis of carbides part of the carbon in the mixture is replaced with organic polymers (polystyrene). As a result, carbides and nitrides with an average grain size of 1–5 μm can be obtained.

One study proposed the SHS of nanosized titanium carbide powders using an inert diluent, namely NaCl, which is chemically inert towards the starting powders of metallic titanium and carbon and towards the titanium carbide TiC product.

During the combustion of titanium and carbon, NaCl, whose melting point is $T_{\text{melt}} = 1074 \text{ K}$, forms a melt that prevents the growth of the synthesised carbide particles. In addition, NaCl is readily soluble in water and is easily separated from the synthesised carbide. The particle sizes of the starting Ti, C and NaCl powders did not exceed 50, 0.1 and 150 μm , respectively. Specimens 30 mm in diameter and 40 mm in height were pressed from the powder mixture.

Synthesis was performed in a standard reactor under argon at a pressure of 0.5 MPa. Combustion was initiated by a current pulse (voltage $U = 15\text{--}20 \text{ V}$, pulse duration 1.0–1.5 s) delivered to the specimen through a tungsten wire. As the amount of sodium chloride added increased, the combustion temperature decreased from 2500 to 1950 K.

During combustion, spontaneous homogenisation of the starting mixture occurred owing to the melting of Ti and NaCl. Microscopic examination revealed titanium carbide particles distributed in the NaCl melt and isolated from one another by a thin layer of this melt, which prevents their further growth.

2. Other Methods for Producing Nanomaterials

2.1. Chemical vapour deposition technologies

This group of technologies is based on chemical reactions of metal compounds in the gas phase. In a certain zone of the reaction chamber, these compounds either decompose thermally to form a solid deposit in the form of nanopowders together with gaseous products, or enter into chemical reactions that likewise yield a powder and gaseous products.

Metal halides (mainly chlorides), alkyl compounds, carbonyls and oxychlorides can be used as the starting materials. This technology has been used to obtain nanopowders of silicon, boron, titanium, zirconium and aluminium oxides, and nitrides with particle sizes from 20 to 600 nm.

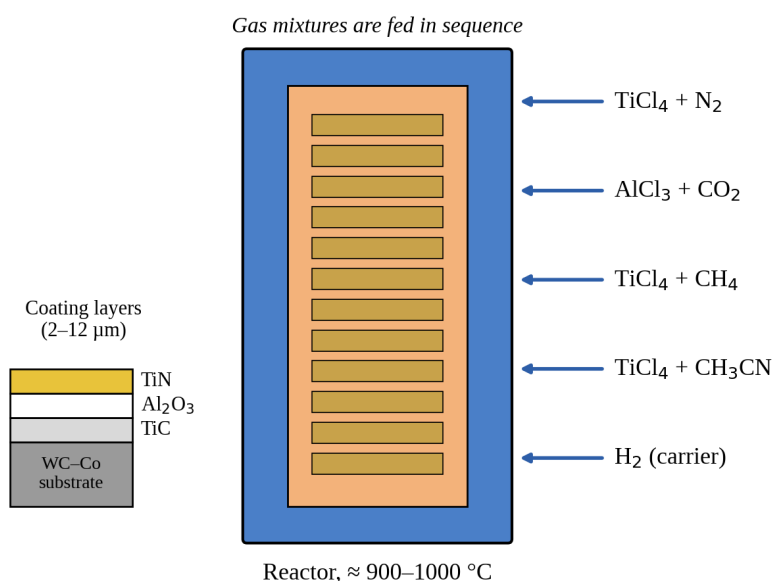


Figure 1. Chemical vapour deposition: inserts on trays or grids are placed in a furnace, and successive gas mixtures are fed into the chamber until a multilayer $\text{TiC}/\text{Al}_2\text{O}_3/\text{TiN}$ coating 2–12 μm thick is formed

Two main methods can be distinguished within this group of technologies:

1. Transport through the gas phase and reduction with subsequent decomposition.
2. A process based on the synthesis and subsequent decomposition of carbonyls.

The recently developed method of *high-temperature hydrolysis* can also be classed among chemical vapour deposition technologies. It is based on the interaction of compounds, mainly chlorides, in a hydrogen–oxygen flame. It enables the production of multicomponent compounds, in particular SiO_2 , TiO_2 , Al_2O_3 and ZrO_2 nanopowders.



Figure 2. *The plasma (violet glow) accelerates the growth of carbon nanotubes in a laboratory PECVD set-up*

2.2. Deposition from solutions

This group of technologies is the most thoroughly studied; its distinguishing feature is that chemical reactions take place in aqueous salt solutions. Several different methods are used.

In the *chemical precipitation* method, after the metal salt solutions have been prepared, favourable conditions for precipitation are created, a precipitating agent is added, and the hydroxide precipitate is separated and converted into a metal oxide powder. Ammonia solutions, ammonium carbonate, oxalic acid and ammonium oxalate are most often used as precipitants, and soluble nitrates as the precipitated substances. As a result, oxide nanopowders are obtained.

The method is widely used to produce multicomponent powders, when several compounds are precipitated simultaneously from multicomponent solutions. Its main drawbacks are the large volumes involved, the considerable content of impurities in the powders and the wide particle size distribution.



Figure 3. *Hydroxide precipitate formed in a test tube during chemical precipitation*

The *sol-gel process* was developed specifically for producing oxide ceramics. It comprises the following stages: preparation of alkoxide solutions, their catalysed interaction followed by hydrolysis, condensation polymerisation and further hydrolysis. The result is an oxide polymer (gel), which is aged, washed, dried and heat-treated.

A *drawback* of the method is the complexity of the equipment, whereas its *advantages* are the high purity and homogeneity of the synthesised compounds and the possibility of obtaining a wide variety of nanopowders.

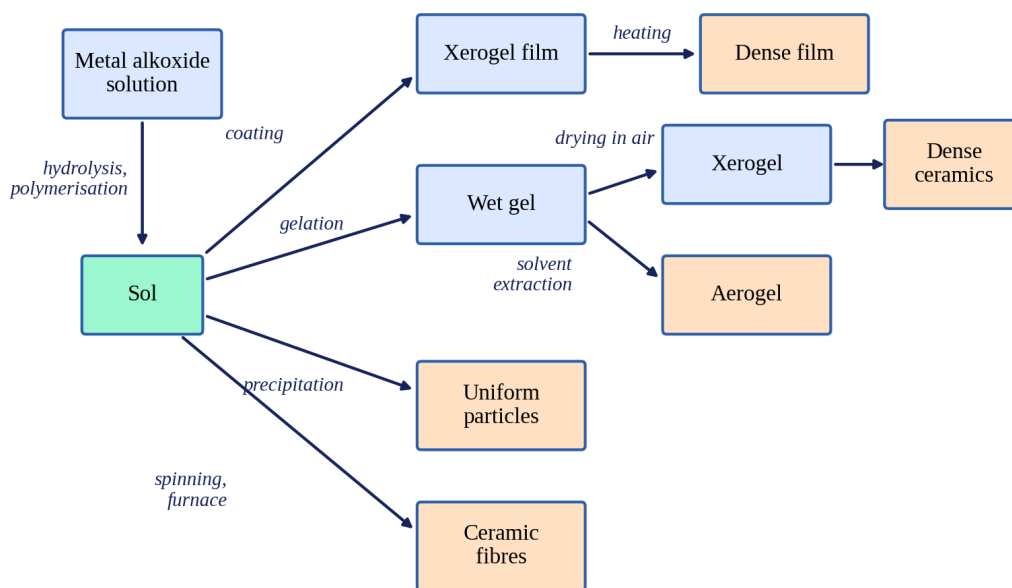


Figure 4. Sol-gel technologies and their products

The method of *liquid-phase reduction from solutions* is used to obtain nanopowders only of metals with low reduction potentials (copper, silver, nickel). For example, copper nanopowders can be obtained in this way from a solution of copper nitrate in 4-methylpentanol. The solutions are mixed to form an emulsion; after it separates, the copper nanopowder is located in the organic phase. To obtain the powder itself, this phase is separated, filtered and dried.

The method of *hydrothermal synthesis* uses hydrothermal decomposition and oxidation reactions that take place in aqueous media at elevated temperatures (100–370 °C) and pressures (up to 100 MPa). The method yields oxide nanopowders with a narrow particle size distribution. Its *drawbacks* are the high cost and complexity of the equipment and the batch nature of the synthesis.

The *microemulsion method* comprises the following stages: preparation of an emulsion of two immiscible liquids, an aqueous solution and an oil; precipitation of the metal hydroxide in the droplets of the aqueous phase by adding an organic precipitant; separation of the components; and drying of the precipitated product. This method was used to obtain a Y_2O_3 powder with spherical particles up to 800–1000 nm in size and a silver powder with a particle size of 2–2.5 nm.

The *cryochemical method* of producing metal oxide nanopowders consists in dissolving salts, rapidly freezing the resulting solutions, subliming the solvent and thermally decomposing the residue. This method was used to obtain copper and yttrium oxide powders. Its advantage is the possibility of obtaining multicomponent homogeneous nanopowders.

2.3. *Decomposition of unstable compounds*

Today this technology is regarded as promising for obtaining nanopowders with particle sizes of 20–300 nm. The process involves three reactions: thermolysis, oxidation and hydrolysis.

The *advantages* of the method are the low process temperature, small reaction volumes, the absence of labour-intensive and inefficient washing and filtration of the final products, controllable dispersity and the high purity of the powders. Its *drawback* is the difficulty of monitoring and controlling particle size, since two competing processes occur simultaneously: decomposition of the starting compound and sintering of the final product particles under the effect of temperature.

For producing metal oxide nanopowders, alkoxides (alcohol derivatives of metals) are promising starting materials.

Another method is the *radiation-induced decomposition* of compounds. Decomposition of silver azide in this way yielded a silver nanopowder containing mainly two groups of particles, 5–30 nm and 170–220 nm in size. Particles up to 100 nm were spherical, whereas the larger ones were faceted.



Figure 5. *Silver azide*

2.4. *Use of reduction processes*

The best-known method here is the *hydrogen reduction of metal compounds*. Metal compounds (hydroxides, chlorides, nitrates, carbonates) undergo reduction in a hydrogen stream at a temperature of about 500 K. For a metal chloride, the reaction can be written as follows: $\text{MeCl}_2 + \text{H}_2 \leftrightarrow \text{Me} + 2\text{HCl}$.

This method can be used to obtain powders of iron, tungsten, nickel, rhenium, molybdenum, copper and calcium, as well as powders of alloys and alloy steels, which are distinguished by a low impurity content and a narrow particle size distribution.

The *chemical–metallurgical method* is also known. First, low-water hydroxides are synthesised by gas-phase interaction, and the resulting hydroxides are then heat-treated in a reducing atmosphere, for example in hydrogen. This yields nanopowders of iron, nickel, molybdenum, tungsten and copper. If the heat treatment is carried out in air, oxide nanopowders are obtained, for example Al_2O_3 , TiO_2 , ZrO_2 or their composites.

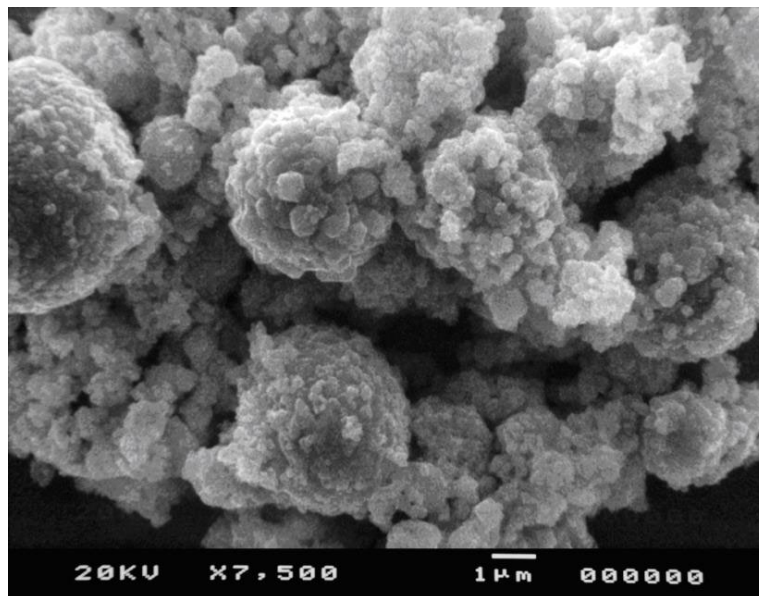


Figure 6. Copper oxide nanopowder (SEM, $\times 7500$)

The *advantages* of the method are the narrow particle size distribution of the nanopowder, low impurity content, relatively inexpensive process equipment and the ease of switching from the production of one powder to another.

2.5. Physical vapour deposition methods

Technologies based on evaporating a substance with various high-intensity energy sources and subsequently depositing it from the vapour phase are well established, easy to control and meet stringent requirements for the purity of the resulting nanopowder, especially when chambers with a controlled atmosphere are used.

Vacuum chambers or chambers filled with inert gases (helium, argon or xenon) are most often used. When metals are evaporated in vacuum or in an inert gas, the metal atoms tend to combine into particles a few nanometres in size, which then settle on a cooled substrate. These methods can produce complex alloyed powders.

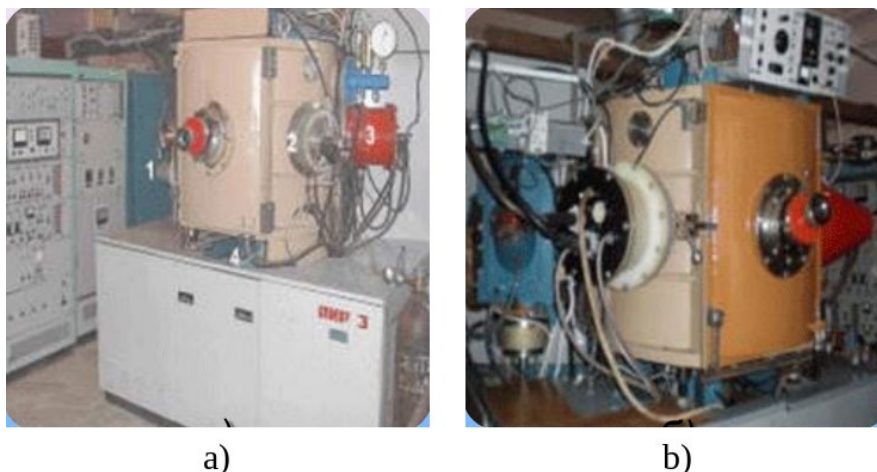


Figure 7. Basic industrial unit AIR-3: a) AIR-3 with arc ionisation of the vapour phase; b) AIR-3M with RF ionisation of the vapour phase

Depending on the method variant and the process parameters, the particle size of the powders can range from 5 to 100 nm.

Depending on the type of evaporation process, the following variants of the method can be distinguished.

Thermal evaporation. Here the material to be evaporated is heated in a crucible. Today various heating methods based on high-intensity energy sources are used: high-frequency induction, electron-beam, electric-arc, plasma and laser heating. A typical schematic of nanopowder production by this method is shown in Figure 8.

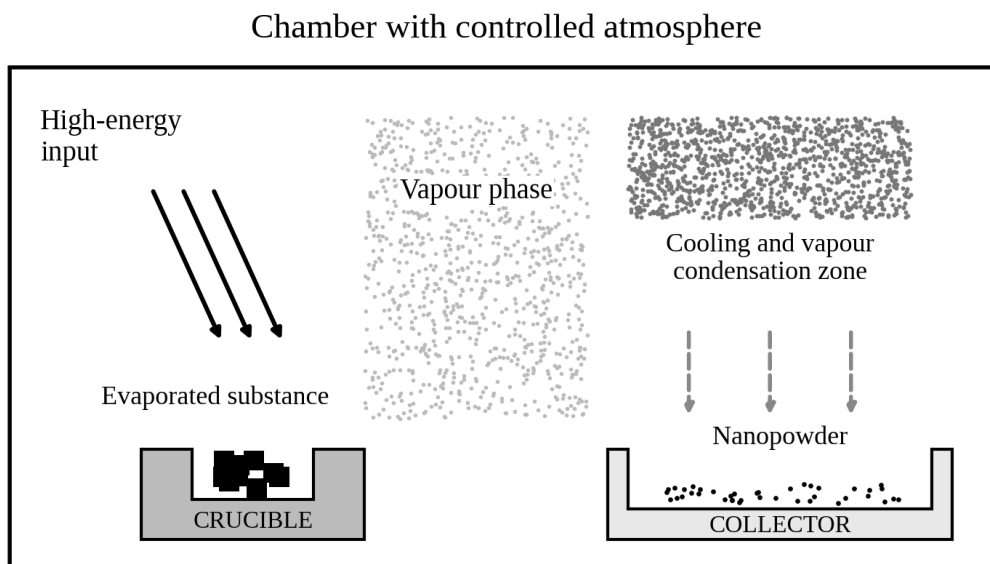


Figure 8. Schematic of nanopowder production by thermal evaporation and condensation of the material from the vapour phase

The powders are spherical or faceted and may be metallic, intermetallic or other compounds. The advantages of the method are pure powders with a narrow particle size distribution; its drawback is low productivity. This drawback is temporary: it results not from the process technology but from the lack of large-scale units for the industrial production of nanopowders.

Explosive evaporation. This rapidly developing method is based on the release of a very large amount of energy within a short period of time. The material evaporates and then, owing to the rapid increase in volume, cools down, and the vapour condenses into small particles.

In some cases, part of the material may not have time to evaporate; it melts and breaks up explosively into liquid droplets. To deliver the required amount of energy, a powerful electric current pulse, an arc discharge or a laser radiation pulse is used.

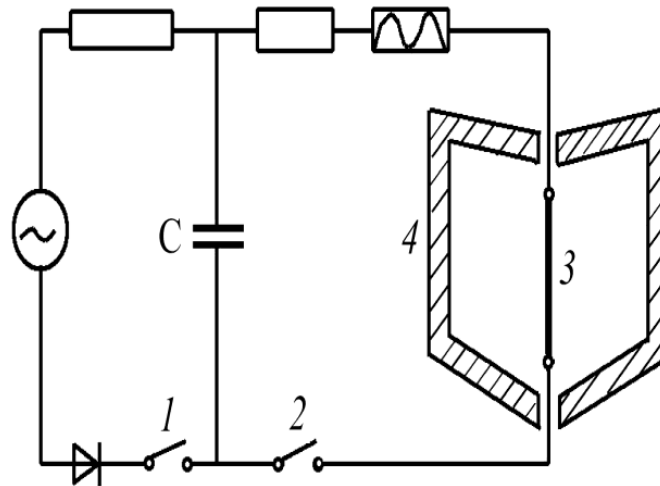


Figure 9. Schematic of powder production from a wire by explosive evaporation: 1 – charging circuit; 2 – discharge circuit; 3 – exploding wire; 4 – inert gas chamber

In this case, the current discharge is generated by a capacitor. The size and structure of the particles are controlled mainly by varying the density and rate of the energy input. The method makes it possible to produce high-purity spherical powders with particle sizes down to 5–10 nm, including powders of metals with high melting points and high chemical activity.

Evaporation in an inert gas flow (levitation-jet method). Here the metal is evaporated in an inert gas flow, for example from a melt droplet at the end of a wire heated by a high-frequency magnetic field.

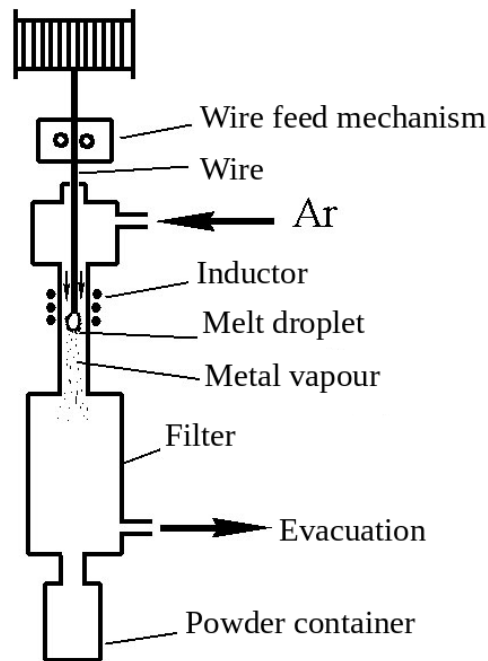


Figure 10. Schematic of a unit for producing nanopowders by evaporation in an inert gas flow

The particle size depends on the gas flow velocity: as the velocity increases, the particle size can decrease from 500 to 10 nm, while the particle size distribution narrows. This method has been used to obtain, in particular, Mn and Sb nanopowders; the latter was amorphous because of the high quenching rate in the gas stream.

A variant of this method is known as *vacuum melting*. In this variant, the wire is melted in a liquid with a very low temperature, for example in liquid nitrogen.

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Lecture 7. Methods for Producing Nanomaterials: Melt Atomisation and Severe Plastic Deformation

Outline

1. Melt atomisation.
2. Deformation methods for producing nanostructured materials.

1. Melt Atomisation

This group of methods is based on the rapid atomisation and cooling of a melt of the starting material. The technology makes it possible to obtain powders with a particle size of not less than 100 nm. The powder can be produced in a protective atmosphere. Today three variants of this technology are used.

Contact cooling by means of a water-cooled disc or drum. This method is based on feeding the molten material onto a rapidly rotating water-cooled disc or drum made of a material with high thermal conductivity.

Copper is usually used as such a material, providing cooling rates of up to 10^8 K/s. The surface of the drum or disc is made rough (toothed), since a smooth surface yields a foil or wire about 10...50 μm thick with an amorphous or nanocrystalline structure. The finished powder is distinguished by flake-shaped particles. Such a shape can lead to a non-uniform structure and anisotropy of the properties of products. For this reason, the powders are usually additionally comminuted mechanically, which is the main drawback of the method.

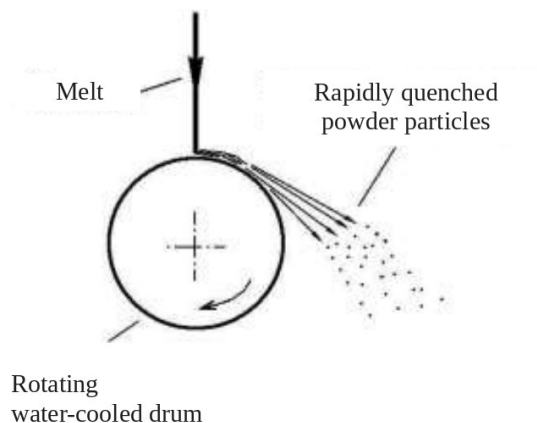


Figure 1. Schematic of powder atomisation from a melt by means of a water-cooled drum

Impact atomisation of the melt. Here a jet or droplets of the melt are mechanically broken up into fine particles on collision with intensively cooled, rapidly rotating metal blades. Cooling rates of up to 10^7 K/s are achieved.

As in the previous method, the powder particles have an irregular shape, and to form high-quality products with a uniform structure the powder must be additionally comminuted.

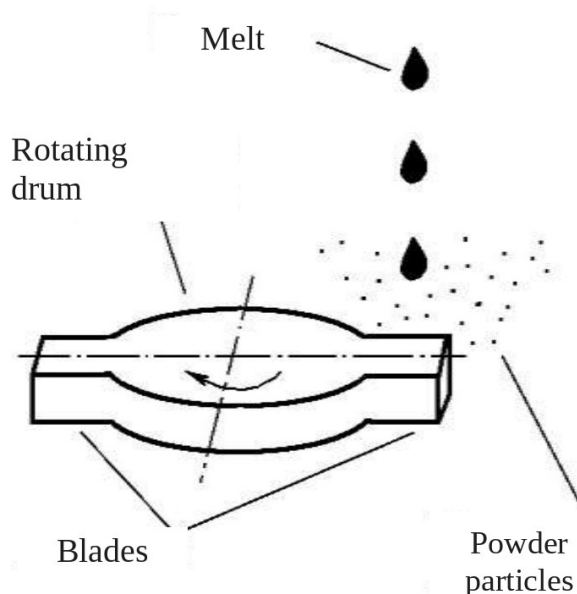


Figure 2. Schematic of impact atomisation of a melt

Electrohydrodynamic atomisation of the melt. In this method, electrostatic forces are used to atomise the melt. The melt jet is fed into a nozzle with an orifice diameter of $\sim 80\ \mu\text{m}$, in front of which an annular electrode is located. A constant voltage of 3...20 kV is applied to it. As a result, positively charged fine droplets of the melt fly out of the nozzle, which form powder particles after cooling.

Depending on the material and the process parameters, the particle size can range from 100 nm to 10 μm . The drawback of this method is its very low productivity (2 g/h from one nozzle).

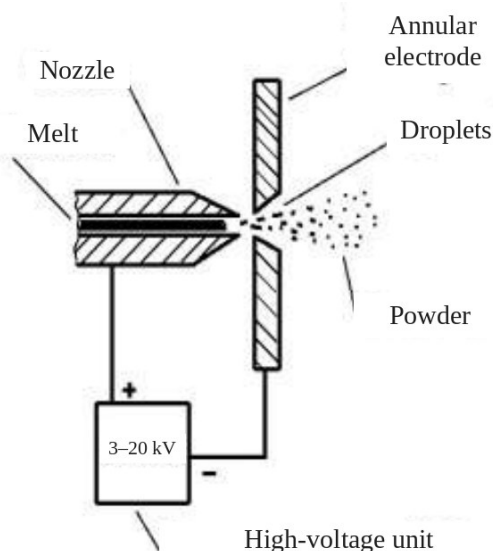


Figure 3. Schematic of electrohydrodynamic atomisation of a melt

Mechanical comminution. This route makes it easier to obtain powders based on brittle materials. The powder obtained by this method meets stringent purity requirements, is more homogeneous and contains particles of approximately the same size. An intensive gas flow substantially reduces the heating of the particles during milling, which makes it possible to process amorphous and nanocrystalline powders. The main drawback is the complexity and high cost of the process equipment.

Depending on the type of material and the required properties of the nanopowder, mainly planetary, ball and vibration mills are used. The average particle size of the powders can range from 5 to 200 nm. Another variant of the method is the use of high-energy grinding devices (attritors) with a stationary drum body and agitators that transmit motion to the balls in the drum.

The main drawback of the method is contamination of the powder owing to wear of the working parts of the equipment.

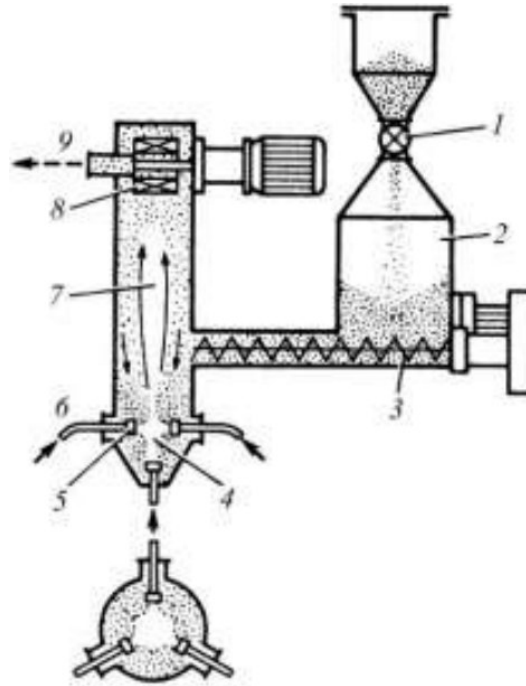


Figure 4. Schematic of a unit for counter-current (jet) milling in a fluidised bed: 1 – feeder; 2 – hopper with the starting particles; 3 – system for feeding the particles into the milling chamber; 4 – fluidised bed; 5 – gas supply nozzles; 6 – high-pressure gas supply pipeline; 7 – milling chamber; 8 – classifier; 9 – gas outlet manifold with fine particles

2. Deformation Methods for Producing Nanostructured Materials

Deformation methods for producing nanostructured materials are based on **severe plastic deformation (SPD)**, which consists in large strains at relatively low temperatures (below $0.3...0.4 T_m$) under high applied pressures, ensuring the production of bulk pore-free nano- and submicrocrystalline metals and alloys.

SPD methods include:

- high-pressure torsion;
- equal-channel angular pressing;
- reversible (alternating) bending;
- twist extrusion;
- accumulative roll bonding;
- multiaxial isothermal forging (MIF).

The following conditions facilitate the achievement of large plastic strains without fracture of the specimen:

- the initial and final cross-sections of the specimen remain unchanged;
- the deformation of the specimen approaches simple shear;
- the deformation is reversed (alternating);
- high pressures.

The requirements for SPD methods that should be taken into account when developing them for the fabrication of nanostructured materials are as follows:

- uniformity throughout the specimen volume to ensure the stability of the properties of the materials obtained;
- the structure must consist of grains and fragments with predominantly high-angle misorientations, since it is in this case that a qualitative change in the properties of the materials occurs;
- the specimens must not contain discontinuities or fractures despite their severe deformation.

SPD schemes are subdivided into two groups:

1. In the first group, high hydrostatic pressures are not possible. It includes multiaxial deformation, reversible bending and accumulative roll bonding. SPD schemes of the first group provide a submicrocrystalline structure ($100 \text{ nm} < D < 1 \text{ }\mu\text{m}$).
2. The second group, which uses high hydrostatic pressure, includes high-pressure torsion, twist extrusion and equal-channel angular pressing. SPD schemes of the second group provide a nanocrystalline structure ($D < 100 \text{ nm}$).

Multiaxial deformation: multiaxial isothermal forging. The MIF scheme is based on multiple repetition of open-die forging operations, upsetting and drawing, with a change in the axis of the applied deforming force.

The billet is deformed stepwise and cyclically. One cycle consists of three passes: the billet is successively deformed along all three coordinate axes. The number of cycles is determined by the attainment of the required degree of accumulated strain.



Figure 5. Billets after multi-axial isothermal forging

The equipment is an open die with heat-resistant nickel-alloy anvils. The temperature of plastic deformation lies in the range $(0.3\text{--}0.6) T_m$ of the alloy.

Advantages of the MIF method:

- it provides the largest dimensions of nanostructured semi-finished products;
- high structural homogeneity and versatility;
- it does not require special equipment or tooling;
- it provides a uniform ultrafine-grained structure down to $D \sim 10\text{--}100\text{ nm}$;
- the material is processed over a wide temperature range ($T = 20\text{...}950\text{ }^{\circ}\text{C}$) under isothermal conditions, which makes it possible, by combining upsetting–drawing schemes, to achieve uniform deformation and hence a uniform ultrafine-grained structure.

Drawbacks of the MIF method:

- the low productivity of the process of obtaining the specified microstructure in billets;
- the low technological ductility of the deformed material, since during upsetting and drawing the billet experiences tensile stresses along two of its axes and compressive stress along the third axis.

High-pressure torsion is performed in devices in which the specimen is placed between anvils. When the upper anvil rotates, the specimen is deformed in shear by surface friction forces. The lower anvil has a recess to prevent the metal from flowing out.

High-pressure torsion provides a high degree of shear strain, as a result of which the finest structure is formed in the specimen material. The process is usually carried out at a pressure of $4\text{...}6\text{ GPa}$.

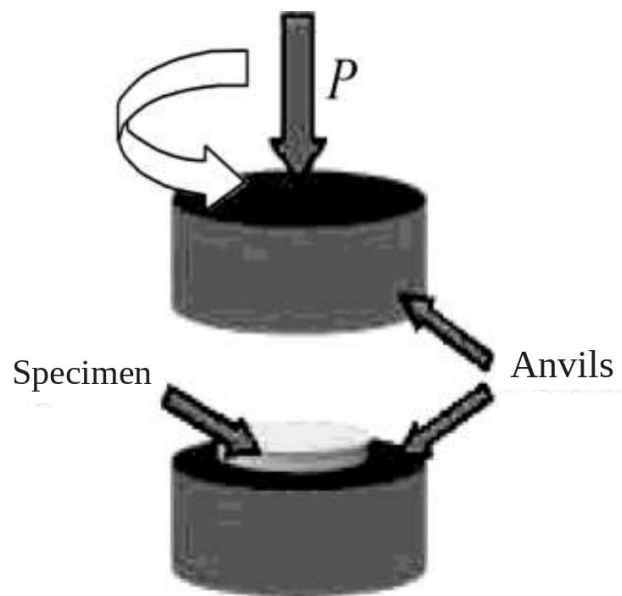


Figure 6. *Schematic of severe plastic deformation by high-pressure torsion*

Twist extrusion. In this method, a prismatic billet is extruded through a die with a helical channel; therefore, in the literature this method is also called twist (helical) pressing.

The angle β of inclination of the helix to the extrusion axis varies along the height of the die, being zero in its initial and final sections. When the alloy is pressed through the helical channel, the shape of the billet does not change, which makes it possible to perform multiple extrusion passes to accumulate the strain that causes refinement of its structural constituents.

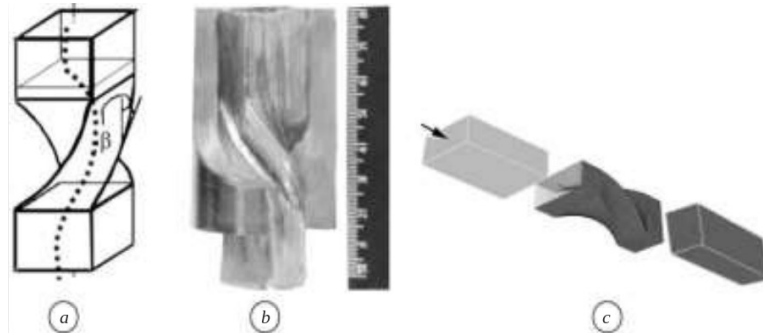


Figure 7. Twist extrusion: *a* – schematic of the helical channel; *b* – extrusion of an alloy through the helical channel (longitudinal section); *c* – schematic of the passage of the billet through the helical channel

The stress state of the metal during twist extrusion is determined by the strain-rate field. As the deformed material moves along the helical channel, the pressure from the active parts and the periphery gradually penetrates into the central zone of the billet. The pressure is distributed more uniformly over the cross-section, although the position of the maximum is retained. Twist extrusion of metals with back pressure makes it possible to increase the strength characteristics of the material while preserving its ductility.

Equal-channel angular pressing (ECAP) was first proposed by Professor V. M. Segal in 1978. During ECAP, the specimen is repeatedly pressed through two channels of equal cross-section that intersect at an angle.

The main parameters of ECAP are the deformation temperature, the channel intersection angle and the pressing route.

The deformation temperature must be below the recrystallisation temperature of the alloy (a smaller diameter of the grains formed, but more non-equilibrium grain boundaries).

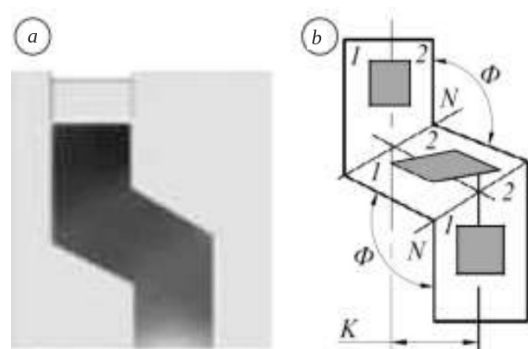


Figure 8. Schematic of ECAP in parallel channels: *a* – longitudinal section of the die with the billet in parallel channels; *b* – schematic of shear deformation of the billet cross-section in different parts of the channels

The principle of the high-productivity process of producing rods of titanium and aluminium alloys with an ultrafine-grained structure is illustrated by the ECAP–Conform scheme (Figure 9).

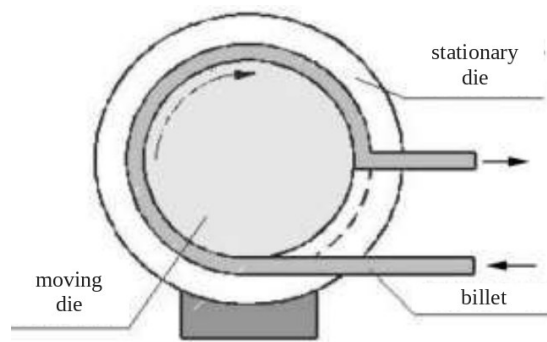


Figure 9. Schematic of the ECAP–Conform process

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Lecture 8. Methods for Studying Nanomaterials: Electron and Scanning Probe Microscopy

Outline

1. General characteristics.
2. Electron microscopy.
3. Scanning probe microscope.

1. General Characteristics

A decrease in crystallite size below a certain critical value can lead to a substantial change in properties. Size effects appear when the average size of the crystalline grains does not exceed 100 nm and are most pronounced when it is less than 10 nm. Thus, **particle size** is one of the most important parameters determining the specific properties and field of application of a nanomaterial.

A conventional classification of substances by absolute grain size can be adopted. Materials with an average grain size of more than 1 μm are *coarse-crystalline*; polycrystals with an average grain size from 100...150 to 40 nm are *submicrocrystalline*; and those with an average grain size of less than 40 nm are *nanocrystalline*.

Physically, the transition to the nanocrystalline state is associated with the appearance of size effects in the properties. If there are no size effects, there is no nanocrystalline state.

To assess the transition to the nanocrystalline state, such physical parameters as the size of magnetic domains in ferromagnets, the electron mean free path and the wavelength of elastic vibrations can be used.

2. Electron Microscopy

Electron microscopy is a visualisation technique. There are two main methods of electron microscopy: *scanning* electron microscopy, which operates with reflected electrons, and *transmission* electron microscopy.

Scanning electron microscopy gives information about the external shape of a particle and its apparent dimensions, but not about its internal structure. Transmission electron microscopy makes it possible to see the structure of particles.

To study the structure of nanoparticles and determine their sizes, the optimal approach is to combine electron microscopy with the diffraction method.

Electron microscopy makes it possible to study objects whose dimensions are substantially smaller than 1 μm . The ability to resolve individual columns of atoms in a crystal led to the emergence of high-resolution transmission electron microscopy.

Electron microscopy can directly determine the sizes of nanoparticles and nanocrystallites; it is therefore widely used both in nanomaterials research and in the

nanotechnologies of modern electronics. It is the only direct method for studying the structure of nanoparticles obtained from colloidal solutions.

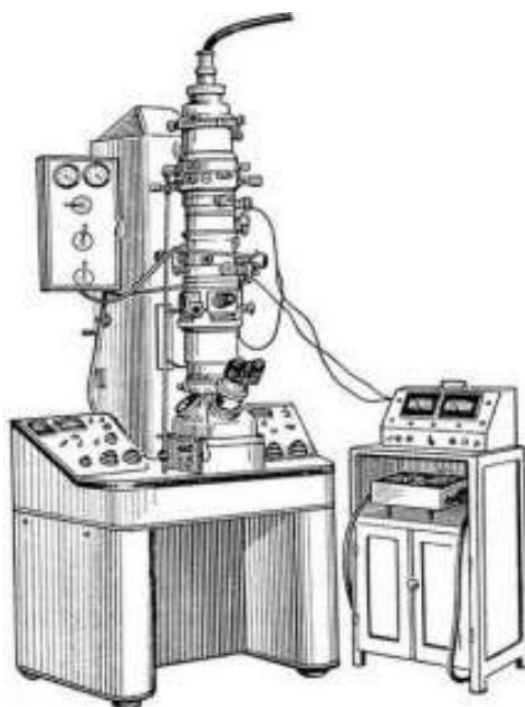


Figure 1. Transmission electron microscope of the 1970s

Electron microscopy has made it possible to observe an unusual nanostructure obtained after ordering of non-stoichiometric vanadium carbide.

Under the microscope at a magnification of about 100 times, only large (up to 20 μm) individual agglomerates of irregular shape are visible in vanadium carbide powder. At a substantially higher magnification, however, it becomes clear that these particles have a complex structure and are an aggregate of a large number of very small particles in the nanometre range.

A micrograph obtained at a magnification of 30 000 times with a DSM 982 Gemini high-resolution scanning electron microscope shows that the vanadium carbide nanocrystallites have the shape of curved petals which, growing together, form a coral-like nanostructure (Figure 2).

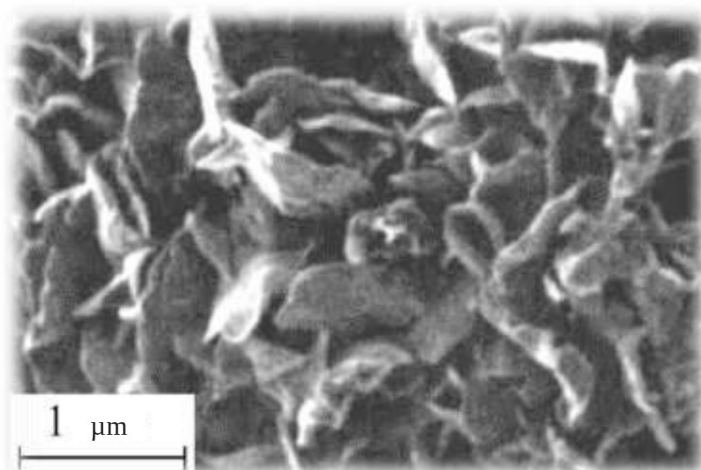


Figure 2. Nanocrystallites of ordered vanadium carbide powder V_8C_7 ($VC_{0.875}$)

For high-resolution transmission electron microscopy, the specimens must be prepared especially carefully.

3. Scanning Probe Microscope

To study the atomic and molecular structure of a surface, **scanning probe microscopy** is often used. Owing to its high resolution, it makes it possible to estimate the sizes of the objects observed, to visualise individual atoms and molecules and to construct three-dimensional images. Its varieties are scanning tunnelling microscopy (STM) and atomic force microscopy (AFM).

In *STM*, the probe is an extremely fine metal (tungsten) needle whose tip may consist of a single atom and have a size of ~ 0.2 nm. Its principle of operation is based on the passage of electrons through the potential barrier formed by a break in the electric circuit, i.e. a small gap between the probing microtip and the specimen surface.

In *AFM*, the force of interaction between the microtip and the specimen surface is monitored, and the instrument is extremely sensitive for measuring the surface profile. The probe is a miniature elastic plate (cantilever) on the free end of which a tip of a hard material is formed by lithographic methods.

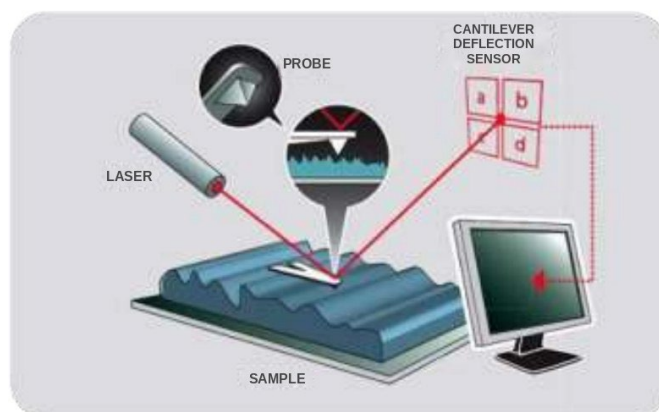


Figure 3. Principle of operation of the AFM

The main drawback of AFM is the lack of simultaneous information about the entire surface, since at any moment information is available only from the area being directly registered by the probe. Modern AFM is used to study any materials.

Scanning probe microscopy is based on the detection of the local interaction that arises between the probe and the surface of the specimen under study when they approach each other to a distance of $\sim \lambda$, where λ is the characteristic decay length of the probe–specimen interaction.

Depending on the nature of this interaction, the following main types of microscope are distinguished:

- the scanning electron microscope (SEM), which measures the current of secondary and reflected electrons;
- the scanning tunnelling microscope (STM), which measures the tunnelling current;
- the scanning force microscope (SFM), which measures the force interaction;

- the scanning near-field optical microscope, which measures electromagnetic radiation.

Scanning force microscopy is subdivided into atomic force microscopy, magnetic force microscopy, etc., depending on the type of interaction. The most important methods of scanning probe microscopy are STM and AFM; it is with them that progress in the development of nanostructure research techniques is associated.

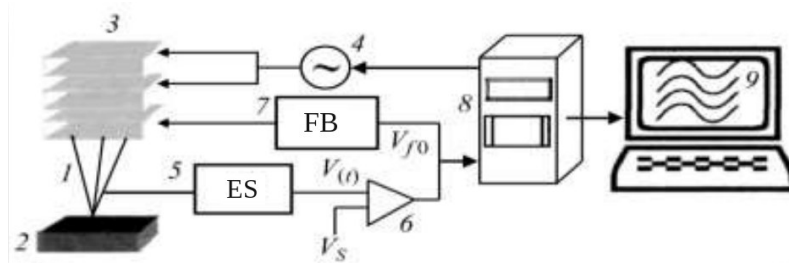


Figure 4. General schematic of a scanning probe microscope: 1 – probe; 2 – specimen; 3 – x, y, z piezoelectric actuators; 4 – scan voltage generator; 5 – electronic sensor (ES); 6 – comparator; 7 – electronic feedback circuit (FB); 8 – computer; 9 – image

When the tunnelling current is measured, a current-to-voltage converter connected into the current path between the probe and the specimen is used in the tunnelling sensor. Two connection options are possible: with a grounded probe (the bias voltage is applied to the specimen relative to the grounded probe) and with a grounded specimen (the bias voltage is applied to the probe relative to the specimen).

The force interaction sensor is usually a silicon cantilever with an optical scheme for registering its bending caused by the force interaction between the specimen and the probe located at the end of the cantilever.

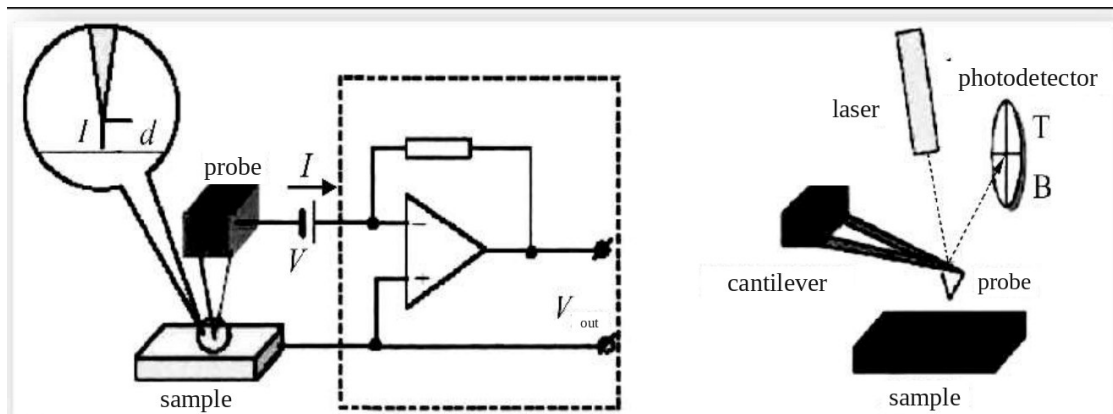


Figure 5. Schematics of sensors: a – tunnelling sensor; b – force sensor

Contact, non-contact and intermittent-contact ("semi-contact") modes of force microscopy are distinguished.

In the *contact mode*, the probe rests against the specimen. In this case, when the cantilever bends under the action of contact forces, the laser beam reflected from it is displaced relative to the centre of a quadrant photodetector, so that the cantilever deflection can be determined from the relative change in the illumination of the upper and lower halves of the photodetector.

In the *non-contact mode*, the probe is removed from the surface and is in the zone of long-range attractive forces. Here the attractive forces and their gradients are weaker than the repulsive contact forces; therefore, a modulation technique is usually used to detect them.

In the *semi-contact mode*, a modulation technique for measuring the force interaction is also used. Here the probe partially touches the surface, being alternately in the region of attraction and in the region of repulsion.

There are simpler methods of measuring the force interaction in which the force interaction is directly converted into an electrical signal, for example, a method based on the direct piezoelectric effect, when bending of a piezoelectric material under the action of the force interaction generates an electrical signal.

For precision mechanical scanning of the specimen under study by the probe, either by moving the probe relative to a stationary specimen or by moving the specimen relative to a stationary probe, *piezoelectric actuators* are used.

The operation of such actuators is usually based on the inverse piezoelectric effect, which consists in a change in the dimensions of a piezoelectric material under the action of an electric field. The piezoelectric material most commonly used is PZT piezoceramics (lead zirconate titanate $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ with various additives).

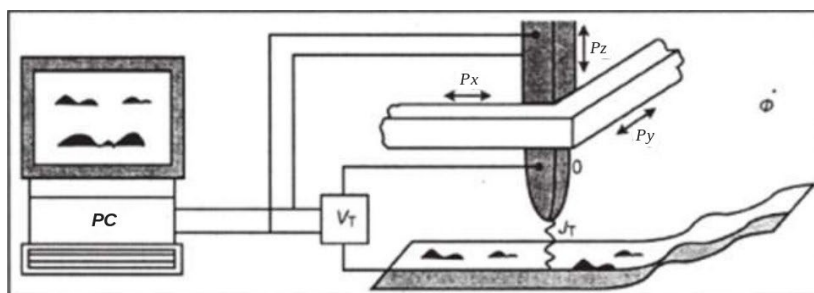


Figure 6. Piezoelectric actuators for linear displacements along the surface (P_x , P_y) and in depth (P_z) and the feedback circuit

Scanning of the surface is similar to the motion of the electron beam across the screen of a cathode-ray tube: the probe moves along a line first in the forward and then in the reverse direction (line scan), and then moves on to the next line (frame scan). The probe is moved by the scanner in small steps under the action of sawtooth voltages supplied by the scan generator.

Scanning electron microscopes are similar in principle of operation to an ordinary television set with a cathode-ray tube.

The idea of SEM is that the specimen surface is scanned by an electron beam produced by an external source at a voltage of the order of several tens of kilovolts. The beam is deflected by a magnetic field produced by an electric current in coils, which is proportional to the voltage applied to the coil.



Scanning electron microscope JEOL JSM-T220A

Figure 7. *Scanning electron microscope JEOL JSM-T220A*

The surface irradiated during scanning begins to emit either secondary electrons or light quanta, which are registered, amplified, converted in intensity, etc., and then fed to the screen of a cathode-ray tube, creating a visible image of the surface.

The methods of obtaining a magnified image in scanning electron microscopes differ substantially from those used in transmission electron microscopy.

By scanning the surface under study with a fine but sufficiently intense electron beam and feeding the signals from the detector of secondary and reflected electrons to the screen, a magnified image of the surface can be obtained. Naturally, the rate of scanning of the surface and that of the screen must be synchronised. The principle of operation is as follows:

1. The irradiating electron beam emitted by the electron gun passes successively through the condenser lens, the deflection coil and the objective lens and creates a small illuminated "spot" on the specimen surface, whose size can be adjusted by the control system.
2. Secondary and reflected electrons are thereby generated, the number of which depends on the characteristics of the surface: roughness, atomic composition and electric potential of the illuminated area of the crystal.

By measuring and analysing the intensity of these electrons, a magnified picture of a specific area of the surface can be obtained on the screen and converted into a photographic image. In scanning electron microscopes, as in transmission microscopes, a high vacuum must be maintained.

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Lecture 9. Nanomaterials for Nanoelectronics

Outline

1. Materials for nanoelectronics.
2. Moore's law and the main functions of nanoelectronics.
3. Improvement of traditional "silicon" electronics.
4. Nanolithography.
5. Main components of microcircuits.

1. Materials for Nanoelectronics

The advent of the era of nanotechnology as a general and systematic approach to solving the most difficult technical problems was stimulated to a very large extent by the unprecedented pace of development of microelectronics.

Nanoelectronics is a priority field of nanoscience and nanotechnology, since it faces the most ambitious, complex, multifactorial and multicomponent tasks, which can be solved only comprehensively by combining the efforts of physicists, chemists, biologists, materials scientists, electronic engineers, systems engineers and programmers.

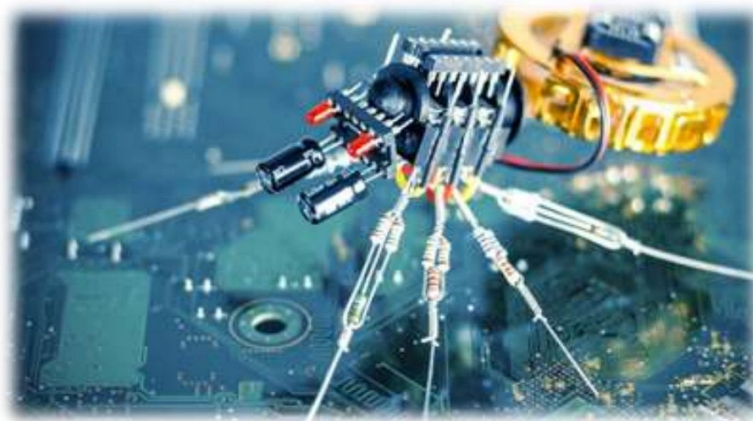


Figure 1. Micro- and nanosystem engineering

In electronics, it is customary to distinguish three main varieties:

- vacuum electronics;
- solid-state electronics;
- quantum (laser) electronics.

In what follows, we shall consider semiconductor solid-state electronics in more detail, although from time to time we shall also refer to the other two classes.

2. Moore's Law and the Main Functions of Nanoelectronics

The improvement of all the essential parameters of large-scale integrated circuits (LSI) follows an exponential law. Thus, for almost half a century, the number of elements in microprocessors and dynamic memory units has doubled approximately

every eighteen months. This trend was predicted more than 40 years ago by G. Moore, one of the founders of Intel.

The essence of the forecast:

- the exponential growth in the number of elements making up a microcircuit (primarily transistors) over several decades has led to a total of about 10^{19} transistors being produced in 2005 (approximately 1 billion for every inhabitant of the Earth), which exceeds by three orders of magnitude the number of wheat grains produced annually in the world;
- moreover, for the price of each of these grains, 1000 transistors can now be bought;
- the characteristic dimensions R^* of individual elements decrease steadily;
- the operating speed increases;
- power consumption and cost decrease;
- the power dissipated by a transistor per switching event has decreased by more than 10^5 times over the last 40 years.

At the end of the 1960s, the technology for producing p-MOS transistors was developed, and somewhat later that for n-MOS transistors, employing hole (p) and electron (n) conduction in the channel, respectively. Their combination gave rise to a device called the complementary MOS transistor (CMOS), which is still the basic element of circuit engineering. Its advantage is that it consumes almost no energy in standby mode (except for a very small leakage current).

In the early 1980s, the first optoelectronic devices based on quantum wells (films of nanometre thickness) were created, and they found wide application in information technologies and computer engineering.

Thus, for almost half a century electronics developed rapidly under the motto "more compact, faster, better, cheaper". Reviews of nanoelectronics can be found in numerous monographs.

Although nano- (micro-)electronics is not an absolute synonym of computer and information technology, with minor reservations one can agree that these concepts are almost fully equivalent at present. Let us distinguish five main functions of information systems.

1. Information processing:

- one of the central tasks of any computer or information system is processing, i.e. rapid handling of incoming information (Figure 2) and the issuing of decisions and control commands;
- it is often vital to perform it online;
- any computer contains a microprocessor (or a group of interconnected microprocessors) and random-access memory with which the processor periodically exchanges information during operation.

At present, these are the most complex and expensive units of information systems (computers), and they largely determine their capabilities.

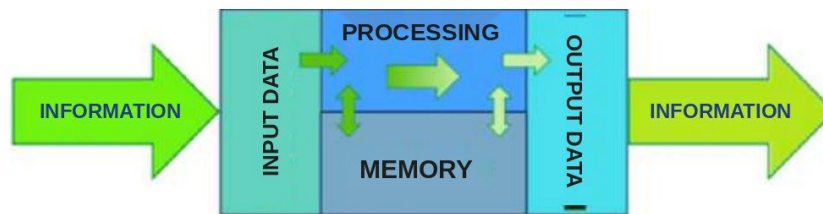


Figure 2. Data processing system

2. Information storage:

- long-term non-volatile storage of large amounts of information, which the information system may access from time to time;
- the corresponding devices need not be as fast as RAM units, but they must have a large capacity and high reliability to guarantee the storage of information for several years without power consumption or refreshing by rewriting;
- at the same time, they must allow new information to be written and unnecessary information to be deleted.

3. Information transmission:

- most technological electronics operates in networks in interaction with other devices;
- there are also internal connections within a computer, a local information or technological module, and each individual microcircuit;
- obviously, in the future the degree of integration at all levels of the hierarchy of electronic systems will only increase and determine their functionality, reliability, production cost and other important characteristics;
- both galvanic connection by means of conductors and contactless connection by means of microwave electromagnetic waves are possible.

4. Information conversion:

- this involves acquiring information from the environment and transforming it into an electrical signal;
- physically, this is accomplished by various sensors, transducers, microphones, video cameras, etc.;
- the other side of this function is the reverse conversion of coded information into sound and visual images, commands and executive actions;
- the homogeneity of the system is disrupted, and it becomes necessary to pass from some physical processes (mechanical, acoustic, thermal, chemical, etc.) to others (electrical) and vice versa, converting electrical signals into actions and images by means of actuators, motors, etc.

For brevity, all devices that convert information about the environment into an electrical signal are most often called *sensors*, and those performing the reverse conversion are called *actuators*.



Figure 3. Digital voltmeter connected to the board of an electronic device

5. Information protection against unauthorised access, use, distortion, erasure, etc. It must be implemented at the physical level as well as at the software and organisational–legal levels.

The general requirements are: increased functionality and intelligence of products; manufacturability; reliability; throughput; memory capacity with a simultaneous reduction in material consumption, power consumption, cost and complexity of use.

From the point of view of novelty and radicalness of approaches, three main paradigms can be identified:

- the development of nanoelectronics through the evolutionary improvement of existing "silicon" planar technologies;
- a deeper modification of planar technology and its extension to other materials and situations;
- the creation of fundamentally new electronics of the next generations based on "non-silicon" devices and physical principles.

These revolutionary ideas envisage the use of quantum superconducting components, nanotubes, fullerenes, graphene and their derivatives, optotronics, bioelectronics, quantum distributed computing, single-electronics, spintronics, etc.

At present, the possibilities of silicon technologies have not yet been fully exhausted (Figure 4). The "alongside silicon" direction appears to experts to be closer and more predictable. In each direction of nanoelectronics development, there are several groups of proposals of varying degrees of novelty and difficulty of implementation.

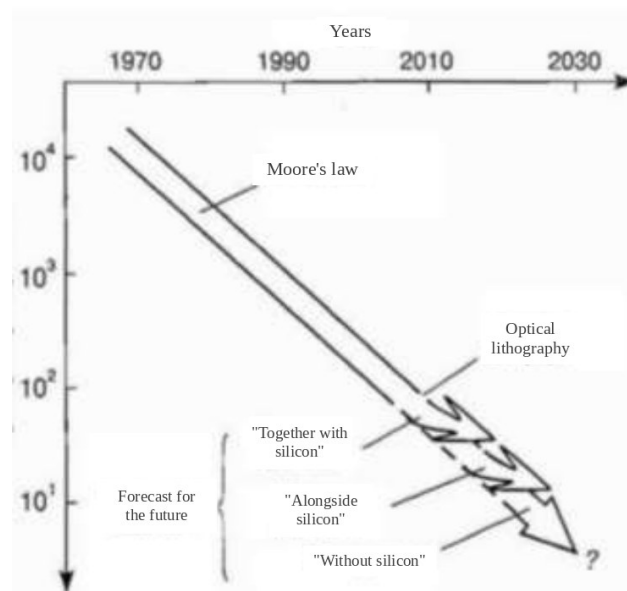


Figure 4. Three possible scenarios for the development of micro- and nanoelectronics in the near and distant future

Three groups of fundamental reasons that impose limitations on further reduction of the dimensions of elements in LSI circuits can be distinguished: thermodynamic, electrodynamic and quantum-mechanical.

Thermodynamic limitations are due to the finite temperature of objects, heat-exchange requirements, heating caused by current flow, the action of the first and second laws of thermodynamics (in particular, the tendency for entropy to increase and for information to be lost in the system), the specific features of reversible and irreversible processes in nano-objects, etc.

Electrodynamic limitations are caused by the inertia of capacitances and inductances in the circuit, which prevents rapid changes in voltages and currents on passing from one state to another. The finite propagation velocity of electromagnetic waves, the finite velocity of charge carriers and the finite rates of magnetisation reversal of ferromagnets or repolarisation of dielectrics impose additional limitations on operating speed.

Quantum-mechanical limitations manifest themselves when the characteristic size of an object R^* is reduced to atomic scales; atomic and electronic discreteness then becomes noticeable in transport phenomena, particle interactions, etc.

Hence, all strategies for improving and developing nanoelectronics can be divided into three groups of approaches, conventionally designated "into the future together with silicon", "alongside silicon" and "without silicon".

3. Improvement of Traditional "Silicon" Electronics

Today it is necessary to overcome various practical difficulties and problems, which can be combined into several groups:

- the creation and selection of efficient materials and of technologies for their production, processing and application;

- the development of new operating principles of individual components and of technologies for their fabrication on an industrial scale;
- the optimisation of electrical circuits at the circuit-design level;
- the improvement of the system architecture of complex devices or complexes.

The main processes used in silicon-based nanoelectronics manufacturing can be grouped into three classes: modifying processes; removing processes; and processes that add new material. Each of these, in turn, is divided into several groups.

With rare exceptions, almost all of these technologies are already used on an industrial scale; however, the transition to a new scale level (below 32 nm) will require serious improvement.

4. Nanolithography

Let us consider in more detail the key stage of LSI manufacturing, namely beam lithography, which precedes the actual creation of the electrical circuit on the surface of silicon wafers.

The word *lithography* originally denoted a method of printing images: a drawing was first applied to the flat surface of a stone and an impression was then made from it on another material. In the second half of the 20th century, the term also came to denote the processes of transferring the patterns of electrical circuits in the microelectronics industry.

Its meaning and main purpose are as follows:

- the layout of the electrical circuit of the device is transferred onto a substrate (in the vast majority of cases a silicon one);
- the required structures and their interconnections are then formed step by step by various physicochemical means;
- this usually requires several dozen operations, resulting in a finished integrated circuit or microelectromechanical system (MEMS).

Modern industrial micro- and nanolithography mainly uses an optical method of transferring the pattern from a template (photomask) to the substrate surface; the process itself is therefore often called *photolithography* (Figure 5).

- An essential part of this process is the fabrication of a photomask with the required pattern and the deposition of a photosensitive layer, the resist, on the surface of the silicon wafer.
- The resist is exposed through the photomask by means of an ultraviolet, X-ray or other source of electromagnetic radiation.
- The photomask may lie on the resist surface or be located at a distance from it.

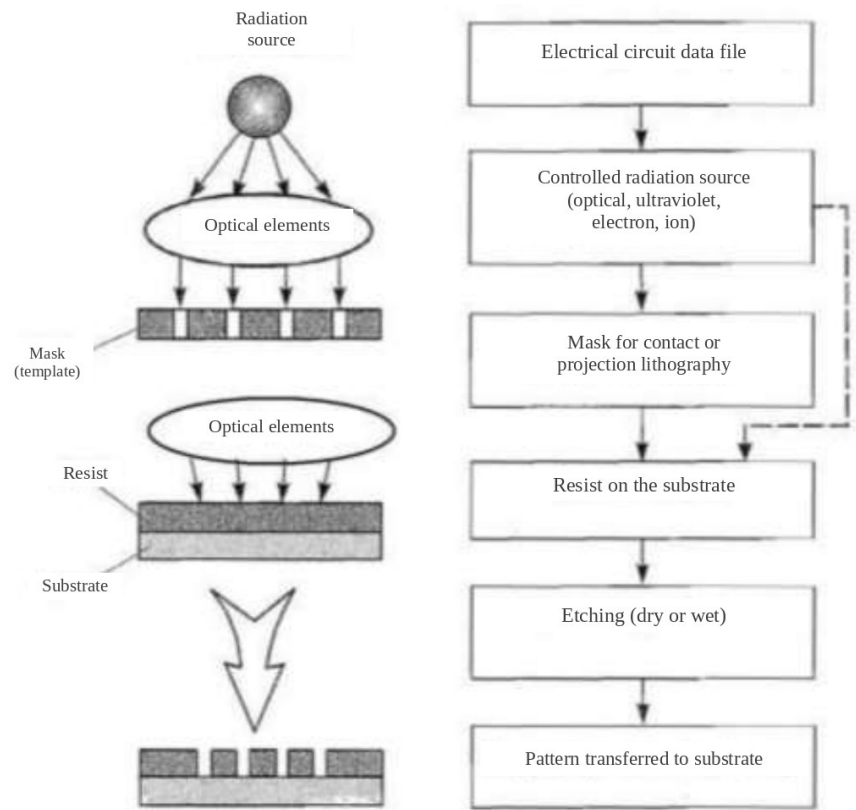


Figure 5. Optical nanolithography

In the second case, the image of the photomask is projected onto the resist surface with a reduction of several times by means of an optical system.

- The photoresist is treated with a selective chemical etchant.
- The exposed areas of the resist are etched at a rate that differs many times from that of the unexposed areas (if it is higher, a positive image of the template is obtained; if lower, a negative one).
- On prolonged etching, the pattern begins to be etched into the substrate (silicon, silicon dioxide, metal, etc.).
- This makes it clear why the film deposited on the substrate surface is called a *resist*.

The use of the optical lithography method (the most convenient and best mastered) imposes a physical limit of miniaturisation of several tens of nanometres (and even then only when the resist is exposed with a short-wavelength ultraviolet source). To increase the resolution further, it is necessary either to use harder radiation (X-ray, electron or ion beams) or to switch to alternative technologies.

The common tasks in developing alternative methods of nanolithography are:

- high productivity;
- high accuracy of positioning and alignment of the masks for each layer of the multilayer structure being created;
- requirements for radiation sources: they must be powerful enough to achieve high productivity, monochromatic to provide high resolution, and stable over time;

- the selection of a highly sensitive resist (to allow a lower exposure dose) with high contrast (to ensure high resolution);
- the need for a separate mask for each individual image (up to several dozen of them are required to produce one LSI circuit); in the transmission regions the mask must transmit radiation without distortion, while in the absorption regions it must not heat up strongly, deform or distort the pattern transferred to the substrate.

Hence, one of the bottlenecks on the way to further integration and miniaturisation of LSI circuits is lithography with ever higher resolution. Let us consider the available proposals and developments aimed at further improving the resolution of nanolithographic processes.

Electron-beam lithography (Figure 6) can be implemented in two ways: by projection, using a defocused beam that irradiates the entire substrate at once, or point by point, using a well-focused beam.

Drawbacks:

- maskless lithography has low productivity, since the object is processed sequentially, point by point;
- it can be used only for the production of high-precision masks, which are then used many times.

A number of effects prevent a further increase in resolution: Coulomb repulsion of the electrons in the beam, shot noise, electron scattering in the resist, etc.

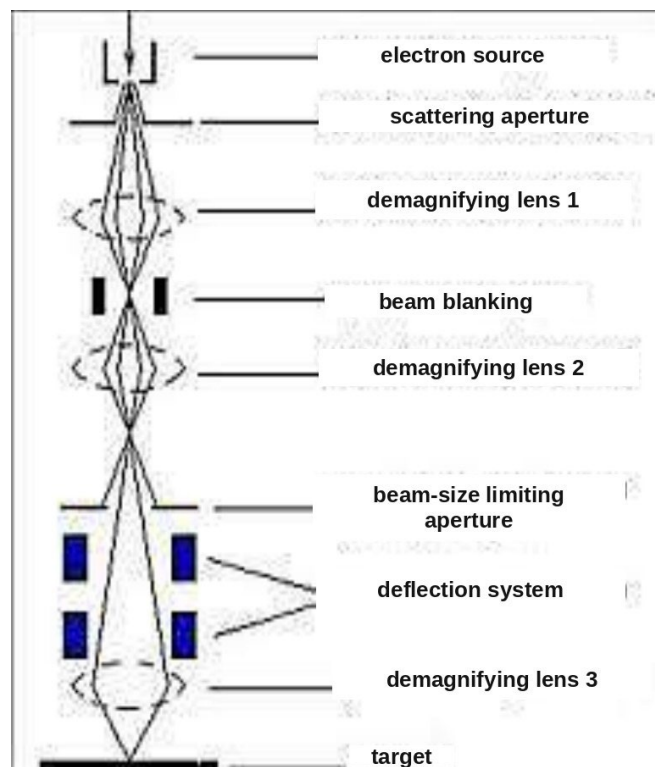


Figure 6. General schematic of the scanning system for electron-beam lithography

Ion-beam lithography is quite similar to electron-beam lithography.

Advantages:

- owing to the much shorter equivalent wavelength, it can operate with a considerably smaller aperture;
- this makes it possible to obtain a large depth of focus and to expose a large area in one step in projection lithography with the possibility of image reduction by a factor of 3...4.

Drawbacks:

- the risk of radiation damage to the substrate;
- these and other difficulties make ion lithography less developed than electron lithography.

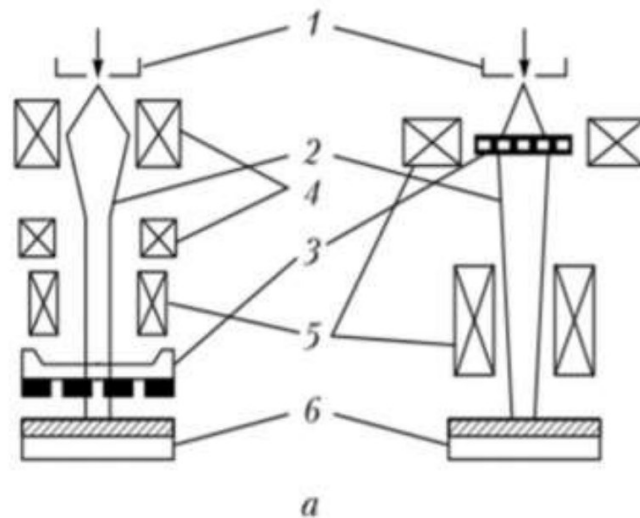


Figure 7. Schematic of ion-beam lithography units using a projection system (a) and collimated ion beams: 1 – ion source; 2 – ion beam; 3 – mask; 4 – collimating system; 5 – focusing system; 6 – wafer

X-ray lithography can be performed using a beam of photons with $\lambda \leq 1$ nm. Obstacles to its rapid mass implementation are the need for a powerful and very bulky radiation source (for example, a synchrotron) and the prior fabrication of high-precision masks on a 1:1 scale, as well as the impossibility of focusing an X-ray beam in the same way as an optical, electron or ion beam. As a result, it is not possible to obtain a substantially reduced image (relative to the scale of the mask template) on the silicon substrate and thereby achieve additional miniaturisation.

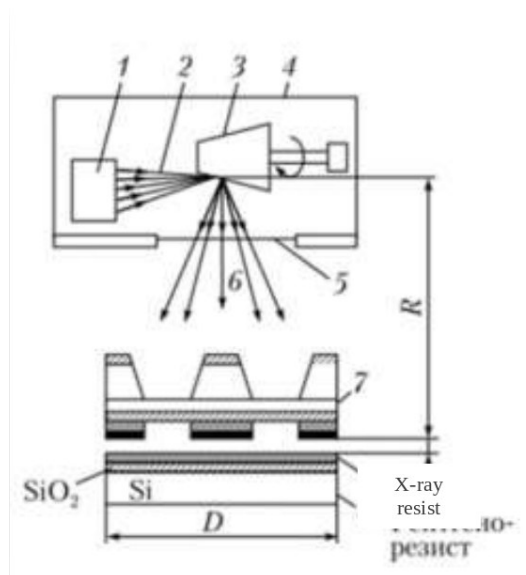


Figure 8. Schematic of X-ray lithography: 1 – electron gun; 2 – electron flux; 3 – target; 4 – vacuum chamber; 5 – beryllium foil window; 6 – X-ray flux; 7 – X-ray mask; 8 – wafer with X-ray resist

Lithography in the extreme ultraviolet. A gas-discharge plasma is proposed as the source of such radiation. At the required wavelength $\lambda \approx 10$ nm, the necessary radiation power is ~ 100 W in a band of $\delta\lambda \approx 0.25$ nm. The main problems are the creation of high-precision defect-free masks and powerful ultraviolet radiation sources.

Microcontact printing. This method is very similar to letterpress printing from lead type. However, it requires high-precision templates and specific polymeric materials for transferring the pattern from the stamp to a substrate coated with gold or silver, and so far it has a low resolution (~ 100 nm).

Probe methods potentially have a very high resolution ($1 \dots 10$ nm) and are relatively simple to implement, as is the necessary equipment. The productivity of such "nanopen writing" is limited by the maximum permissible velocity of lateral probe motion (~ 100 $\mu\text{m/s}$), i.e. approximately 10^3 elements per second.

Nanoimprinting is considered the most promising of the non-beam methods of nanolithography. It resembles the technology for producing gramophone records on vinyl discs in the mid-20th century, which consisted in pressing a metal stamp into the heated surface of a polymer. Several variants of implementing this process on the nanoscale have been proposed (Figure 9): a literal reproduction of the old technology at a new technical level (Figure 9, *a*) and a number of modifications, two of which are shown in Figure 9, *b* and *c*.

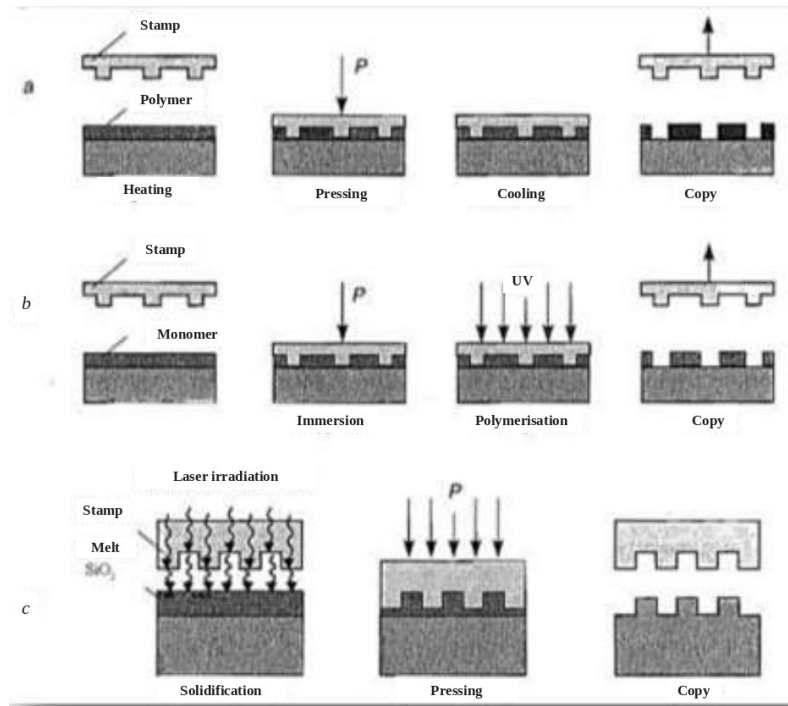


Figure 9. Three variants of nanoimprinting

In mass (as opposed to experimental laboratory) production, the decisive role in choosing a particular technology is played by economic considerations, in particular the cost of the product, the cost and complexity of the equipment and tooling, their reliability and durability, the stability of the results obtained, etc. A very approximate order-of-magnitude comparison of various characteristics of the nanolithography methods discussed is given in Table 1.

Table 1. Comparison of various nanolithography technologies

Characteristic	Technology						
	Industrial	Existing		Under development			
	Optical [†]	Electron-beam (projection)	Electron-beam (point)	Ion-beam (point)	Extreme UV	Probe	Nano-imprinting
Resolution, nm	100	50	20	30	30	10	10
Mask alignment accuracy, nm	20	10	2	3	3	1	100
Productivity, elements/s	10 ¹⁰	10 ¹⁰	10 ⁴	10 ¹ ...10 ²	10 ¹¹	up to 10 ³ per probe	10 ¹²
Equipment cost, US\$	10 ⁷	10 ⁷	10 ⁶	10 ⁶	5·10 ⁷	10 ⁵	10 ⁵

[†] Used on an industrial scale.

5. Main Components of Microcircuits

The key role in any microcircuit is played by the active elements, diodes and transistors. Let us consider the design and operating principle of field-effect (unipolar)

transistors, as well as another element which is the main component of such a transistor and is important in its own right, namely the capacitor on the surface of a silicon wafer (Figure 10).

Dry or wet thermal oxidation technology is used: a thin layer of silicon dioxide is created by passing a stream of dry or wet oxygen over the heated wafer. Other methods exist, but they have not become widespread because of the poorer structure of the oxide layer.

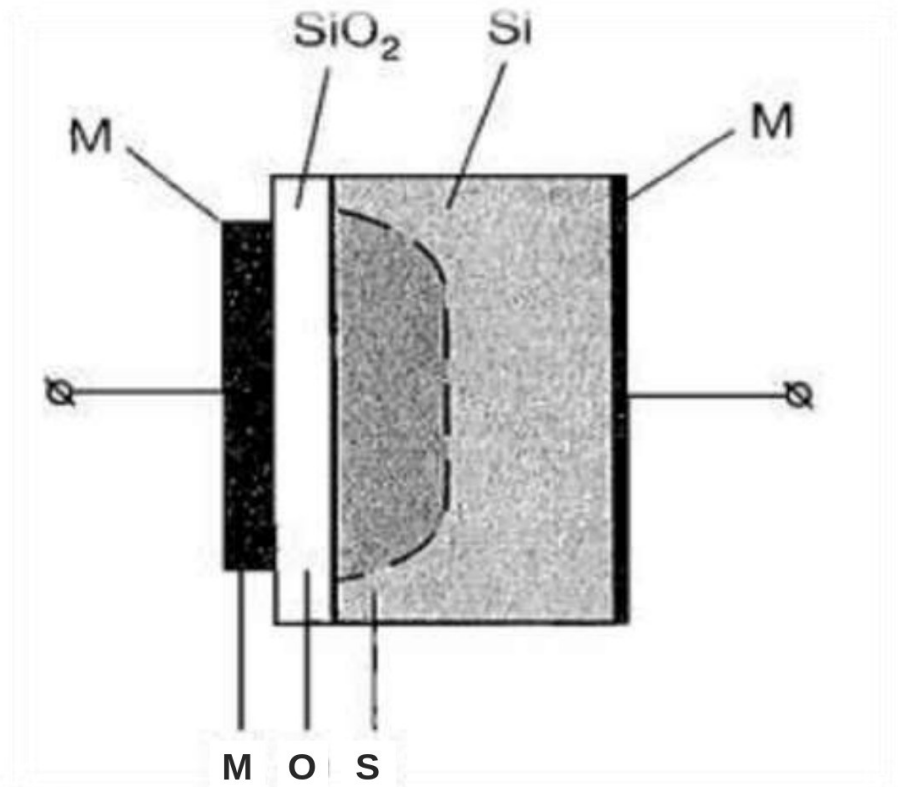


Figure 10. Metal–oxide capacitor on the silicon surface

The silicon oxide film has excellent dielectric properties and can serve both as a mask material through which subsequent structures are deposited and as insulation between individual circuit elements.

- Its usual thickness in modern LSI circuits is a few nanometres, but as all the dimensions of the device decrease it must become less than 1 nm.
- As the film thickness decreases, quantum tunnelling effects begin to manifest themselves; this is a fundamental obstacle to the miniaturisation of such devices, since tunnelling leads to a sharp increase in leakage current.
- To combat this effect, it is proposed to use materials with a very high dielectric permittivity ϵ (from several tens to several hundreds).
- At low voltages, oxide capacitors exhibit strong non-linearity, i.e. a dependence of capacitance on the applied voltage. It arises from the depletion of charge carriers in the silicon layer adjacent to the silicon oxide layer from below (Figure 10).

As a result, the conductivity of this silicon layer drops sharply, and the equivalent thickness of the dielectric gap between the metal layer and the conducting silicon substrate increases substantially.

Such structures find wider application in metal–oxide–semiconductor (MOS) transistors. A schematic explaining the design and operating principle of a field-effect transistor (also called a MOS or MIS transistor) is shown in Figure 11. SCR is the space-charge region depleted of majority carriers.

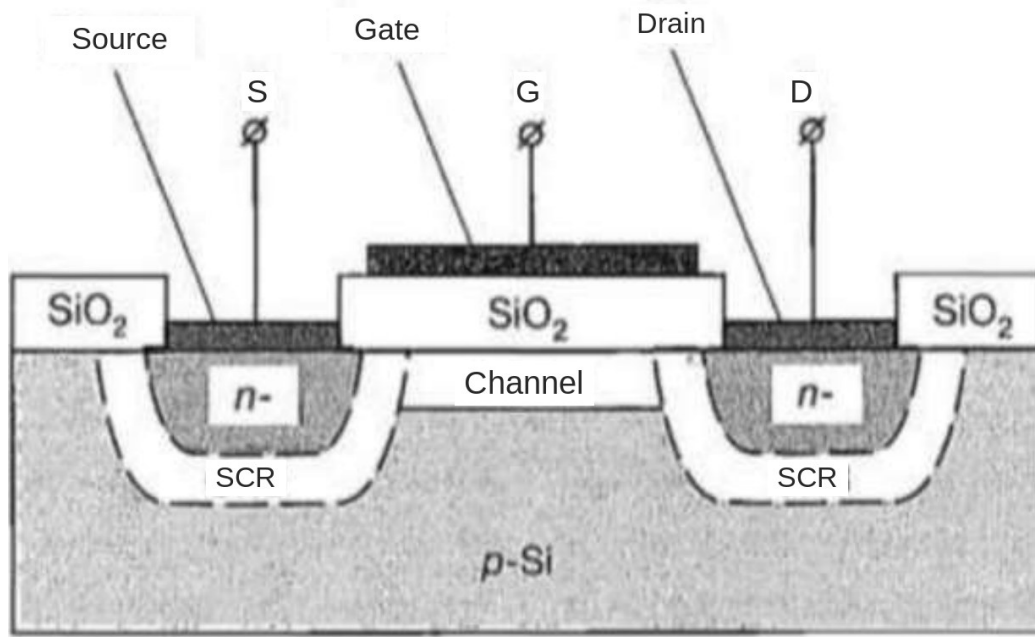


Figure 11. Schematic of a field-effect MOS transistor on the surface of a silicon wafer

Recently, a layer of heavily doped polysilicon has been created between the metal gate film and the silicon oxide. This makes it possible to reduce the transistor size and provides additional control of the gate properties.

Review Questions

1. Define the term "nanoelectronics" and name its varieties.
2. Describe Moore's law.
3. Name the fields of application of the technology for producing p-MOS and n-MOS transistors.
4. How are nanoelectronics and computer and information technology related?
5. Describe the main functions of information systems.
6. Name and describe the limitations on further reduction of the dimensions of elements in LSI circuits.
7. Define the term "nanolithography". What is its meaning and purpose?
8. Into what types is nanolithography divided? Name the advantages and drawbacks of each.
9. Define the term "nanoimprinting".

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Lecture 10. General Regularities of the Structure and Properties of Nanocrystalline Materials

Outline

1. Structural features and crystallography of nanoparticles.
2. Characteristics of surface structures.
3. Grains, layers, inclusions, clusters and pores.

1. Structural Features and Crystallography of Nanoparticles

The highly developed surface of isolated nanoparticles substantially affects their properties.

The non-additivity of thermodynamic functions associated with the contribution of interphase boundaries, which is taken into account by introducing the surface energy, leads to size-dependent thermodynamic effects. For nanoparticles, the dependence of surface tension on particle size must also be taken into account.

Surface energy, in particular, affects the thermodynamic conditions of phase transformations. Phases that do not exist in the given substance in the bulk state can arise in nanoparticles. As the particle size decreases, the contribution of the surface energy to the free energy increases.

The surface energy substantially exceeds the bulk energy. To reduce the total energy of the system, a deformation of the crystal that reduces the surface energy may prove more favourable. Such a reduction can be achieved by changing the crystal structure of the nanoparticle in comparison with a coarse-grained bulk specimen.

The surface energy is minimal for close-packed structures; therefore, the face-centred cubic (FCC) or hexagonal close-packed (HCP) structures are the most favourable for nanocrystalline particles, which has been confirmed experimentally.

Particular attention should be paid to the structure of **clusters**, i.e. particles containing fewer than $2 \cdot 10^3$ atoms (giant clusters may contain up to 20 thousand atoms).

A distinctive feature of clusters is the non-monotonic dependence of their properties on the number of atoms they contain. In nanocrystalline dispersed and bulk materials, there is no such dependence; instead, a dependence of the properties on the size of the particles (grains, crystallites) appears.

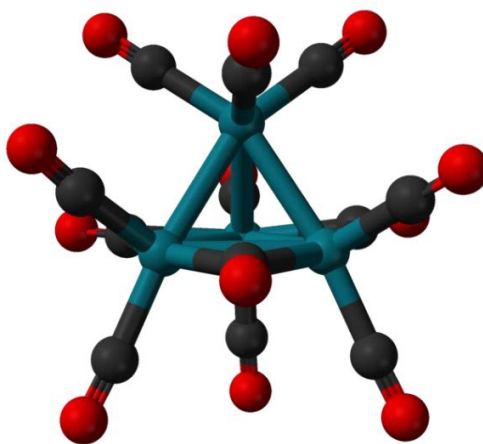


Figure 1. Cluster obtained from a platinum-group metal, $[Rh_{13}(CO)_{24}H_3]^{2-}$; single-crystal X-ray diffraction data were used for this area of cluster chemistry

A cluster is a group of a small (countable) and, generally, variable number of interacting atoms, ions or molecules. The minimum number of atoms in a cluster is two. The upper limit of a cluster corresponds to the number of atoms at which the addition of one more atom no longer changes its properties. Most chemical changes come to an end when the number of atoms in the group reaches 1–2 thousand.

Theoretical calculations have shown that, along with the FCC structure characteristic of a bulk crystal, clusters can have a crystallographic symmetry characterised by fivefold symmetry axes. Two main principles are taken into account when modelling the structure of clusters with a small number of atoms:

1. Clusters must be close-packed and built of the simplest stable atomic configurations; the relative fraction of tetrahedra among all the atomic configurations of the cluster should be as large as possible.
2. Clusters must be energetically stable. The tetrahedron, octahedron, cube, cuboctahedron, pentagonal pyramid and icosahedron are usually considered as the structural elements of clusters.

In general, an analysis of the results of various authors on the size dependence of the melting temperature of small particles shows that the melting temperatures of bulk crystals and of small particles larger than 10 nm hardly differ. A noticeable decrease in the melting temperature caused by the size effect is observed when the nanoparticle size becomes smaller than 10 nm.

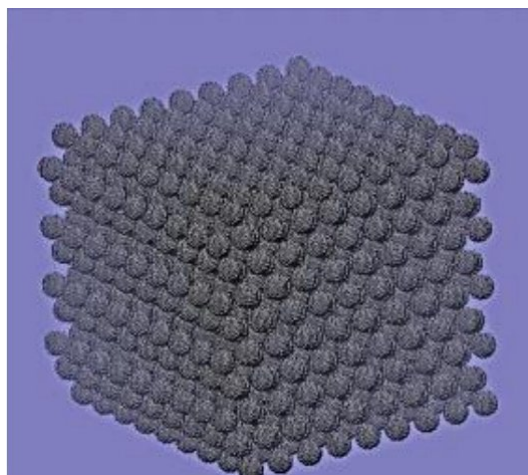


Figure 2. Clusters with a face-centred cubic crystal lattice arranged in a hexagonal lattice

The transition from bulk crystals to nanoparticles is accompanied by a change in interatomic distances and crystal lattice periods. The main question is whether the lattice periods decrease or increase as the particle size decreases, and at what nanoparticle size this change becomes appreciable.

One of the methods of determining the lattice parameters of nanoparticles is *electron diffraction*. An analysis of the systematic errors of this method has shown that only certain diffraction lines are suitable for accurate calculation of the lattice period of nanoparticles.

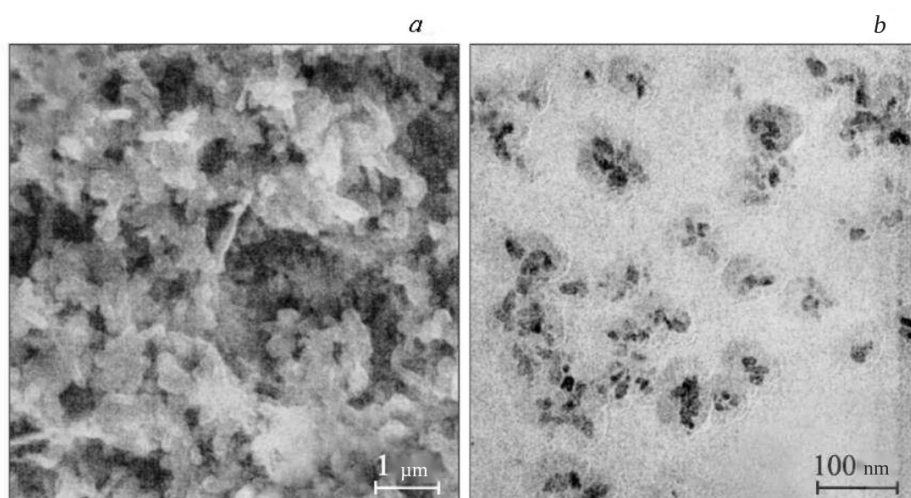


Figure 3. Images of ZnO particles obtained by scanning (a) and transmission (b) electron microscopy

The influence of nanoparticle size on the lattice parameter has been observed not only for metals but also for compounds.

The experimental results on the size effect of the nanoparticle lattice parameter are ambiguous, which may be related to the adsorption of impurities, the different chemical composition of the particles and structural transformations caused by the reduction in particle size.

According to the definition proposed by H. Gleiter, *nanostructured materials* are metastable systems in which the characteristic size of a structural element does not exceed 100 nm in at least one direction.

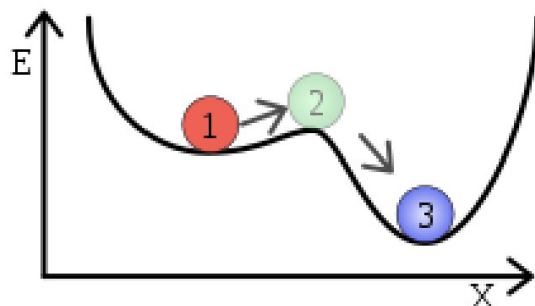


Figure 4. Illustration of metastability

The upper limit of the nanostructural scale is taken to be 100 nm, although most of the phenomena caused by the scale factor fall within the range of 1...50 nm. The lower limit is not strictly defined; however, there is a thermodynamic limiting size of an ensemble of atoms or molecules at which the ensemble is either a phase with an interface or a cluster without such a surface.

The concept of a structural element requires additional explanation. It is known that in the hierarchy of structural levels characterising the structure of a physicochemical system, the following can be distinguished:

- atomic–molecular (0.1...1 nm);
- supramolecular and cluster (0.5...5 nm);
- microscopic, or grain–heterophase (5 nm...100 μm);
- macroscopic (> 100 μm).

According to this classification, nanostructured systems can be assigned to the second and third levels, the cluster and grain–heterophase levels. Thus, the structural elements are considered to be clusters, particles, grains, phase inclusions or interlayers, between which there are structural objects that fall under the thermodynamic definition of a phase.

Among nanostructured systems, there are systems with a cluster structure, for example crystallised amorphous alloys. Cluster nanomaterials are a separate type of consolidated materials, and molecular clusters become structural elements of nanocomposites.

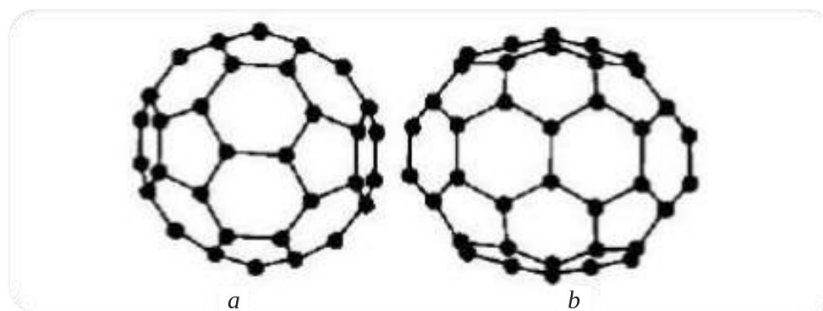


Figure 5. Structure of fullerenes (molecular carbon clusters): a – C_{60} ; b – C_{70}

2. Characteristics of Surface Structures

The definition of nanostructured materials implies the existence of four categories of objects according to their dimensionality:

- zero-dimensional: nanoclusters, nanoparticles, quantum dots;
- one-dimensional: nanotubes, nanowires, fibres;
- two-dimensional: thin and nano-multilayer films;
- three-dimensional: nanopolycrystals.

H. Gleiter proposed classifying consolidated nanostructured objects according to the shape of the structural elements, their arrangement in space and their chemical composition.

The **first group** comprises isolated or weakly bonded small particles, thin fibres or thin films. The structural elements in such systems are nanosized in three, two or one dimension, respectively. According to topological features, the first group of nanostructured systems can be divided into *granular systems*, *fibrous systems* and *film or layered systems*.

The **second group** comprises surface layers that are nanostructured in thickness and are not separated from the bulk substrate or differ from it in chemical composition and structure. These layers may themselves be nanostructured, i.e. consist of nanosized grains. Within a layer, the structure may be homogeneous, heterophase, periodically layered or graded.

The **third group** comprises bulk nanostructured bodies, which may be single-phase (microhomogeneous) or heterophase (microheterogeneous) but macroscopically homogeneous. Such materials are predominantly nanocrystalline, i.e. their structural elements have a crystalline structure and characteristic nanodimensions, and the grain boundaries are high-angle boundaries.

H. Gleiter proposed combining systems that differ in structural complexity and chemical composition into four groups:

1. The grains and interfaces have the same chemical composition; these are single-phase nanostructured polycrystals, semicrystalline polymers separated by non-crystalline interlayers of the same composition, and thin crystalline films separated by amorphous layers.
2. A more complex structure than in the first case arises if the chemical composition of the phases differs and the system is multiphase; such nanocomposite systems can be formed naturally or artificially, for example by mixing highly dispersed constituents.
3. The number of possible combinations in the structure of a nanosystem increases if both the grains (fibres, layers) and the grain (interphase) boundaries differ in chemical composition, as, for example, in nanostructured ceramics in which a new phase precipitates at the grain boundaries.

4. The fourth group comprises combined nanocomposites, the distinctive feature of which is a matrix with nanostructured elements embedded in it; in this case the inclusions and the matrix have different chemical compositions. Examples of materials of this group are dispersion-strengthened alloys, ceramics and polymers.

All types of nanostructured systems may differ in the mutual arrangement of their structural elements in space; accordingly, they can be divided into:

- *regular* systems, which have symmetry elements, including translational symmetry; special regular structures are created by interweaving fibres;
- *stochastic* (random) systems; stochastic spatial fibrous structures can be formed from both discrete and continuous fibres.

Nanostructured surface layers are divided into *single-layer* and *multilayer* ones. They can be classed as nanosized according to two features: their thickness and their average grain size.

Within each layer, the structure may be *homogeneous* or *heterogeneous*. An important heterogeneous structure is the *graded* (gradient) structure, characterised by a continuous, predominantly monotonic, dependence of the chemical composition and structural parameters on thickness. Such structures have a pronounced anisotropy of properties.



Figure 6. Graded structure of tungsten carbide

The layers themselves can be either *continuous* or *island-like*. There are two types of discontinuity. One of them is porosity, and the pores must be nanosized; such a structure is characteristic of relatively *thick layers*. Conversely, *ultrathin layers* and *films* are characterised by in-plane discontinuity, when the entire coating area is divided into separate segments of the same or different chemical composition. Such a structure of a surface layer or thin film is called *island-like*, since it consists of islands separated by wide grooves.

Table 1. Main types of surface nanostructures on substrates

Number of layers on the substrate	Continuity	Homogeneity, interfaces, gradient
One	Continuous, porous, island-like	Discretely homogeneous Graded Incoherent Coherent (epitaxial)
Many	Continuous	Discretely homogeneous

Number of layers on the substrate	Continuity	Homogeneity, interfaces, gradient
		Discretely graded Incoherent
	Porous	Coherent non-periodic Coherent periodic

3. Grains, Layers, Inclusions, Clusters and Pores

The structural elements of nanomaterials are considered to be clusters, particles, grains, inclusions or interlayers, between which, as a rule, there are incoherent interfaces.

Nanodispersed systems are characterised by a number of size-related features:

- the main one is that nanomaterials contain an anomalously large number of solid–solid interfaces between the nanosized structural elements;
- the structural elements listed are bounded by solid–gas or solid–liquid interfaces.

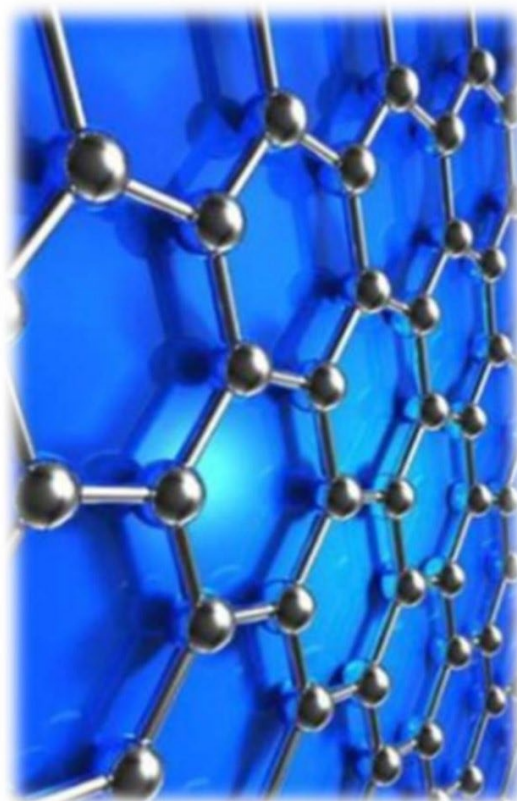
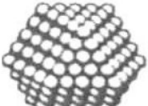


Figure 7. Model of a carbon nanostructure (graphene-like atomic network)

The simplest structural elements are clusters or domains in which a considerable fraction of the atoms is located at the surface. A close-packed hexagonal or cubic cluster can be regarded as a central atom surrounded by a first shell of 12 atoms, then a second shell of 42 atoms, a third shell of 92 atoms, etc. The properties of the geometric packing of clusters are given in Table 2.

Table 2. Properties of the geometric packing of clusters

Number of atomic shells	Total number of atoms	Atoms on the surface, %	Cluster appearance
One	13	92	
Two	55	76	
Four	309	52	
Seven	1415	35	

Clusters form nanoparticles which, in turn, become the grains of nanostructured materials through coalescence. In this connection, control of the size, shape and structure of nanoparticles is technologically important because of the strong correlation between these parameters and the optical, electrical and catalytic properties.

Nanoparticles usually contain twins, since clusters nucleate and grow as twinned particles. A twin is the result of the formation of a common plane between two clusters.

Thermodynamically, a nanodispersed particle is a non-equilibrium system with excess free energy. It is customary to distinguish three types of non-equilibrium: *morphological*, *structural* and *compositional*. The highly developed surface determines the morphological instability of nanoparticles.

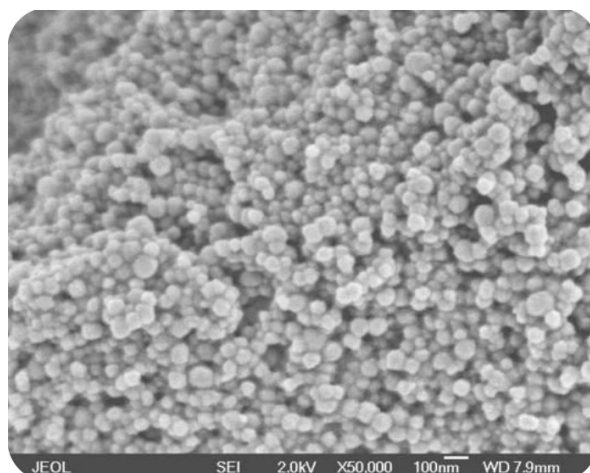


Figure 8. Silver nanoparticles

Inhomogeneity of the phase or chemical composition of nanoparticles is the cause of their compositional metastability.

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Lecture 11. Nanomaterials for Devices, Machines and Apparatus

Outline

1. Sensors.
2. Actuators, manipulators and motors.
3. Integrated systems.
4. Nanomaterials in the aerospace industry.

1. Sensors

Modern microelectronics and personal computers have transformed the information and production spheres and then, to a considerable extent, everyday human life.

To create an interface, i.e. channels and means of interaction between the surrounding environment and an electronic device, a set of engineering tools equipped with sensors is required; in the broadest sense, sensors are devices that perceive information about the state of the environment. The more flexible and intelligent the production, transport or household systems we intend to create, the greater the number of parameters that must be taken into account, and with a higher speed.

Sensors are primary transducers that convert a signal (energy) of one physical nature into a signal of another nature. They include:

- *electronic* sensors, which convert external influences and stimuli of thermal, optical, chemical, mechanical or magnetic nature into an electrical signal (Figure 1);
- *deformable* devices, which, as a rule, can also operate in the reverse mode, i.e. convert an electrical signal into mechanical motion.

Formally, sensors can be subdivided according to their main design feature into: deformable and non-deformable membrane sensors; and string and cantilever-beam sensors.

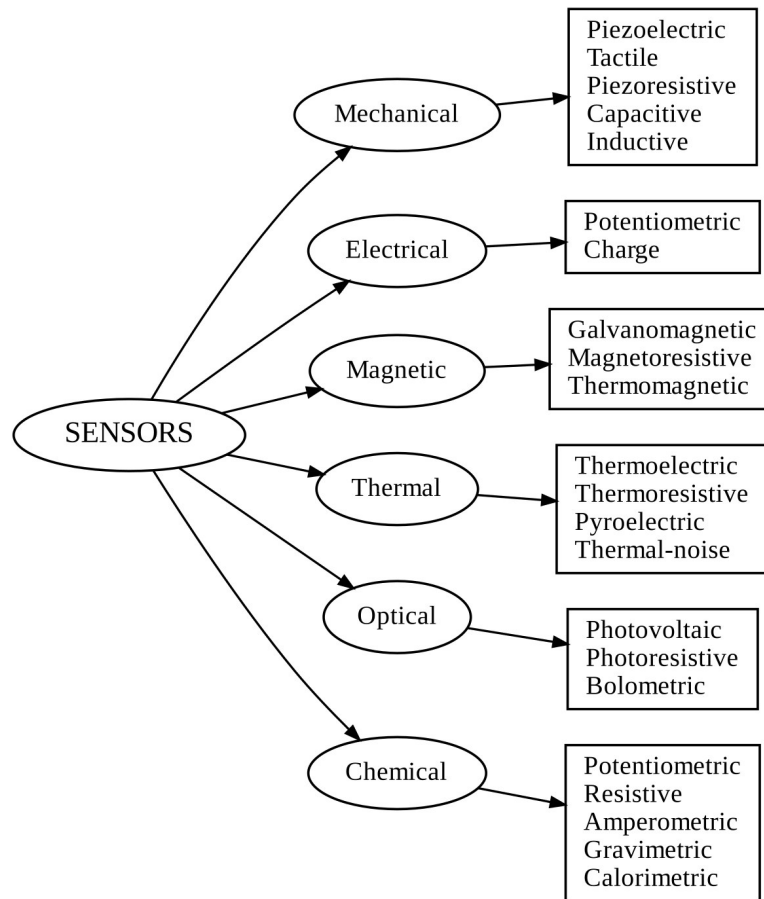


Figure 1. Basic types of electronic sensors

Sensors are subject to various and often *mutually exclusive requirements*; therefore, it is impossible to satisfy all of them simultaneously in a single design. As in any engineering activity, the task can be solved on the basis of compromises. The requirements usually imposed on these transducers are listed below:

- high sensitivity;
- a wide dynamic range of input quantities;
- a simple (preferably linear) functional relationship between the input and output signals;
- absence of hysteresis (differences in the output response for increasing and decreasing input signals of the same magnitude);
- absence of drift and ageing;
- small dimensions and mass;
- high speed of response;
- high reliability and long service life;
- ease of manufacture;
- low cost.

All the sensors shown in Figure 2 are manufactured by a single technology that includes chemical etching, surface oxidation, sputtering of metal contacts and diffusion bonding of the parts into a single whole.

The upper one (Figure 2, *a*) is a **piezoresistive pressure sensor**. Its principle of operation is based on the change in the resistance of a silicon diaphragm as a result of its deformation. Doped silicon is used to increase the conductivity and the piezoresistive effect.

Sensors of this type can have dimensions of several tens of micrometres and can measure pressure in the range from 0.1 to 10^8 Pa. Their weak points are temperature sensitivity and continuous energy consumption.

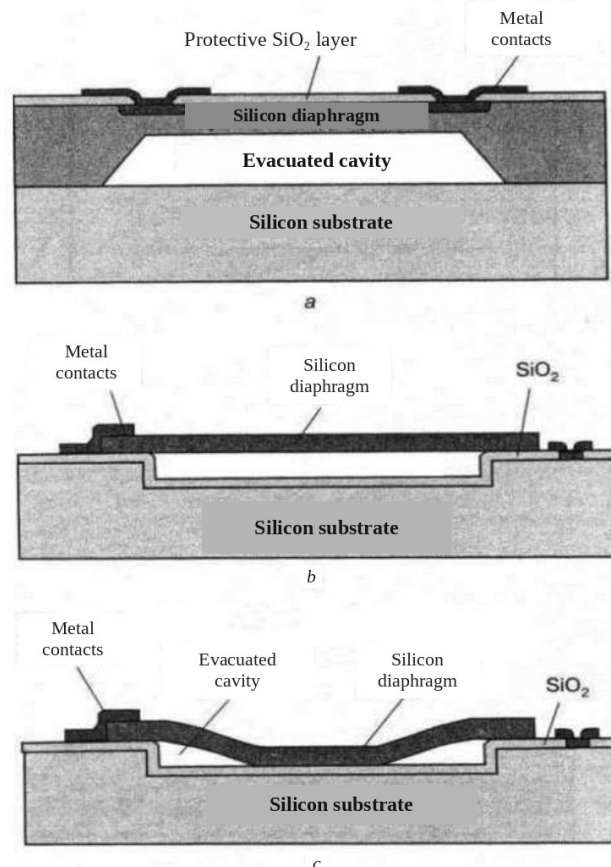


Figure 2. Three types of diaphragm sensors: piezoresistive (*a*) and capacitive (*b*) sensors for pressure measurement; capacitive sensor for touch registration (*c*)

The **capacitive pressure sensor** shown schematically in Figure 2, *b* is largely free of these drawbacks.

- Instead of resistance, it measures the capacitance between the diaphragm and the base, which depends on the deflection of the elastic element.
- The more rigid design makes it more resistant to mechanical damage.
- A modification of this design, in which the centre of the diaphragm is brought into contact with the base (Figure 2, *c*), converts it into a sensor that registers touch from the change in capacitance.
- It is worth noting that pressure sensors of all kinds form the largest market segment of micromechanical devices.

The external appearance of pressure sensors is shown in Figure 3, which presents, as an example, a fragment of a matrix of capacitive sensors used to determine the instantaneous local pressure in liquid or gas flows with a spatial resolution of 20 μm .



Figure 3. Matrix of membrane pressure microsensors

Among membrane sensors, a special group of **tactile** sensors can be distinguished, i.e. sensors that feel a touch to their surface. They can be divided into two classes.

First-class sensors react to the very fact of contact and produce a signal in a binary "yes–no" code. They are used in various keyboards, object counters, control systems of technological processes and household appliances.

Second-class sensors are more complex: they make it possible to obtain additional information about the force acting on the pad, the location of its application in one- or two-dimensional space, and the geometric and physical characteristics of the object.

The force must be known and taken into account in various manipulators and robots in order to provide feedback between the object being manipulated and the actuating devices, which ensures a reliable but non-damaging grip.

The possibility of determining the coordinates of the contact spot is useful in creating *touch screens*: they are more convenient than ordinary monitors for human–computer interaction and do not require a separate remote device (a mouse).

More complex sensors make it possible to determine a number of characteristics of living organisms on contact with them.

- Devices for reading the pattern of papillary lines on the fingertips have become widespread (for personal identification in criminology, as a key or password for access, for the prevention of terrorist acts, etc.).
- The role of the simplest sensor can be performed by a contact pad or an electrode covered with a thin insulating layer, a touch to which changes the resistance, capacitance or leakage current of the circuit.

Sensors that are triggered by closing the circuit between the membrane and the base when a given force is reached are not much more complex; the potential is then taken from one or another part of a voltage divider (Figure 4).

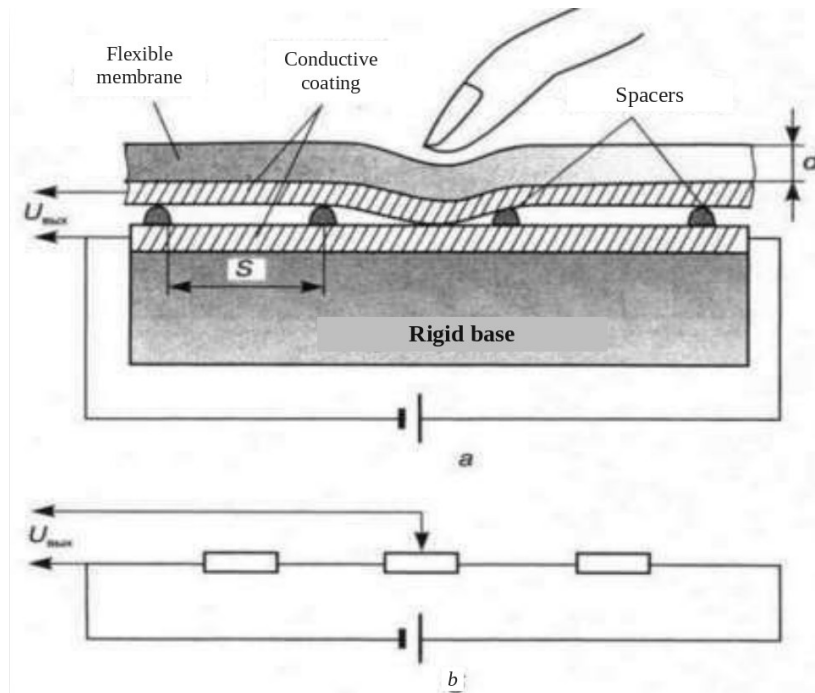


Figure 4. Simplified schematic of the operation of a resistive tactile sensor (a) and its equivalent electrical circuit (b)

In engineering, it is often necessary to determine the parameters of the mechanical dynamics of an object: displacements, velocities and accelerations. Among the whole variety of principles and systems, **inertial sensors** should be singled out; their mass production by nanotechnology methods was mastered several years ago. They are widely used for deploying airbags in cars, in security systems, gyroscopes, etc.

Principle of operation:

- a body of known mass is suspended on flat springs, and the gap between the surface of this body and a cover plate, which together form a capacitive sensor, is measured;
- motion with acceleration causes deformation of the springs and a change in capacitance, which is registered by the corresponding electronic circuit;
- knowing the acceleration, one can obtain the change in the velocity of the object after a single integration, and the change in its position in space after a second integration.

Two designs of such sensors for measuring different components of acceleration are shown in Figure 5.

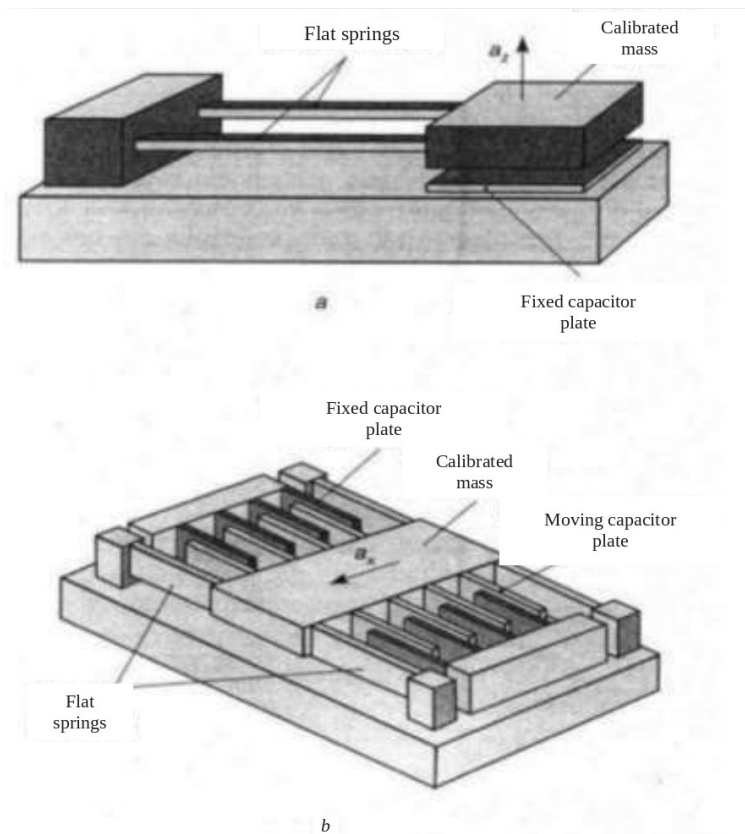


Figure 5. Schematics of inertial sensors for measuring the vertical (a) and horizontal (b) components of acceleration, a_z and a_x , respectively

Many tasks require contactless determination of the distance to bodies, their size and shape, velocity of motion, etc. A significant part of them can be solved by *machine vision* methods, which use appropriate optics, a high-resolution photosensitive matrix and an image analysis system comprising a computer and specialised software packages.

Optical systems for three-dimensional capture and image analysis can be divided into five types: triangulation; interferometric; tomographic; time-of-flight; and those based on analysis of the shadow shapes of an object.

Modern photosensitive matrices (Figure 6) contain several million pixels, and their sizes (in the image plane) are of the order of a few micrometres.

- Processing and amplification of the signal of each photodetector require primary electronics consisting of no fewer than several dozen elements.
- High noise immunity (signal-to-noise ratio) can be achieved only if all the electronic components are located directly under the photosensitive element.
- *Thin-film structures*, formed by the same methods as large-scale integrated circuits for microprocessors and dynamic memory in computers, are the most attractive for this purpose.
- The photosensitive elements in them are p–n photodiodes with different spectral sensitivities, obtained by ion implantation on the same silicon chip as the service electronic circuit.

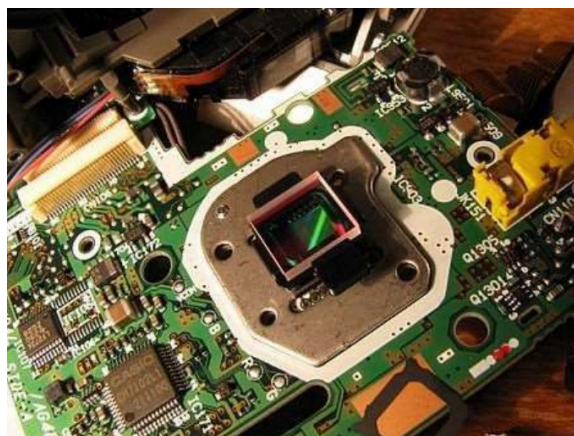


Figure 6. Matrix on the printed circuit board of a digital camera

There are also *pyroelectric matrices*, which operate in the infrared range and are capable of registering the actual thermal radiation of an object with a resolution of ~ 0.1 K. Cameras with such matrices make it possible to:

- detect heat leaks in houses and buildings;
- find overheated elements in electronic devices;
- diagnose certain human diseases;
- they are also used in night-vision devices, sights and security systems.

A beam, a single-crystal whisker, a nanowire, a nanotube or similar structures (Figure 7) supported at both ends can form the structural basis of various sensors.

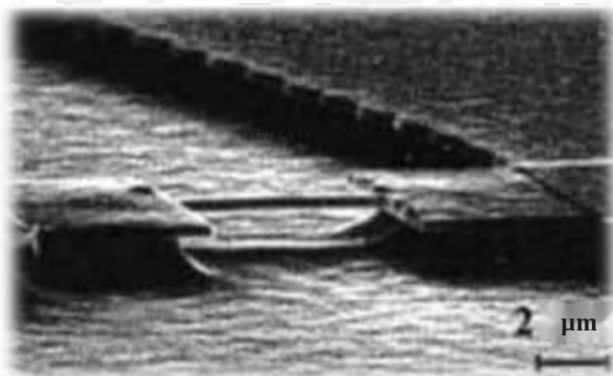


Figure 7. String nanosensor

The principle of operation of **string (nanowire) sensors** is based on the change in the natural frequency of vibration, the electrical conductivity and the electric potential on interaction with the substance being tested. For example, sensors based on single-walled carbon nanotubes sensitive to nitrogen dioxide and ammonia molecules have been created.

When functionalised with bioactive substances (for example, an enzyme), *nanosstring sensors* become highly selective sensors that react to only one of the substances present in the environment.

String nanosensors sensitive to changes in the acidity of a solution in the pH range from 2 to 9 have been created, which make it possible to construct microscopic pH

meters. Ensembles of strings with different resonant frequencies and different functionalisation can be fabricated; they make it possible to create microanalysers that recognise several substances and determine their concentrations in parallel.

A structural element in the form of a beam clamped at one end, the *cantilever*, is widely used in atomic force microscopes for measuring small forces (Figure 8).



Figure 8. Atomic force microscope

One of the first *gas sensors* based on a cantilever, created in the mid-1990s, was designed to register *mercury vapour*. A silicon microbeam coated with gold on one side bent and changed its natural frequency in the presence of mercury vapour owing to the adsorption of mercury.

Despite its high chemical inertness, gold can nevertheless enter into active interaction with certain organic molecules, in particular *mercaptans* (thiols). Mercaptans contain one or more thiol groups ($-SH$), which are capable of forming strong covalent bonds with gold. Besides mercury, such sensors detect the presence of thioethanol molecules, hydrogen and other substances in a gas.

However, the *selectivity* provided by inorganic coatings (other metals are used besides gold) is not very high, and the range of substances that such sensors can detect is narrow.

Increasingly, cantilevers are therefore functionalised with *organic molecules*. To determine air humidity, the cantilever is coated with a layer of gelatine, which readily adsorbs water molecules; a polymethyl methacrylate (PMMA) coating provides sensitivity to alcohols.

The next logical step in the development of cantilever sensors is the creation of *arrays* consisting of sets of cantilevers with different coatings (besides PMMA, polystyrene, polyurethane and various copolymers are used). This makes it possible to analyse gas mixtures and determine the presence of volatile organic components, humidity and other parameters, which brings us closer to the creation of universal gas analysers, known in the literature as the *artificial* or *electronic nose*.

- Coating the two sides of a cantilever with different materials provides high sensitivity to changes in thermal energy.

- Specially prepared arrays can detect heavy-metal ions in liquids (for example, in drinking water, waste water, etc.) at concentrations starting from 10^{-11} (for mercury) and serve to determine pH, etc.

Functionalisation of a cantilever with biologically active molecules transforms it into a highly sensitive selective sensor that can be used in biomedical research, diagnostics and DNA analysis.

- Differential methods of registering the mechanical response (one cantilever is functionalised, while the other serves to compensate for temperature drift, vibrations, etc.) make it possible to detect single mismatches in DNA base pairs.
- Another method of recognising biomolecules is *mechanical spectroscopy of single molecules*, which are "stitched" at one end to the substrate and selectively captured by the tip of a functionalised probe under an oscillating or monotonically increasing force; the features of the mechanical behaviour of the molecule make it possible to analyse its composition and structure.

Potentiometric and amperometric probes, which are immersed in a medium and register the potentials and currents arising in it, can conventionally also be classed as cantilever-type sensors.

2. Actuators, Manipulators and Motors

Actuators and **motors** are understood as mechanisms that convert various kinds of energy into mechanical work (motion).

- They can be created from inorganic materials using "silicon" nanotechnology, which is applied in the production of large-scale integrated circuits.
- An alternative approach is to use organic molecules, which make it possible to construct and drive devices of monomolecular size.

Piezoelectric actuators are widely used:

- in the designs of scanning probe microscopes;
- in precision positioning stages (for example, for aligning masks/stencils over a silicon wafer during nanolithographic transfer of the image of electrical circuits onto the resist surface in integrated-circuit production);
- in active vibration-isolation devices, etc.

Their *advantages* are mechanical strength and reliability, simplicity and ease of control. Their *drawbacks* are that without additional mechanisms they cannot provide large displacements, and they are not completely linear and are unstable over time. Devices with *electrostatic drive* serve as an alternative or supplement to them.

Figure 9, *a* and *b*, shows two schemes of electrostatic actuators with one translational degree of freedom. The first scheme provides high linearity at small displacements; the second, conversely, gives large displacements with low linearity.

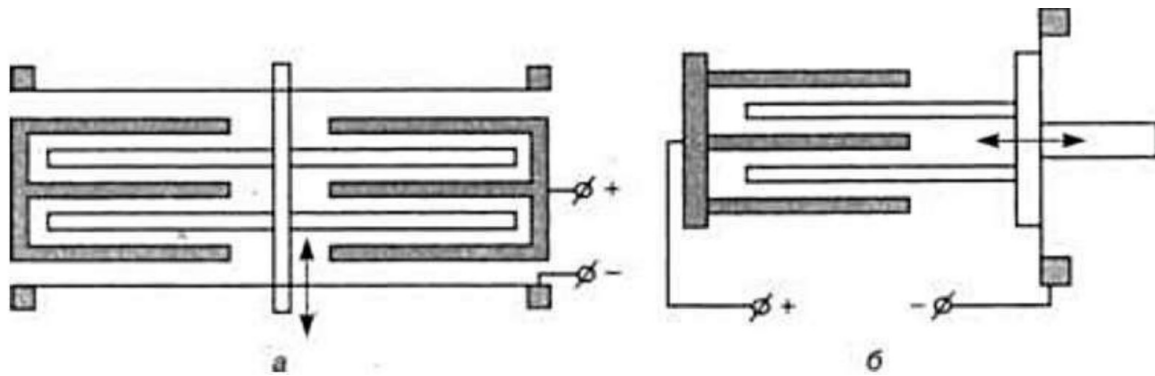


Figure 9. Schematic diagrams of electrostatic actuators with one translational degree of freedom

The scheme of an electrostatic actuator with two rotational degrees of freedom is shown in Figure 10. Principle of operation:

- applying a potential difference between electrodes 1, 2, 3, 4 and the movable disc 5 leads to a controlled rotation of the movable part on the torsion suspensions 6 and to a change in the orientation of platform 5 in space;
- actuators similar to the one shown in Figure 10 are widely used to control micromirrors, probes, tunable capacitors, resonators, etc.

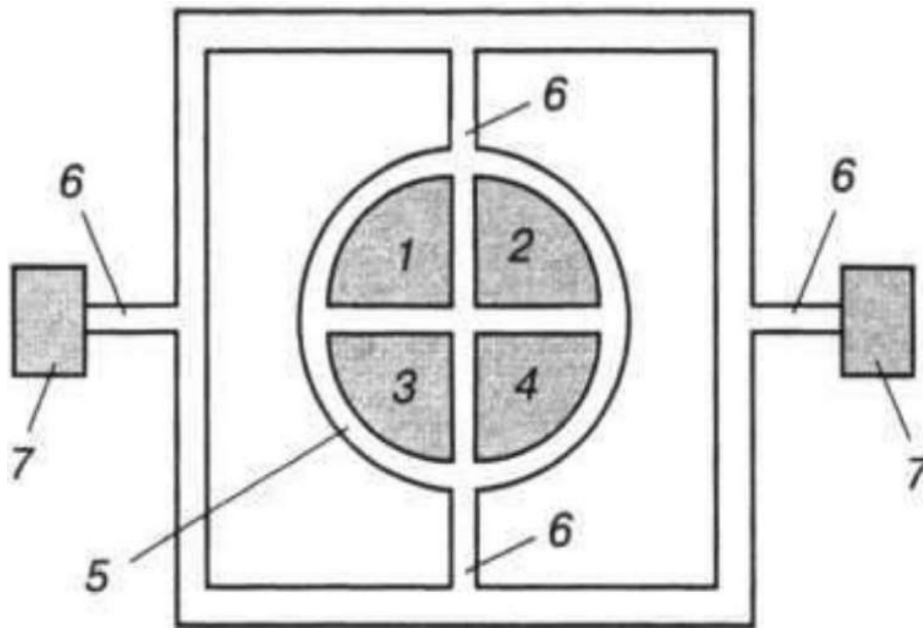


Figure 10. Schematic diagram of an electrostatic actuator with two rotational degrees of freedom

For convenience of consideration, molecular devices are usually divided into two large groups.

Electronic devices, whose main point of interest is charge transfer under the action of various factors: illumination, radiation, electric fields, heat flow, chemical reactions, etc.; and *machines*, whose ultimate purpose is *mechanical motion*.

Biomimetics is the imitation of nature in the creation of new technology. The corresponding branches of electronics and mechanics are called *bionics*.

The basis of the functioning of any machine is the type of energy used, the ways of converting it into mechanical motion and of interacting with the environment, design features and control methods.

Molecular machines:

- the main type of energy that drives molecular motors is *chemical* energy;
- it is usually stored in adenosine triphosphate (ATP) molecules and released as a result of their hydrolysis with the formation of adenosine diphosphate (ADP) and inorganic phosphate;
- the second most important energy source is *sunlight*, whose energy enables photosynthesis in green plants and is partly accumulated in ATP molecules.

The direct conversion of light energy into mechanical motion can, in principle, occur without the formation of any chemical waste, which favourably distinguishes such machines from those running on the chemical energy of ATP.

Photochemical reactions have other advantages over purely chemical ones:

- simplicity of controlling the machine, since light can be switched on and off quickly;
- a laser can be a convenient energy source, since its light beam can be concentrated in a small space for a short time;
- photons can not only supply energy for the motion of a machine but also identify its state, which is also useful for control.

Electrical (electrochemical) methods of driving artificial biomachines also have a right to exist if they are carried out in the liquid phase.

Like macromachines, molecular devices can perform all types of motion required in nanotechnology: translational and rotational motion, contraction and elongation (artificial muscle), and gripping and moving objects.

Molecular tweezers. Capturing (especially selectively) individual atoms and molecules from mixtures and transferring them to a specified place is one of the most demanded operations in nanotechnology. Molecular tweezers were among the first examples of nanodevices consisting of a single molecule; publications about them appeared as early as the beginning of the 1980s.

The principle of operation consists in a change in the conformation of organic molecules under the action of light quanta of appropriate energy. Figure 11 shows one of the first proposed molecular tweezers based on azobenzene molecules.

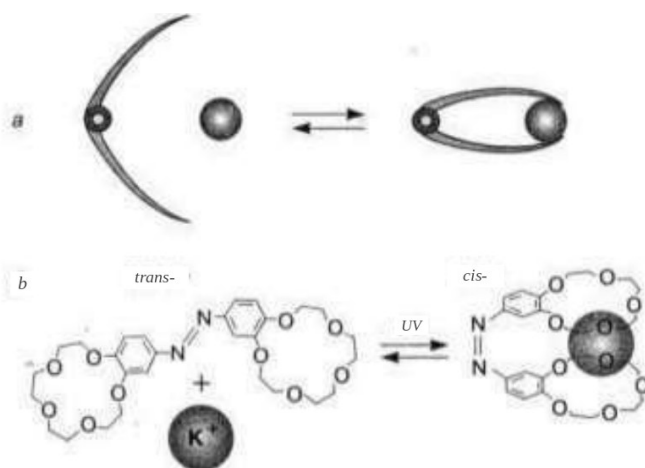


Figure 11. Molecular tweezers based on the photosensitive azobenzene molecule: *a* – principle of operation; *b* – scheme of capture of a potassium ion when UV light is switched on

In **laser tweezers**, a laser beam focused to a point attracts molecules from solution owing to the difference in the dielectric properties of water and individual molecular groups. By controlling the light beam, single macromolecules can be captured and moved to the desired place.

Another common method is the *stretching of long macromolecules in an electric field*:

- one end of the molecule is usually fixed on a stationary substrate or on balls of submicron size;
- in DNA analysis, the molecule is unfolded and stretched along a capillary: the microspheres to which it is fixed at one end are captured by laser tweezers and passed into a capillary liquid flow, which straightens the macromolecule.

The molecule can then be purposefully cut into the required fragments with another laser (usually an ultraviolet one) or with the needle of an atomic force microscope functionalised with an appropriate enzyme.

Another principle of operation is used in *optical tweezers–manipulators*, in which light causes intramolecular charge transfer, as a result of which one end of the molecule becomes charged opposite to the other. Owing to the Coulomb forces of attraction, these ends are attracted to each other and can capture various particles.

- In a number of cases, the photoinduced capture of an ion, atom or molecule can bring about serious structural changes in the "tweezers" themselves, which may also find useful application, in particular for functionalising the manipulator.
- Molecular machines similar to optical tweezers can also be organised on DNA molecules, as has been demonstrated in a number of recent works.

In the last few years, many compounds suitable for the role of atomic manipulators have been found or synthesised, so that researchers and engineers can choose the optimal combination of their characteristics for the task at hand. Besides atomic–molecular manipulation and design, these molecules can be used in selective sensors and in other nanoscale electronics.

Rotaxanes and catenanes. Complex molecular devices can be built on the basis of these two types of supramolecular structures.

- The shape of a rotaxane molecule resembles a dumb-bell with a ring encircling its thin part (Figure 12, *a*).
- Catenanes are supramolecular structures consisting of two or more closed rings linked to each other like the links of a chain (Figure 12, *b* and *c*). As in rotaxanes, these links are not bonded to each other covalently but are held together only mechanically, which allows them to rotate and move relative to each other in different planes.

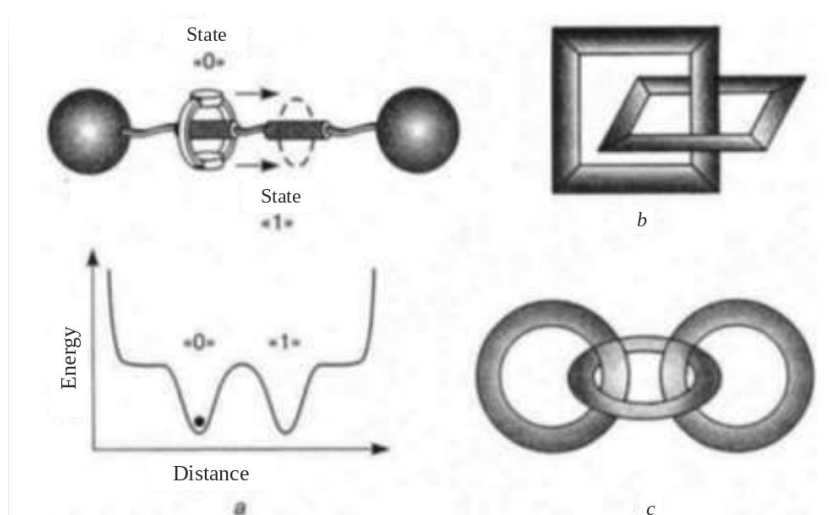


Figure 12. Schematic of the structure of a rotaxane molecule and its double-well potential profile (*a*); one of the stable states can be assigned the logical value "0" and the other the logical value "1". Topological schemes of catenanes with two (*b*) and three (*c*) rings

Rotational motion. Examples of such motion at the molecular level in nature are the motion of side groups in linear polymers, of individual units of an organic molecule, and of whole molecules and their ensembles in the drive of bacterial flagella, etc. The energy source for these motions is usually ATP.

For technical applications this is not very convenient; therefore, let us consider other possibilities that make it easy to control the speed of rotation of one part of a complex relative to another.

- The biporphyrin metal complex in Figure 13 has two quasi-planar "decks" capable of rotating about the central axis of symmetry.
- Its rotation can be accelerated by means of a redox process in a solution of anthracene nitrate in dioxane. At 20 °C, the range of regulation of the angular velocity of rotation of one deck relative to the other is 1:300.

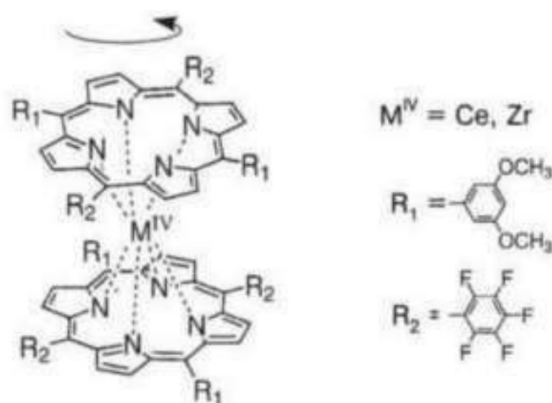


Figure 13. Biporphyrin metal complex that implements regulated reversible motion of one part relative to the other

Photochemical and electrochemical control of molecular motors is more convenient. Figure 14 shows the structural diagram of a molecular motor with distinct upper and lower parts connected by a double bond, whose photoisomerisation (cis–trans transition) *substantially changes the rotation speed*.

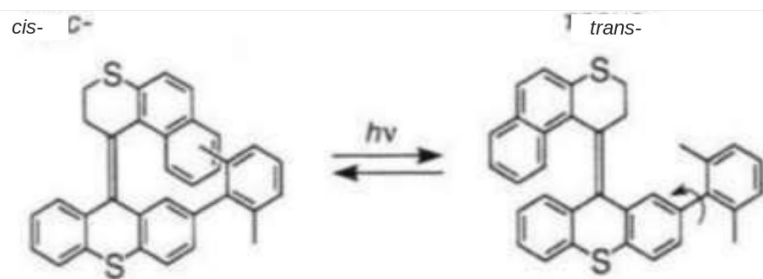


Figure 14. Molecular motor whose rotation speed is controlled by light

- In a number of structures, photoisomerisation leads to a *complete stop of rotation*, and they can be regarded as molecular brakes that serve to stop the motor.
- One may expect that applying an alternating electric field will lead to pulsation or rotation of one part of the system relative to another (when appropriate conditions are created).

Supramolecular structures adapted to operation in an alternating field have also been synthesised; they implement the direct conversion of electric current into rotational motion.

Reciprocating motion is widespread both in biological objects and in engineering. In nanotechnology, *rotaxane* and *pseudorotaxane* structures can be used to organise reciprocating motion. For example, an artificial muscle can be constructed from several links connected in parallel, as shown in Figure 15.

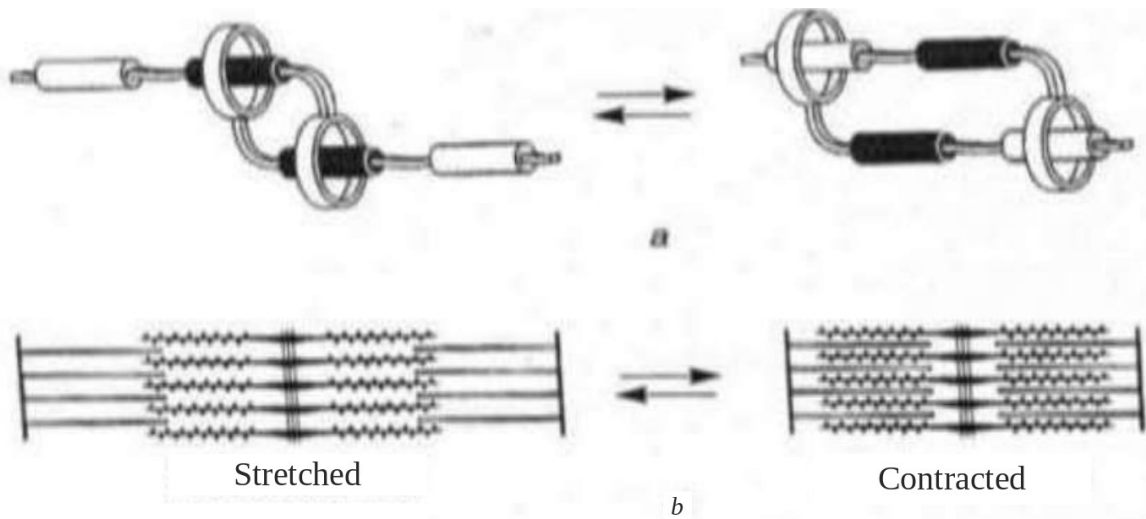


Figure 15. Scheme of a synthetic analogue (a) of a real muscle (b) in the stretched and contracted states

3. Integrated Systems

The planar methods and other types of nanotechnology developed make it possible to create systems integrated on a single chip within one production and technological concept and even one set of well-known operations.

- A large part of them are **microelectromechanical systems (MEMS)**, which contain moving mechanical parts and electronic components.
- Together with electronics, which is moving into the nanoscale region, mechanical components are also decreasing in size and acquiring nanometre dimensions. Such systems are called **nanoelectromechanical systems (NEMS)**.
- There is currently no clear boundary between MEMS and NEMS (as, indeed, between micro- and nanoelectronics).

MEMS/NEMS are becoming widespread and play a key role:

- in telecommunication systems and information technologies;
- in automated production;
- in ground and aerospace vehicles;
- in health care and environmental monitoring;
- in defence and reconnaissance systems.

Their functionality is continuously increasing, while their dimensions, mass and cost are decreasing.

Two types of inertial devices have been mastered in mass MEMS technology: *acceleration sensors* (accelerometers) and *gyroscopes*.

Inertial acceleration sensors are used:

- in the safety systems of modern cars (for generating and issuing commands to the airbag activators in accidents);
- in active vibration-isolating suspensions;

- in biomedical means of monitoring human motor activity and in a number of consumer goods.

Such sensors are easily manufactured by the microtechnology methods described above and are integrated with electronics; their dimensions do not exceed several hundred micrometres in length and width and a few micrometres in thickness. Along with the reduction in size, their price has fallen until it stopped at a few dollars per device, mounted in a hermetic package the size of a small pea.

Microgyroscopes are more complex devices that serve to register the rotation of an object about one, two or three spatial axes. They are used in aviation, astronautics, shipbuilding and military rocket technology for course stabilisation, navigation, motion control, etc.

Gyroscopes with one degree of freedom usually use electrostatic vibromechanical actuators to make an element oscillate at its resonant frequency (Figure 16). The sensors respond to the transfer of energy between two vibration modes under the action of the Coriolis acceleration if the object begins to rotate about the z axis. A real gyroscope sensor occupies an area of $1 \times 1 \text{ mm}^2$ and is about $2 \text{ }\mu\text{m}$ thick, and the whole chip with the service electronics has a size of $4 \times 4 \text{ mm}$.

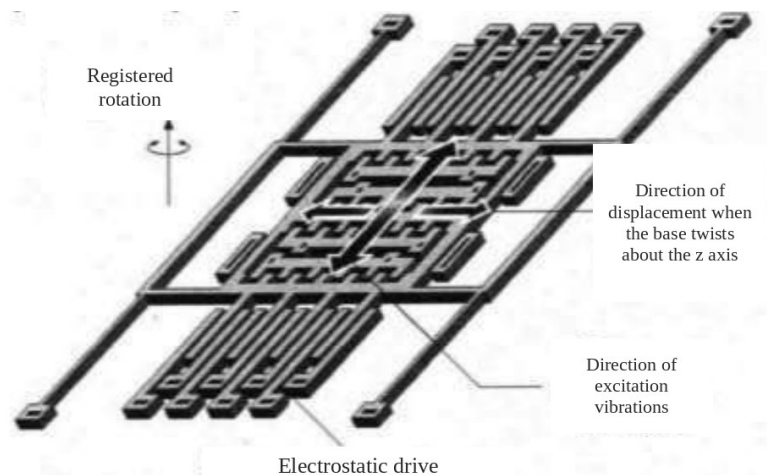


Figure 16. Schematic of a single-axis vibration gyroscope

The ever-increasing information flows and the need to transmit them at high speed have stimulated the development of fibre-optic technology. Traditionally, switching operations in optoelectronics were carried out by converting the optical signal into an electrical one, then switching, again converting the electrical signal into light and transmitting it further.

MEMS technologies offer simpler routing devices that consume practically no energy in static mode and introduce no delays into the communication channels (Figure 17).

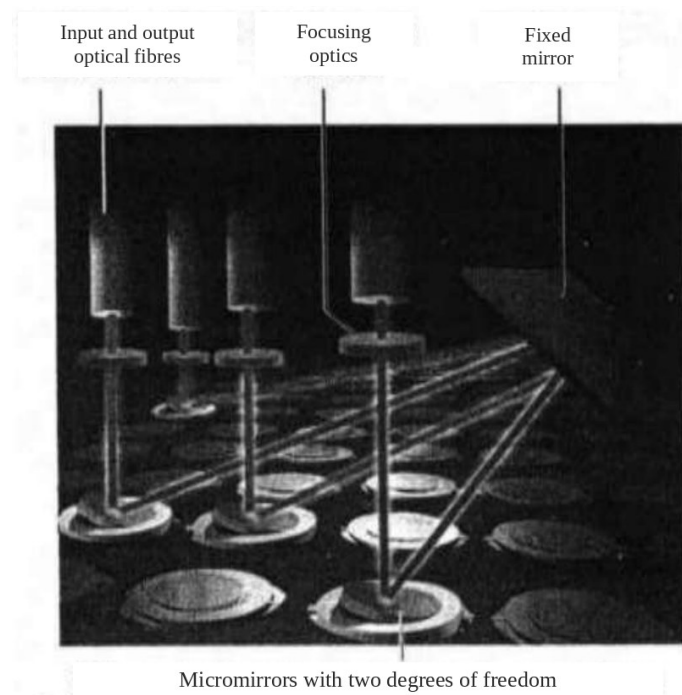


Figure 17. *Schematic of a three-dimensional router of light fluxes for fibre-optic communication channels*

The micromirrors of such light switches are mounted on torsion suspensions with one or two degrees of freedom (Figure 18), which makes it possible to control them in order to disconnect or redirect each channel separately.

In traditional *high-frequency and microwave radio engineering*, on which mobile communication, television signal transmission and satellite communication and navigation systems are now based, there are many tasks that can potentially be solved successfully with MEMS/NEMS.

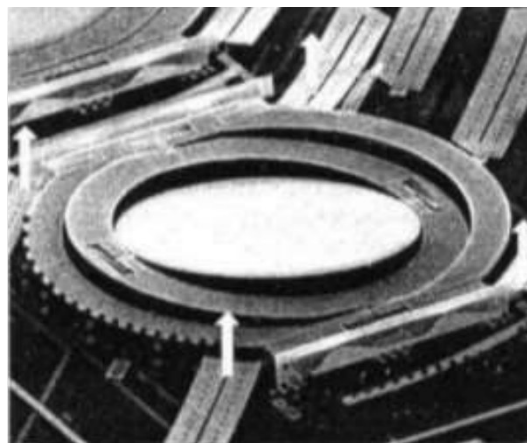


Figure 18. *Micromirror with two degrees of freedom, a part of the electro-optical-mechanical matrices for fibre-optic technology*

- In particular, the tuning of generators and resonant circuits is usually performed with *variable capacitors*.
- In silicon technology, they are made in the form of *combs of micrometre size* (Figure 19) and are controlled by means of similar comb electrostatic actuators (Figure 20).

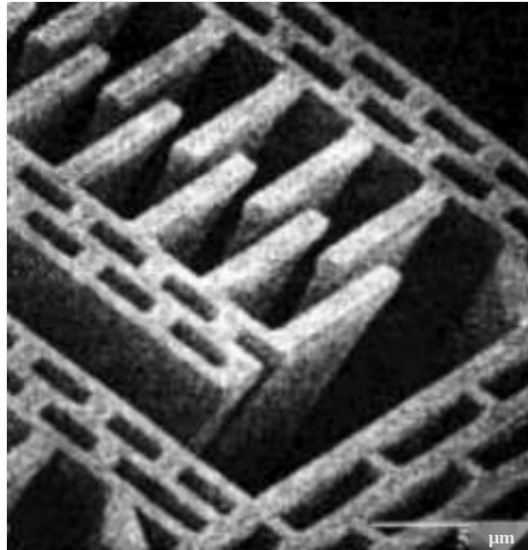


Figure 19. Appearance of a tunable capacitor for radio electronics

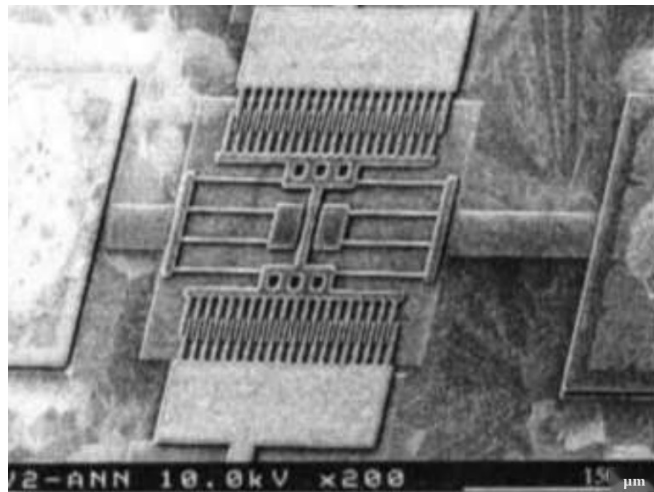


Figure 20. Image of a trimming structure for radio engineering made by dry etching of polycrystalline SiC

Microwave resonators also require tuning and adjustment, which can be performed by movable elements manufactured on the same chip as the service electronics.

- Microelectromechanical filters with a high quality factor, reaching 10^5 in vacuum, have been proposed for signal filtering;
- one example, a filter with a resonant frequency of 156 MHz, is shown in Figure 21.

The simplest switches and commutators based on the electromechanical principle of operation are also used in radio links.

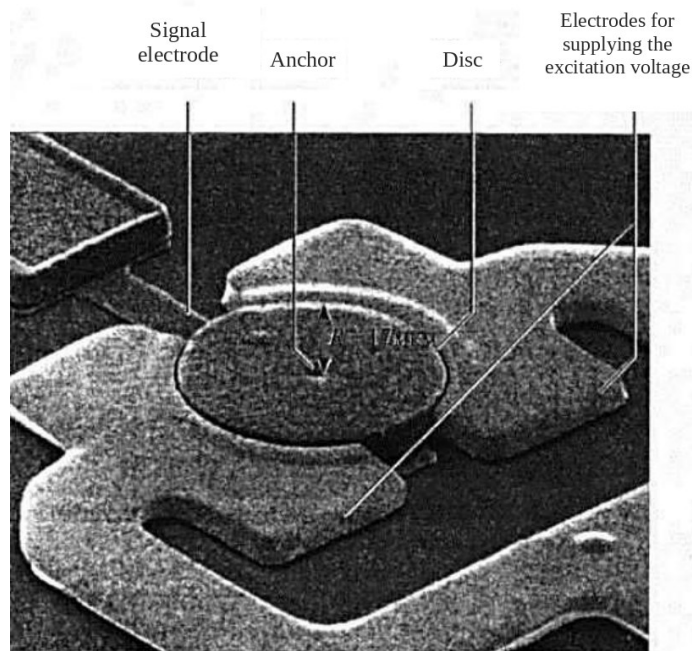


Figure 21. *Silicon electromechanical microresonator for a frequency of 156 MHz*

Thus, nanotechnology has come close to the practical design and creation of devices, machines and integrated systems with submicron and nanometre dimensions of parts, components and units.

- The development of this field of activity, new for engineering practice, requires more fundamental grounds and approaches than those traditionally adopted in the design and production of macro-products.
- They must be based on the laws of quantum mechanics, molecular dynamics, biochemistry and molecular biology.

So far only the very first steps have been taken. However, the grandiose prospects stimulate scientists and practitioners to make the fastest possible use of the almost boundless potential laid down by nature in nanostructures for solving a wide range of vitally important tasks.

4. Nanomaterials in the Aerospace Industry

Experts predict that over the next 20 years world air passenger traffic will grow at a rate of about 5% per year. The main reasons are globalisation and the growth of prosperity and of the planet's population.

In this connection, the fleet of aircraft will have to grow, while satisfying ever more stringent requirements for improved flight safety, etc. Aircraft structural materials must have high strength, stiffness, resistance to brittle fracture and survivability under extreme conditions at low densities.

Nanocomposite materials reinforced with carbon nanotubes are considered very promising:

- they can be tens of times stronger than steel at a six times lower density;

- in conceptual aircraft designs using such materials, the mass of airframe structures is halved compared with traditional ones;
- an additional reserve lies in the transition to new principles and materials for control devices (avionics) and the internal equipment of the aircraft.

Any polycrystalline metals can be strengthened in accordance with the Hall–Petch relation by reducing the grain size and bringing the structure to the nanocrystalline state.

- It is known that aluminium and titanium alloys strengthened in this way acquire a 2...3 times greater fatigue life.
- *Nanophase ceramics* demonstrate increased strength and fracture toughness under high-temperature service conditions; they can be used as heat-protective and corrosion-resistant coatings for nanocomposite materials reinforced with nanofibres or nanotubes.
- As the statistics of failures and accidents due to technical reasons show, a large proportion of them are associated with the destruction of the surface layers of the material of parts (as a result of corrosion and fatigue).
- It would therefore be logical in many cases to protect and strengthen only the surface, rather than to make the whole part of a high-strength and expensive material.

In promising projects of new aircraft, the use of the following types of coatings for various purposes is envisaged:

- anodic coatings for corrosion protection of light magnesium alloys, and nanostructured boron oxide and cobalt phosphide coatings for other materials;
- protective coatings that counteract abrasive wear (for friction pairs, the fuselage and front glazing and portholes, the leading edges of propellers), thermal and chemical effects more effectively than traditional ones;
- antibacterial coatings;
- antifriction wear-resistant coatings with a reduced friction coefficient, including nanostructured paints;
- polymers and rubber modified with carbon nanotubes for "healing" defects and restoring damaged surfaces;
- anti-icing coatings and technologies, in particular those passing an electric current through the leading surfaces;
- coatings with new functional properties (self-healing, self-cleaning, with variable transparency, aerodynamic and thermal properties, etc.).

The addition of nanoparticles to aviation and rocket fuel makes it possible to increase its efficiency, including attaining higher combustion temperatures and rates, which increases the degree of combustion and the engine power while simultaneously reducing fuel consumption.

Nanorobots are devices capable of autonomous functioning in difficult conditions, of collecting data, analysing the physical, chemical and biological characteristics of the environment and collecting samples.

- They must maintain communication with the carrier ship or with Earth to exchange information and allow their operation to be controlled from outside.
- These are the most complex systems, containing the largest number of interacting subsystems.
- They must be cheap enough to be sent in large numbers to remote cosmic bodies.

An example of the development of such projects is ANTS (Autonomous Nano Technology Swarm), carried out by NASA.

At present, laboratory devices and systems already exist that can be applied in rocket and space technology in the near future (nanodispersed additives to rocket fuel, nanocomposite functional and structural materials, nanosensors and nanoelectronics). In the long term, futurological nanotechnology projects such as the space elevator, colonisation of the nearest celestial bodies and fully automated exploration of the entire Solar System may be developed.

Review Questions

1. What are "sensors", and into what types are they divided?
2. List the main requirements for sensors.
3. Describe the principle of operation of a piezoresistive pressure sensor.
4. Describe the classes into which tactile membrane sensors are subdivided.
5. Describe inertial sensors, their principle of operation and application.
6. What are modern photosensitive matrices used for?
7. What properties do cameras with pyroelectric matrices possess?
8. What is the purpose of gas sensors, and how are they related to mercaptans?
9. How are cantilevers functionalised, and what does the coating of a cantilever provide?
10. What are actuators used for?
11. Describe piezoelectric actuators and name their advantages and drawbacks.
12. Describe the principle of operation of an electrostatic actuator with two rotational degrees of freedom.
13. Into what groups can molecular devices be divided?
14. How are molecular and laser tweezers used?
15. Describe the shape of rotaxane molecules.
16. Give examples of rotational motion at the molecular level in nature.
17. Which systems are called nanoelectromechanical (NEMS)?
18. Describe inertial acceleration sensors.
19. Define the term "microgyroscope". Where are microgyroscopes used?

20. Which nanomaterials are considered promising for application in the aerospace industry, and why?

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Lecture 12. Applications and Properties of Nanomaterials

Outline

1. Mechanical properties of nanomaterials.
2. Structural, tool and tribotechnical materials.
3. Electrical and optical properties of nanomaterials.
4. Magnetic characteristics.
5. Reactivity. Catalysis.
6. Porous materials and materials with special physicochemical properties.
7. Electrically conductive materials and insulators.
8. Semiconductors.
9. Emitters, transistors and switches.
10. Micro- and nanoelectromechanical systems.

1. Mechanical Properties of Nanomaterials

The hardness, strength, plasticity and elastic characteristics of nanomaterials are being intensively studied at room, low and high temperatures. Regardless of the field of application, any material must meet certain mechanical requirements.

Figure 1 (*a, b*) shows the influence of grain size on the hardness, strength and relative elongation of iron specimens obtained by hot pressing of powders subjected to intensive milling. Hardness, as the least structure-sensitive characteristic, naturally increases as the grain size decreases, whereas strength increases and plasticity is significantly reduced.

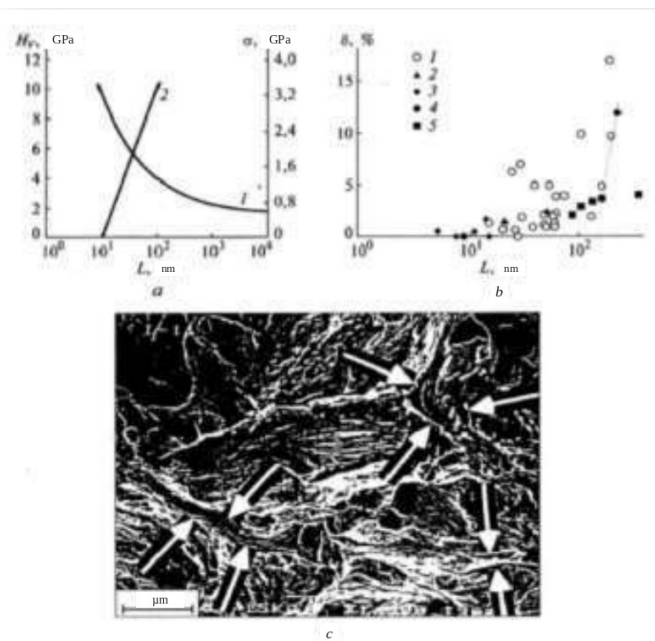


Figure 1. Influence of grain size L on the properties of nanomaterials: *a* – dependence of the hardness (1) and strength (2) of compacted iron on grain size; *b* – dependence of the relative elongation of copper (1), silver (2), palladium (3), an aluminium–zirconium alloy

(4) and an aluminium–titanium alloy (5) on grain size; *c* – micrograph of compacted iron obtained with a scanning electron microscope (arrows show pores and discontinuities)

Electron microscopic examination of the specimens reveals discontinuities and pores in the structure (Figure 1, *c*), which provoke the nucleation of cracks that reduce the strength and especially the plasticity, diminishing the positive influence of the nanostructure.

The presence of pores and other defects, residual stresses, impurities in the grain volume and at interfaces, and texture must all be taken into account when considering the mechanical properties of nanomaterials.

Figure 2 shows the influence of the relative density τ ($\tau = 1 - \theta$, where θ is the porosity) on the hardness and elastic modulus of nanocrystalline TiN. The dependence is linear:

- as τ increases, H_V increases;
- the smaller the grain size, the higher the hardness.

As regards the elastic modulus E , the grain size practically does not affect the dependence $E = f(\tau)$.

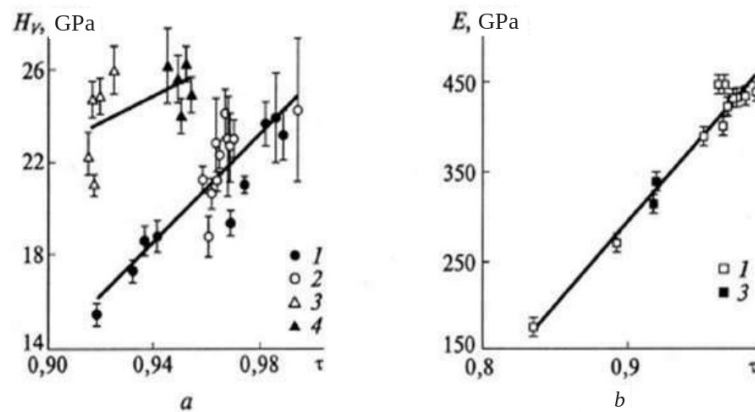


Figure 2. Dependence of the microhardness H_V (a) and Young's modulus E (b) on the relative density τ of nanocrystalline TiN specimens obtained at high pressures and temperatures from ultrafine TiN powders with particle sizes of 80 (1), 70 (2), 18 (3) and 16 (4) nm

The increase in hardness of metallic nanomaterials can reach 500–600%, and for brittle materials up to 200–300%.

For coarse-grained metallic materials, the influence of grain size on hardness (strength) is described by the **Hall–Petch relation**:

$$H_V(\sigma_T) = H_0(\sigma_0) + kL^{-1/2},$$

where H_V is the hardness, σ_T is the yield stress, H_0 is the hardness of the grain body, σ_0 is the internal stress that hinders the propagation of plastic shear in the grain body, and k is a proportionality coefficient.

The Hall–Petch relation also holds for some nanomaterials: in many cases the value of H_V increases as L and the layer thickness δ decrease. However, for a number

of objects a non-monotonic dependence and even an inverse one (the so-called "anti-Hall–Petch" behaviour) is observed, for example in TiN–CrN multilayer films. The change in hardness of multilayer films (e.g. TiN–CrN) is related to the fact that, starting from a certain thickness, the two-phase system is transformed by thermal effects during deposition into a single-phase solid solution with the disappearance of interfaces, which is accompanied by a decrease in hardness.

One of the methods of producing nanomaterials is severe plastic deformation by **equal-channel angular pressing**. The initial coarse-grained copper ($L \sim 30 \mu\text{m}$) is characterised by low strength and high plasticity (Figure 3). After severe plastic deformation ($L \sim 100 \text{ nm}$), both strength and plasticity increase.

The method of severe plastic deformation makes it possible to form a large number of high-angle boundaries, which affect the increase in strength. A certain influence here is also exerted by the deformation defects that arise during severe plastic deformation.

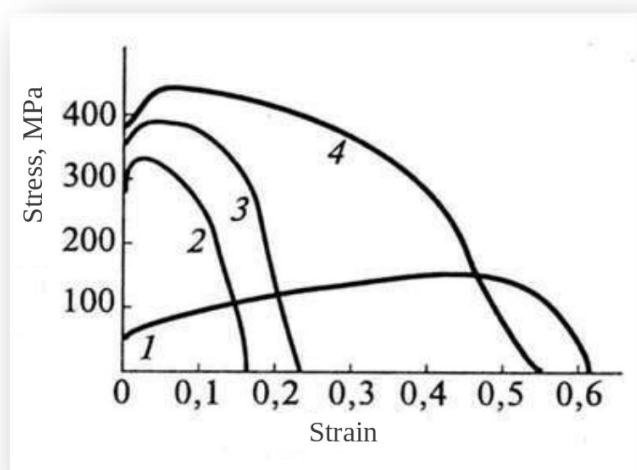


Figure 3. Stress–strain curves obtained in testing copper specimens: 1 – initial coarse-grained copper; 2 – the same after cold rolling; 3, 4 – the same after 2 and 16 passes of equal-channel angular pressing, respectively

The mechanical properties of nanomaterials are related to the features of the dislocation structure of these objects.

- The presence of dislocations in the crystallites of nanomaterials becomes unlikely, starting from a certain size, owing to the ejecting action of image forces; plastic deformation in such materials is therefore unlikely, and fracture is brittle in nature, which is promoted by the presence of pores.
- The structure of nanomaterials contains a large proportion of interfaces (intergranular boundaries), which necessitates taking into account the role of rotational modes and slip along grain boundaries.
- Along with slip processes (at grain sizes above 70 nm), rotation of nanograins takes place, i.e. rotational deformation modes manifest themselves, which are preferable at $L \leq 30 \text{ nm}$.

The rotation of grains and the absence of dislocations within crystallites ($L = 10$ nm) are the basis for qualitative models of the deformation of nanomaterials, in which cooperative rotational modes arise as the grain size decreases. The development of such a shear is shown in Figure 4.

Let us consider the features of the deformation mechanism of nanomaterials:

1. The initial stage of deformation of nanomaterials is associated with grain-boundary sliding, which is accompanied by the generation of dislocations from the intergranular boundaries into the grains. This generation stops at certain grain sizes.
2. Modelling of the deformation of a nanomaterial has shown that plastic deformation is realised by sliding along grain boundaries with a large number of small shears.

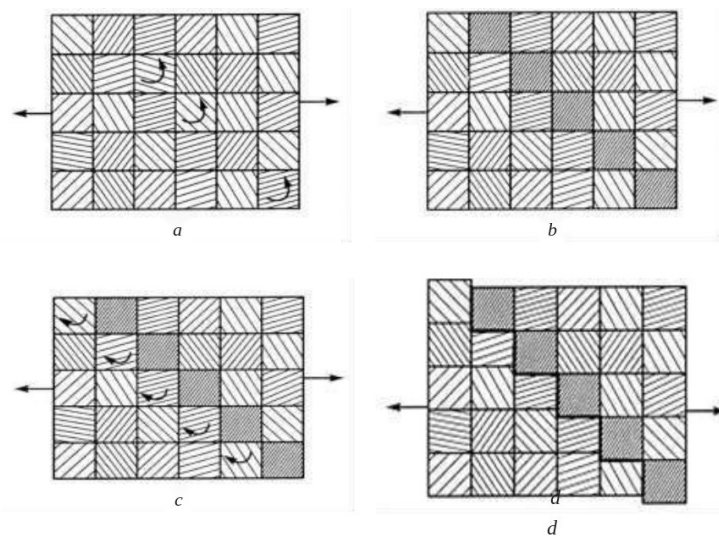


Figure 4. Scheme of the development of a large-scale rotational deformation mode (a, b) and the emergence of mesoscopic shear (c, d). Squares with different hatching correspond to nanograins of different orientation

Figure 5 shows a computer image of nanocrystalline copper ($L = 5.2$ nm) before and after deformation to 10%. A noticeable broadening of the intergranular boundaries can be seen; two partial dislocations are shown, whose motion causes the formation of a stacking fault.

1. An analysis of the role of triple junctions has shown that dislocation nucleation can actively occur in these regions owing to misfit resulting from plastic rotations; moreover, triple junctions can cause plastic deformation in the absence of noticeable diffusion mobility.

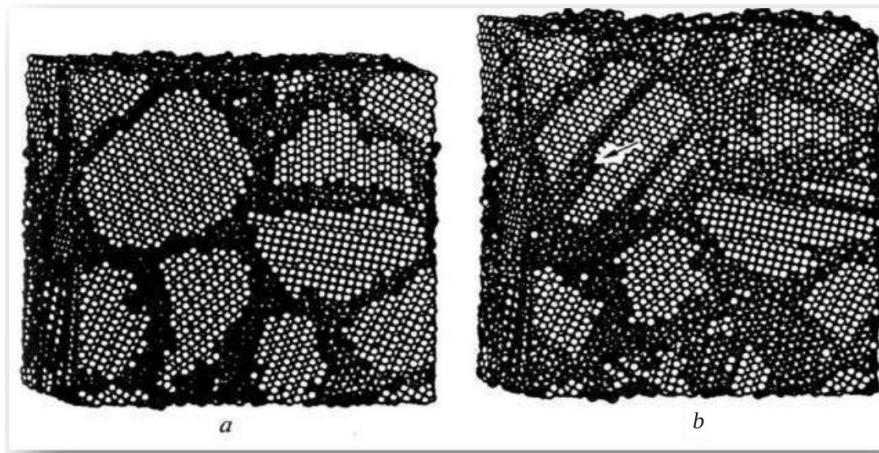


Figure 5. Calculated model of the structure of nanocrystalline copper before (a) and after (b) deformation

Let us note some features of the mechanical properties of nanomaterials:

1. The multilevel nature of the influence on strength and especially on plasticity of not only the grain size but also of porosity, impurities, boundary segregations and inclusions, texture, residual stresses and the nature of boundaries.
2. In many cases, the grain size distribution must be taken into account. Small numbers of large grains can be quite significant in volume and accordingly can influence certain properties of nanomaterials.
3. Owing to the limited number of specimens, many results are considered insufficiently reliable and require additional and independent verification, which indicates the need for further work.

A fractographic study of the deformation of nanomaterials revealed substantial *intercrystalline fracture*, i.e. the propagation of cracks along grain boundaries (Figure 6, a). It is also characteristic that the transition from nanostructures to coarser grains is accompanied by *transcrystalline fracture* (Figure 6, b).

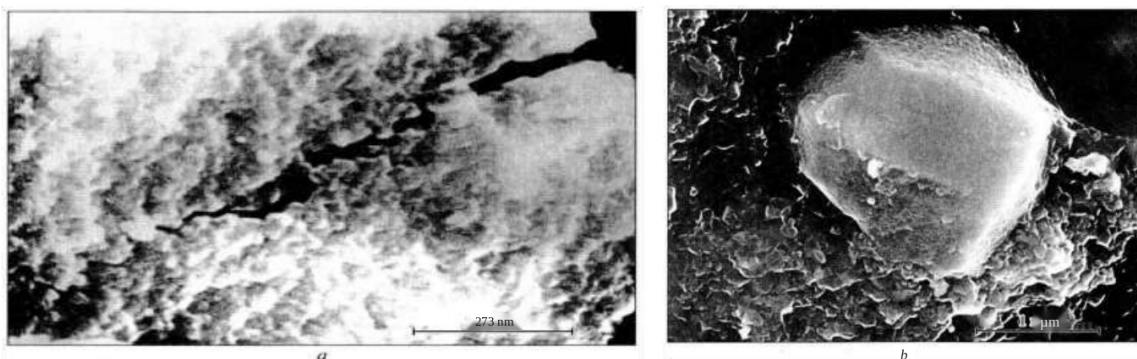


Figure 6. Fracture surfaces of TiN specimens sintered from ultrafine powder at 1200 °C and 4 GPa: a – initial powder with a particle size of ~18 nm; b – initial powder with a particle size of ~80 nm and individual large particles > 1 μm

2. Structural, Tool and Tribotechnical Materials

Structural nanomaterials for general mechanical engineering have not yet become widespread.

- For powder consolidated nanomaterials, this is associated both with the limited size and shape of the products and with the difficulties of preserving the nanostructure during sintering.
- Low flowability and compactibility, easy oxidation and contamination, and powder agglomeration create difficulties in the use of powder nanomaterials.

The drawbacks of powder and other nanomaterials (such as low plastic properties and residual porosity) have not yet been eliminated.

Metallic nanomaterials:

- their strength and hardness are 4–6 times higher than those of conventional materials;
- their plasticity parameters are lower, and they often behave as brittle materials.

The use of metallic nanomaterials requires designs of parts that operate under compression (rather than tension), which hinders the propagation of brittle cracks and raises the permissible level of fracture stress several times.

The service conditions of nanomaterial products in the tool industry and elsewhere involve, in most cases (except for impact and alternating loads), a compressive stress state; the reduction in plastic characteristics is therefore not so catastrophic here.

- The increase in hardness entails an increase in the wear resistance of cutting tools and of friction units in antifriction and friction products.
- High service properties are exhibited by nanocrystalline *hexanite*, a material based on boron nitride ($K_{IC} = 15\text{--}18 \text{ MPa}\cdot\text{m}^{0.5}$), which is obtained by the high-pressure–high-temperature method and used for high-precision cutting.

New tool nanomaterials have been developed: hard alloys, high-speed steels, tools made of diamond nanocrystals, new superhard materials, etc. Additions of tungsten carbide nanopowders (5–8%) to standard hard alloys increase the homogeneity of the structure and reduce the scatter of strength values.

Owing to their high hardness ($H_V = 22\text{--}24 \text{ GPa}$) and crack resistance ($\approx 10 \text{ MPa}\cdot\text{m}^{1/2}$), nanocrystalline hard alloys are also considered promising for the production of drilling tools intended for deep-sea marine oil exploration.

Specimens of *superhard fullerites* (consolidated C_{60} fullerenes) have been obtained by compaction at high pressure (9–13 GPa) in the temperature range 200–1600 °C:

- the optimal hardness of these specimens is 100 GPa, and the bulk modulus is higher than that of diamond, exceeding 500 GPa;
- they are used to manufacture indenters in devices for measuring the hardness and tribological characteristics of hard materials, including nanostructured films.

Nanostructured carbide, nitride and boride films (TiC, TiN, TiB₂, Ti(C,N), (Ti,Al)N) are used as wear-resistant coatings on metal-cutting tools, increasing their service life several times. Multilayer CrN/NbN coatings, in addition to high wear resistance, also have corrosion resistance in various aggressive media.

In industry, nanopowders ($\text{Al}_2\text{O}_3\text{--TiO}_2$, WC--Co , $\text{Cr}_3\text{C}_2\text{--Ni}$) are used to obtain wear-resistant coatings and to restore worn products by thermal spraying, as a result of which hardness and wear resistance increase 1.3–2 times.

- Polishing pastes and antifriction and anti-wear compositions based on nanoparticles have long been used effectively in industry.
- Additions of particles and fibres to polymer matrices provide a significant improvement in the physical and mechanical properties of polymers, as well as in their fire resistance.
- For aerospace technologies, new film antifriction composite nanomaterials based on TiN/MoS_2 and $\text{TiB}_2/\text{MoS}_2$ have been developed. These materials are characterised by significant hardness (about 10–20 GPa), which provides high wear resistance, and a low friction coefficient (less than 0.1) owing to the presence of so-called *solid lubricants* in the structure.

These materials can be used stably under friction conditions in various environments over a wide temperature range.

3. Electrical and Optical Properties of Nanomaterials

It is known that the electrical resistance of metallic solids is determined mainly by the scattering of electrons by phonons, structural defects and impurities.

A significant increase in the specific electrical resistance ρ with decreasing grain size has been noted for many metal and compound nanomaterials. For example, the electrical resistance of nanostructured nickel specimens increases as the grain size decreases, owing to changes in the phonon spectrum and the possible influence of impurities and structural defects.

Practically all metal-like nanomaterials have a high residual electrical resistance at $T = 1\text{--}10\text{ K}$ and a small temperature coefficient of resistance (TCR).

- A noticeable change in electrical resistance begins at $L \approx 100\text{ nm}$.
- As L (grain size) decreases, the TCR decreases; this change is associated with a significant increase in the electrical resistance of nano-objects.

A study of the superconductivity of nanomaterials, i.e. ultradispersed powders of refractory compounds (NbN , VN , TiN , NbCN), revealed a significant influence of particle size on the critical magnetic field:

- the field increases by about 200% when the particle diameter changes from 75 to 15 nm;
- for NbN nanoparticles 28–44 nm in size, a decrease in the superconducting transition temperature in comparison with coarse-crystalline specimens has been noted.

Carbon nanotubes have very specific electrical properties:

- a very wide range of electrical resistance values;

- band-structure calculations for carbon nanotubes of the "zigzag" and "armchair" types have demonstrated a typical metallic electronic spectrum;
- for chiral tube structures, a band gap of about 0.5 eV has been found, which depends on the tube diameter.

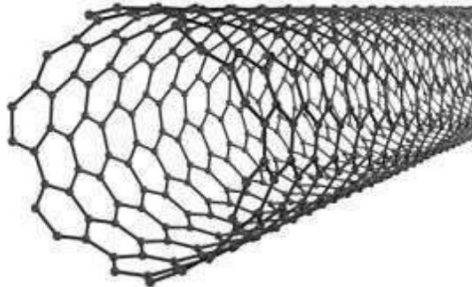


Figure 7. Schematic representation of a nanotube

The thermal conductivity of nanomaterials consists of electronic and lattice components.

- For metallic objects, the electronic component prevails.
- For semiconductors and dielectrics, heat transfer by phonons constitutes the main part.
- Reducing the crystallite size significantly reduces the thermal conductivity of nanomaterials owing to the scattering of electrons at intergranular boundaries.

For example:

- the thermal conductivity, proportional to the thermal diffusivity, of silver with a grain size of 20–47 nm is 3.5–4.0 times lower than that of coarse-grained silver;
- for zirconium oxide, the transition to the nanocrystalline state is also accompanied by a significant decrease in thermal conductivity, which is associated with increased phonon scattering at interfaces. The phonon mean free path in this case is smaller than that in a single crystal.

The combination of electrical and thermal conductivity parameters is important for thermoelectric materials, whose quality is characterised by the figure of merit:

$$Z = \alpha^2 / (\rho\lambda),$$

where α is the thermopower, ρ is the electrical resistivity and λ is the thermal conductivity. The transition to nanomaterials is accompanied by an increase in the figure of merit.

The optical properties of nanoparticles and films are being actively studied:

- a theory of the reflection, absorption and transmission of light by metal films has been developed taking various factors into account;

- sintered specimens of nanocrystalline Y_2O_3 proved to be transparent to visible light, since the nanopore sizes are smaller than the wavelength of light, whereas ordinary sintered yttrium oxide is optically opaque.

The optical and luminescent characteristics of semiconductor nanoparticles have been studied in detail:

- they are characterised by the appearance of luminescence;
- intense luminescence in the visible region of the spectrum is observed in cluster silicon (nanoporous and nanocrystalline);
- this is associated with size quantisation of electrons in clusters or with electronic transitions.

4. Magnetic Characteristics

Crystalline materials characterised by hysteresis phenomena and martensitic transformations are called **ferroics**. Their common feature is the presence of *domains*, regions with maximum values of magnetisation (or dielectric permittivity and elasticity). The domains of ferroics have mobile walls (boundaries), which are planes of twinning.

In large crystals, the rearrangement of the domain structure under the influence of external fields is accompanied by a hysteretic (delayed) response of the material to the change in field. For ferromagnets, the transition from a multidomain to a single-domain structure occurs at a particle size of about 30 nm.

Superparamagnetism manifests itself in nanoparticles (nanocrystallites) of ferro-, ferri- and antiferromagnets under conditions when the energy of thermal fluctuations becomes comparable with the energy of rotation of the magnetic moment of the particle.

The magnetic properties of solids depend significantly on interatomic distances; therefore, the saturation magnetisation I_s , the Curie temperature T_C and other parameters of the ferromagnetic state of nanomaterials will change compared with ordinary coarse-crystalline objects. For example:

- the value of I_s for nanocrystalline iron ($L = 6$ nm) is 40% lower than for ordinary polycrystalline iron;
- for nanocrystalline nickel, this decrease is much smaller, only 5%, when the grain size is reduced from 1000 to 10 nm;
- nanocrystalline nickel obtained by severe plastic deformation and pulsed electrodeposition shows a decrease in T_C by 10–30 K as the crystallite size decreases.

The characteristics (coercive force, remanent induction B_r and maximum magnetic energy product $(BH)_{\max}$) of hard magnetic materials of the Fe–Nd–B and Fe–Sm–N types also depend significantly on grain size:

- for permanent magnets made of such materials, the maximum magnetic energy is an important characteristic;

- the highest values of the magnetic characteristics of these alloys are achieved at a grain size of about 20 nm.

A reduction in crystallite size in ferromagnets affects the shape of the magnetisation curve of both soft and hard magnetic materials.

In multilayer films (superlattices), the *giant magnetoresistive effect* is observed: the films consist of nanometre-thick layers of ferromagnetic and non-magnetic materials (Fe/Cr, Co/Cu, Ni/Ag). The same effect is observed in powder nanocompositions of this composition: in nanomaterials in a magnetic field, a significant reduction in electrical resistance is observed in comparison with homogeneous materials of similar composition.

For soft and hard magnetic materials, a transition to the superparamagnetic state can be observed as the film thickness and crystallite size decrease; it is accompanied by a violation of the magnetic order, which causes a decrease in the high magnetic characteristics.

5. Reactivity. Catalysis

It is known that the corrosion resistance of clusters and isolated nanoparticles is quite high.

- The corrosion resistance of electrodeposited nanocrystalline nickel is entirely satisfactory even in such severe technological tests as stress corrosion at 350 °C in a 10% NaOH solution for 3000 hours; by comparison, traditional nickel alloys are not competitive.
- Owing to the features of their structure, nanomaterials are free of so-called localised corrosion, since the overall average localisation of harmful impurities at the numerous boundaries and triple junctions can be much lower than in ordinary materials.

Diffusion saturation of pure nanomaterials, for example with hydrogen, nitrogen, oxygen and carbon, begins at lower temperatures owing to the intensification of boundary fluxes. For example:

- for nanocrystalline iron, the nitriding temperature was found to decrease approximately by half;
- in a number of cases, the oxidation of nitride and other single- and multilayer films is characterised by very high oxidation resistance of these objects.

The interaction of nanomaterials with gaseous media is of special interest in connection with the development of highly sensitive *gas sensors* intended for the detection of toxic (carbon monoxide), explosive (hydrogen, methane, butane, propane, etc.) and environmentally polluting (nitrogen and sulphur oxides, water vapour, etc.) gases.

The transition to nanomaterials makes it possible to:

- reduce the energy of defect formation and increase the diffusion mobility of components;

- change the physical and mechanical properties of materials;
- control the processes of formation of boundary segregations and non-equilibrium phases;
- in the case of powders, reduce the sintering temperature of ultradispersed powders.

All of the above expands the possibilities of creating sensors with improved performance characteristics (sensitivity, selectivity, response speed, stability and durability). The sensitivity of interaction with the gas medium increases as the particle size decreases.

Traditional small-sized objects, *catalysts*, belong to nanomaterials. *Heterogeneous catalysis* is one of the oldest fields of application of nanotechnology, and in the development of new catalysts the basic principles of nanotechnology are of great importance.

- Gold, which is catalytically inactive in the bulk, in the form of nanoparticles on appropriate nanostructured substrates is more active than traditional palladium and platinum catalysts.
- Ultradispersed platinum is a more active catalyst than platinum black in certain catalytic processes (e.g. isomerisation of *n*-heptane and hydroxylation of benzene).
- The specific catalytic activity of metal nanoparticles depends on the particle size and their distribution, i.e. the distances between them.

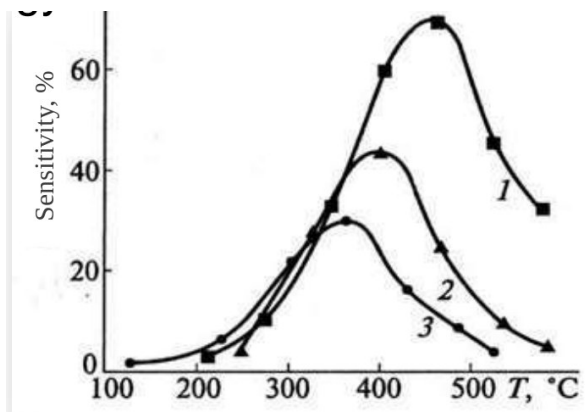


Figure 8. Temperature dependence of the sensitivity of SnO_2 obtained by sintering powders with particle sizes of 4 nm (1), 8 nm (2) and 15 nm (3) in the presence of 0.1 wt.% hydrogen

6. Porous Materials and Materials with Special Physicochemical Properties

Porous nanostructures are used for diffusion separation of gas mixtures (for example, isotopes and other complex gases that differ in molecular mass).

- The pore ("window") size in conventional zeolites varies in the range 0.4–1.5 nm and depends on the number of oxygen atoms in the cyclic structures that form the zeolite.

- From the point of view of donor–acceptor interactions, porous carriers are classified as acidic, neutral (silica gel) and basic (oxides of Mg, Al, Ti, alkaline zeolites).

The surface of many porous nanostructures itself has catalytic properties. For example, aluminosilicate zeolites (MCM-41), whose cylindrical pore size is 2–10 nm, are used in catalytic processing of oil and petroleum products. High selectivity in various separation processes is achieved owing to catalytic phenomena; the economic effect of this in the USA over the next 10–15 years is estimated at 100 billion dollars.

Carbon nanotubes have catalytic, sorption and filtering properties. They also have high sorption characteristics in the removal of carcinogenic organic compounds from exhaust gases, where these compounds are destroyed.

The photocatalytic properties of nanocrystalline TiO_2 have found application in devices for cleaning air of organic pollution of household and industrial origin in various premises (apartments, workshops, offices). The principle of operation of such devices is based on the photocatalytic oxidation of organic impurities on the surface of nanocrystalline TiO_2 under the action of ultraviolet radiation. Photocatalytic oxidation is effective:

- the air cleaned in this way contains a small amount of harmful compounds (far less than permitted by standards);
- the oxidation products are carbon dioxide and water vapour.

Films and highly porous layers of TiO_2 and CdSe are considered promising for solar cells and LEDs.

Ultradispersed powders are used for the production of multilayer fine filters. A wide range of plate and tubular filter elements made of porous stainless steel with a layer of ultrafine powder based on TiN or TiO_2 has been developed. The fineness of filtration of gaseous media reaches 10 nm, and for liquid media 10–100 nm (at a pressure difference of 2–5 bar).

Fields of application of fine filters:

- separation of water–oil emulsions;
- purification of waste water and liquid radioactive waste;
- filtration of cell decay products;
- clarification of fruit juices.

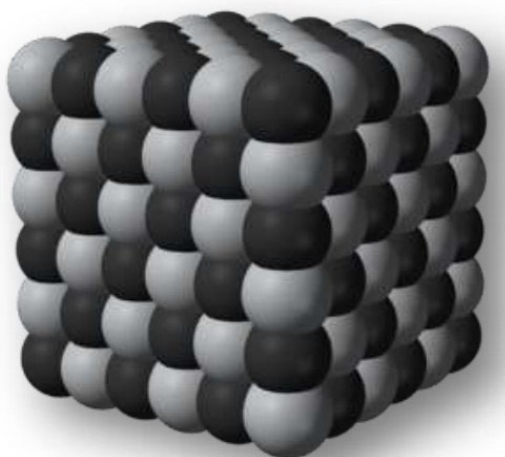


Figure 9. *Crystal structure of titanium nitride (TiN)*



Figure 10. *Titanium dioxide nanopowder*

Hydride hydrogen accumulators are now widely used (for example, the FeTi–H₂, LaNi₅–H₂ and MgH₂ systems).

- The most radical approach is the use of intensive milling (mechanochemical processing) to obtain nanocompositions of the types Mg(MgH₂)–V(Nb), Mg(MgH₂)–FeTi, Mg(MgH₂)–LaNi₅ and Mg(MgH₂)–TiO₂.
- A significant activation of the sorption properties of Mg hydride is observed when graphite or vanadium additives are introduced during intensive milling.

For hydrogen-storage purposes, the use of fullerenes and carbon nanotubes is promising: theoretically, without destroying the fullerene framework, C₆₀H₆₀ molecules containing 7.7 wt.% H₂ can be obtained.

Mechanochemical processing is used to improve the main properties of cathode materials for lithium-ion and nickel–hydride batteries, which contributes to their lower cost and wider use.

The most important characteristics of batteries, namely capacity, service life and charge–discharge rate, are considerably improved when nanomaterials are used, in particular nanopowders of lithium and tin compounds (Li₄Ti₅O₁₂, LiMnO₂, LiVO_x, SnO₂). Such powders are used for the electrodes of lithium batteries in automotive, space and military technology.

Carbon nanotubes are also used in lithium batteries: high discharge characteristics are achieved owing to the increased concentration of lithium in nanotubes compared with ordinary graphite electrodes.

Ultradispersed powders of Zn, Al, TiO₂, ZnO and others have long been used in the paint and varnish industry, for anticorrosion protection and in cosmetics.

In connection with the problems of environmental monitoring, *gas sensors* based on semiconductor oxides (SnO₂, MoO₃, WO₃, TiO₂, In₂O₃, etc.) are of special interest. The positive qualities of nanosensors, namely high sensitivity, selectivity, fast response and the possibility of changing their physicochemical and physicomechanical properties, determine the broad prospects for their application.

Magnetic materials. Japanese scientists discovered a new class of soft magnetic materials with high static and dynamic magnetic properties: alloys based on Fe–Si–B with small additions of Nb, Cu, Zr and some other transition metals.

- After quenching from the melt, these alloys become amorphous.
- Optimal parameters are achieved after partial crystallisation at 530–550 °C, when an ordered nanocrystalline Fe–Si (18–20%) phase with a particle size of about 10 nm precipitates.
- The alloys have a low coercive force (5–10 A/m) and a high initial magnetic permeability at ordinary and high frequencies with low magnetisation-reversal losses (200 kW/m³).

Fields of application: in electrical engineering and electronics as transformer cores, magnetic amplifiers and pulsed power supplies, and in magnetic recording and playback technology, etc., ensuring significant miniaturisation of these devices and stable operation over a wide range of frequencies and temperatures.

For high-density magnetic recording heads, nanocrystalline iron films with additions of refractory compounds (ZrN, AlN) are promising: the presence of refractory nanoparticles in the structure provides sufficient thermal stability and high strength.

Nanocrystalline hard magnetic materials based on Fe–Nd–B and Fe–Sm–N, obtained mainly by mechanochemical synthesis, have become widespread.

Devices for recording information (heads, media, disks) are an important field of application of magnetic nanomaterials. The *giant magnetoresistive effect*:

- manifests itself in multilayer magnetic/non-magnetic films of the Fe/Cr and Co/Cu types;
- is used for efficient recording of information when registering very weak magnetic fields in the heads of magnetic disk drives;
- has made it possible to increase considerably the recording density and the speed of reading information.

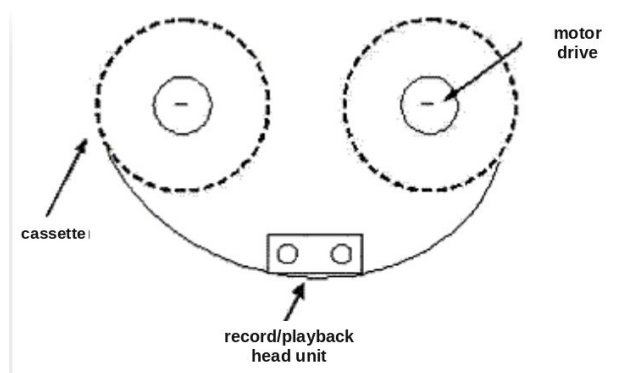


Figure 11. Principle of operation of a magnetic tape storage device

The magnetic properties of ultradispersed powders are also applied in ferrofluids, which are used as vacuum seals, vibration dampers and in other fields.

7. Electrically Conductive Materials and Insulators

A combination of high electrical conductivity and strength is necessary for creating materials for large magnetic systems with high magnetic field strength.

- Promising in this respect are wire nanocomposites of the Cu–Nb type, the manufacturing technology of which consists in joint cold drawing of copper and niobium rods.
- In the final structure of the Cu–Nb (18 wt.%) composite, the average transverse size of the niobium fibres is about 100 nm, the tensile strength is 1.25 GPa and the conductivity is 70% of that of pure copper.

Good prospects are expected from the application of mechanochemical synthesis for the manufacture of powder electrical contact materials, which are used in switching units of high-current and low-voltage electrical equipment (relays, switches, starters, contactors, etc.).

The requirements imposed on them, namely low specific and contact resistance, insignificant erosion, mechanical strength and chemical inertness, high thermal conductivity, etc., can be met only by composite structures, i.e. a combination of highly conductive materials (Cu, Ag) and refractory components (W, Mo, CdO) that are difficult to evaporate. Heterogenisation of the structure down to nanoinclusions, with the possibility of an increased concentration of the conductive components, can promote the formation of new highly efficient contact materials.

The introduction of metal nanoparticles to change electrical conductivity and strength is widely used in polymer materials science. Varying the particle size makes it possible to:

- significantly change the percolation threshold, i.e. the concentration of the conductive component at which a sharp increase in electrical conductivity occurs;
- an increase in the electrical conductivity of polymeric materials has been noted when carbon nanotubes are added.

The range of use of such materials includes heaters, seals, measuring devices, antistatic agents (including in medicine), cables and electromagnetic radiation shields.

Nanowires made of metals and semiconductors are promising for nanoscale devices such as transistors, diodes and logic gates.

The problem of increasing the efficiency of gas turbine engines requires the development of *thermal barrier materials*. The efficiency of gas turbine engines depends on the working temperature of blades made of heat-resistant nickel alloys, whose melting points are relatively low, so that a further increase in working temperatures is now problematic. In this connection, developments aimed at creating coatings with low thermal conductivity, the application of which to the surface of metal blades can help increase the working gas temperature in turbines, are of great importance. Nanocrystalline coatings based on zirconium oxide are very promising for this purpose.

Thermoelectric nanomaterials, especially those of the layered-system type, are promising both for the direct conversion of solar energy into electrical energy and for cryotechnology.

The main basic elements of integrated circuits, including large-scale and very-large-scale ones, are metal–dielectric–semiconductor structures. Ultrathin single-crystal or amorphous films of Si_3N_4 , Al_2O_3 , ZrO_2 , HfO_2 , etc. are considered as promising materials for the dielectric layer, which is about 1 nm thick.

8. Semiconductors

In the case of semiconductors, the transition to nanostructures is accompanied by a spectral shift of luminescence to the short-wavelength region, an increase in the band gap and other phenomena.

- Single-crystal CdSe nanoparticles in polymer matrices are considered as possible light emitters and optical switches for laser systems, as well as sensors in biological objects.
- The transition to heterostructures with quantum wires and dots gives even more significant results, important for lasers, modulators, detectors and emitters operating in the far-infrared region.

The application of heterostructures with quantum wells and superlattices of the AlGaAs/GaAs type in semiconductor lasers has made it possible to:

- significantly lower threshold currents;
- use shorter-wavelength optical radiation;
- improve other performance characteristics in high-speed fibre-optic information transmission systems.

Semiconductor nanostructures are promising for solar energy conversion systems. Progress in the creation of heterostructures with quantum dots will make it possible to improve qualitatively the performance characteristics of many devices of present and future technology.

9. Emitters, Transistors and Switches

Among the numerous potential fields of application of carbon nanotubes, their use in electronic engineering is considered one of the most promising.

- The high emission properties of carbon nanotubes are the basis for the development of electronic devices with cold cathodes (electronic displays, X-ray sources, cathodoluminescent light sources, etc.), which differ from conventional analogues in lower supply voltages and power consumption, as well as in their small size and mass.
- Experimental diodes and transistors, i.e. two- and three-electrode elements based on carbon nanotubes and other nano-objects, have been created.
- Thanks to nanomaterials, electronics is gradually moving from micro-sized to nanoscale objects.

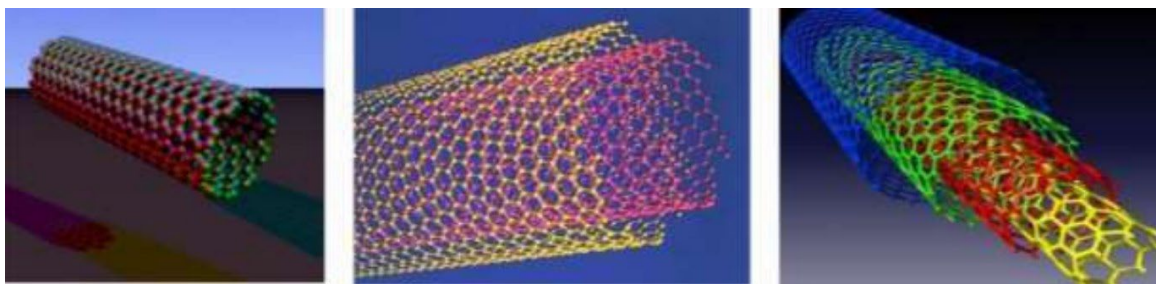


Figure 12. Carbon nanotubes: single-walled (a), double-walled (b) and multi-walled (c)

10. Micro- and Nanoelectromechanical Systems

One of the important advantages of nanomaterials is that their special physicochemical and physicomachanical properties give rise to many opportunities for creating new miniature and subminiature systems.

- Using molecular machines as an example, the operation of nanorobots that perform computer-controlled assembly and disassembly and the creation of individual nanocomponents and nano- and macrosystems has been described.
- Scanning tunnelling microscopes make it possible to carry out nanodoping and other manipulations in nanostructures.
- Microelectromechanical and nanoelectromechanical (below 100 nm) systems are used in the field of subminiature sensors, electric motors, transducers, etc.

There are two approaches to the design of nanodevices: the creation of very small copies of known macro-objects, and the development of fundamentally new designs that have no traditional analogues.

The manufacture of structural parts on the micro- and nanoscale requires the application of special techniques of powder and polymer nanotechnology, as well as special methods of design, inspection, etc.

Review Questions

1. How does grain size affect the mechanical properties of nanomaterials?

2. Describe the Hall–Petch relation.
3. Describe the method of severe plastic deformation.
4. How does the presence of dislocations in the crystallites of nanomaterials affect their properties? What do grain rotation and the absence of dislocations within crystallites provide?
5. Name the features of the deformation mechanism of nanomaterials.
6. Name the features of the mechanical properties of nanomaterials.
7. Characterise metallic nanomaterials.
8. How is the electrical resistance of metallic nanomaterials determined? How does grain size affect electrical resistance?
9. Name the electrical properties of carbon nanotubes.
10. Into what components is the thermal conductivity of nanomaterials divided? Describe them and give examples.
11. Define the term "ferroics" and describe them.
12. Why do gas sensors arise, and what is their purpose?
13. What opportunities does the transition to nanomaterials create?
14. What are catalysts? Give an example of a metal that is catalytically inactive in the bulk.
15. What are porous structures used for?
16. What is made from ultradispersed powders? Name their fields of application.
17. Describe the new class of soft magnetic materials based on Fe–Si–B and name their fields of application.

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Lecture 13. Applications and Properties of Carbon Nanomaterials

Outline

1. Nanodiamonds and their transformation into onions: application and properties of nanodiamonds; electronic structure of nanodiamonds; transformation of nanodiamonds into onions.
2. Fullerenes: properties of fullerenes; structures based on fullerenes; electronic structure of fullerenes; mechanisms of fullerene formation; non-carbon fullerenes; potential fields of application of fullerenes.
3. Carbon nanotubes: structure and types of carbon nanotubes; topological and metric characteristics of nanotubes; properties of carbon nanotubes and prospects for their production.
4. Carbon nanofibres: properties of nanofibres; structural characteristics of carbon fibres; electronic structure of carbon fibres.

1. Nanodiamonds and Their Transformation into Onions

1.1. Application and properties of nanodiamonds

Nanodiamonds, which can exist in meteorites and can also be synthesised by various methods, have unique properties owing to their large specific surface area of 150–450 m²/g.

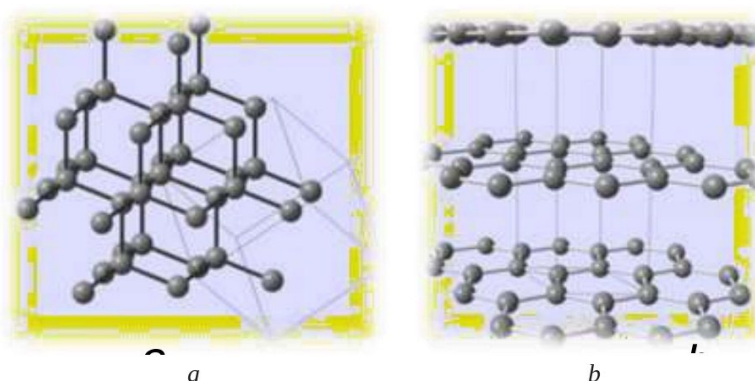


Figure 1. Structures: *a* – diamond; *b* – graphite

Nanodiamonds make it possible to reduce surface roughness to several nanometres; they are therefore used for *polishing*. In addition, nanodiamonds:

- are widely used in the manufacture of composite electrochemical coatings;
- can be suitable for the manufacture of wear-resistant and corrosion-resistant coatings, polymers, antifriction lubricants and additives for industrial equipment;
- have high sorption activity with respect to organic substances, gases, ions and electrolytes;
- are stable under radioactive irradiation, which allows their use as highly effective sorbents of radionuclides.

Nanodiamonds are extremely stable, and functional groups can be chemically attached to their surfaces.

Finely dispersed nanodiamonds with high surface energy and a developed specific surface exhibit *catalytic activity* in various reactions.

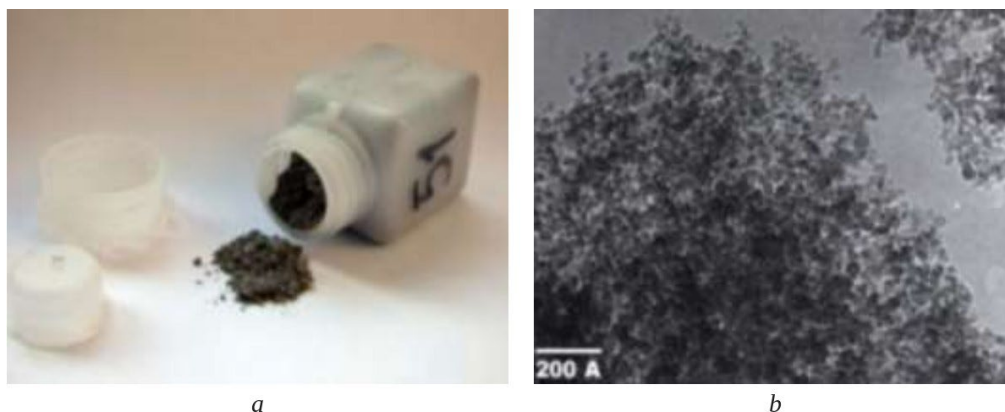


Figure 2. *a* – nanodiamond powder; *b* – nanodiamond under the microscope (particle size from 2 to 8 nm)

Owing to their special properties, the use of nanodiamonds is not limited to industry. For example:

- nanodiamonds are able to retard antigens;
- owing to the large number of ionogenic groups (carboxyl, carbonyl, hydroxyl, ether), hydrocarbons and metal fragments, nanodiamonds can be used for protein separation and purification.

Researchers at a university in the south-western United States have shown that nanodiamonds effectively deliver drugs into diseased cells without particular negative effects, unlike current delivery methods.

1.2. Electronic structure of nanodiamonds

Diamond is a substance with saturated covalent bonding provided by valence-band electronic states that are hybridised according to the sp^3 type.

However, as shown by spectroscopic methods, small-angle X-ray scattering and X-ray diffraction, *nanodiamonds contain both sp^3 - and sp^2 -hybridised bonds*, owing to the presence of amorphous phases at the surface of the cores of a small number of nanodiamond particles. The structure of nanodiamond particles is shown in Figure 3.

The amount of the amorphous component in nanodiamonds can be varied, up to its complete removal by treating the particles with nitric acid. Depending on the surface treatment, only the graphite-like nanoplates are removed from the diamond cores, or the onion-like shell is also removed (if it is closed).

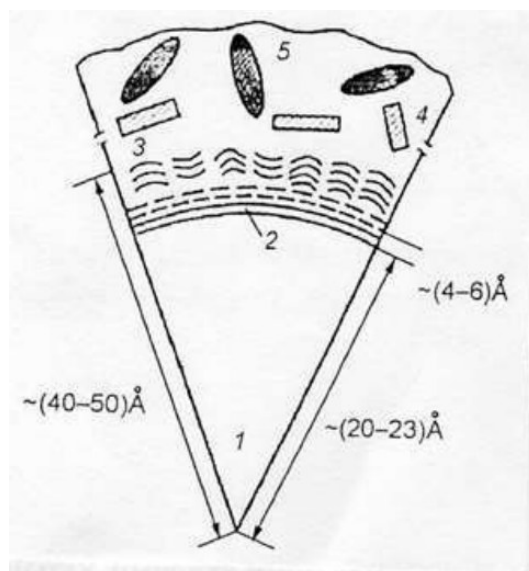


Figure 3. Structure of nanodiamond particles: 1 – diamond core; 2 – onion-like layer; 3 – graphite nanoplates; 4 – graphite particles; 5 – metal oxides

Most detonation nanodiamond particles have a regular faceting: the main structural components are tetrahedra and rectangular prisms with smoothed vertices.

- The particle size ranges from 1 to 7 nm.
- The largest components contain microtwins on (111) planes no more than 1 nm thick.
- Inclusions in the form of thin (no more than 50–100 nm) plates with a microdomain substructure have been found in conglomerates; the diamond in such regions is in a strongly disordered state.
- X-ray analysis of nanodiamond powder revealed a strongly disordered form of non-diamond carbon.
- Infrared absorption spectra have shown that the surface of the nanodiamond powder particles interacts with chemisorbed atoms and molecules of CO₂, O₂, etc.

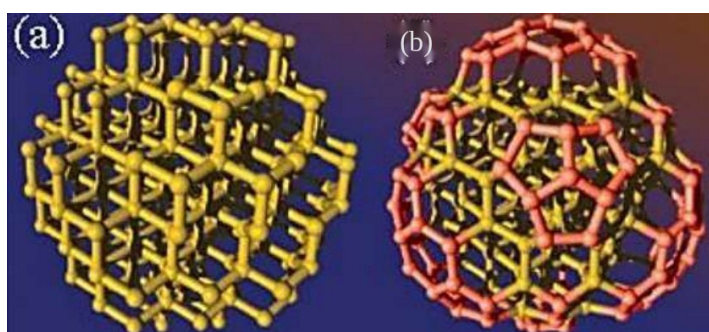


Figure 4. a – bulk diamond structure; b – diamond nanoparticle with a fullerene-like surface

When nanodiamonds are treated in a hydrogen atmosphere, they are cleaned of chemisorbed atoms.

1.3. Transformation of nanodiamonds into onions

Carbon onions are synthesised from nanodiamonds in various ways (for example, by annealing at 1500 °C (1773 K) for 5 and 10 minutes).

- As a result, partially transformed nanodiamonds (after annealing for 5 minutes) and nanodiamonds fully transformed into onions (after annealing for 10 minutes) are formed.
- Under thermal action, the nanodiamond begins to collapse, forming a *new molecule* consisting of a diamond core and graphene layers around this core (Figure 5).

The onion particles formed are characterised by different distances between the layers that form the particle. This may be caused by the unequal densities of the components that form the onion: diamond $\rho = 3.5 \text{ g/cm}^3$, graphite $\rho = 2.27 \text{ g/cm}^3$.

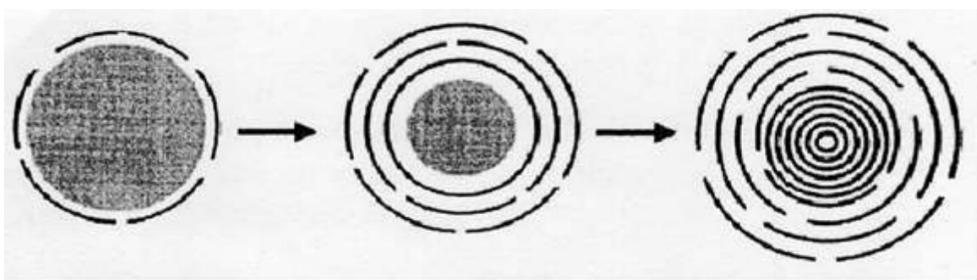


Figure 5. Scheme of the formation of onions from nanodiamonds

Owing to the *higher density of the diamond core* (3.5 g/cm^3) compared with the amorphous shell (2.27 g/cm^3), the inner layers of the molecule are located at much smaller distances from each other than the layers remote from the centre (Figure 6). Moving deeper into the onion particle, the interlayer distance decreases from 0.42 to 0.34 nm.

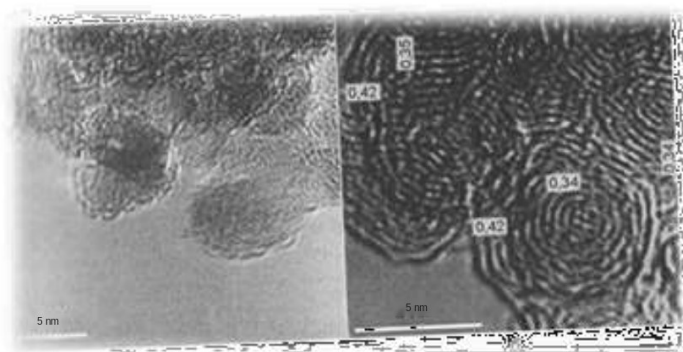


Figure 6. Electron microscopy images of nanodiamond particles (a) and onions (b)

The results of high-resolution transmission electron microscopy of nanodiamonds (Figure 7) showed the presence of *clusters of identical particles* (diameter $\approx 5 \text{ nm}$). Two white parallel lines show an interplanar distance of 0.21 nm, which corresponds to the $\{111\}$ planes of the diamond crystal structure.

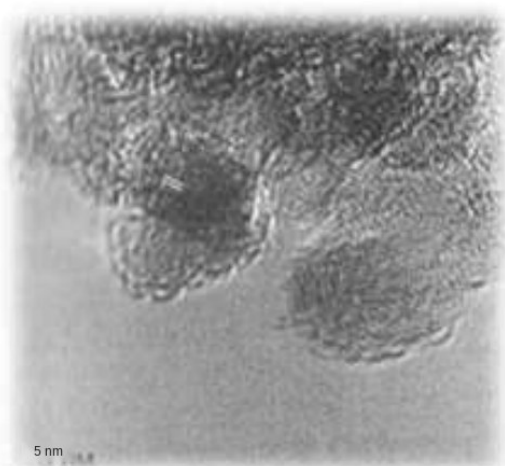


Figure 7. Electron microscopy image of nanodiamond

All onion particles consist of clearly outlined *crystalline cores* (central particle) and *amorphous outer shells*.

An analysis of general areas (0.1 μm in diameter) of nanodiamond particles showed the presence of sp^2 -bonded carbon atoms on the surface of the nanodiamond particles; the fraction of sp^2 -bonded carbon atoms on the surface of the nanoparticles is 40%.

Even after cleaning by boiling in acid, the surface of nanodiamond nanopowder particles remains coated with non-diamond carbon layers, possibly owing to mixed sp^2/sp^3 bonds of carbon atoms at the boundaries between the core and the outer shells.

Partially transformed nanodiamond contains both particles that form a carbon network with a disoriented onion-like structure in the outer shell and traces of diamond-like cores (Figure 8, *a*), and actually spherical particles with an ordered onion-like structure with distances between neighbouring shells of 0.35–0.38 nm (Figure 8, *b*), which is slightly larger than the period of the graphene layers in the ideal graphite structure (≈ 0.335 nm).

In the structure of carbon onions, at the boundaries between amorphous carbon and diamond clusters, as well as in the structure of amorphous carbon, mixed sp^2/sp^3 -bonded carbon atoms are observed.

- In fully transformed nanodiamonds, the diamond-like structure is absent.
- In Figure 8, *c*, onions with polyhedral features are observed.
- The particle sizes coincide with those of the initial nanodiamond particles (≈ 5 nm), with some enlargement to ≈ 10 nm (Figure 8, *d*).
- The distances between neighbouring onion shells range from 0.35 to 0.38 nm.

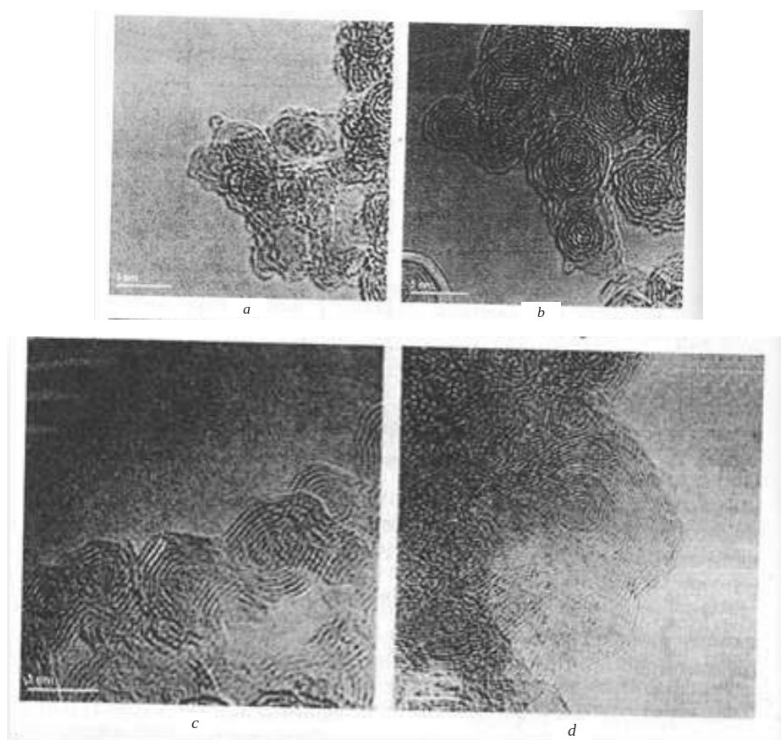


Figure 8. Images of nanodiamonds annealed in vacuum at 1723 K for 5 min (a, b) and for 10 min (c, d), recorded under Scherzer defocus

Polyhedral carbon onions (Figure 8, c), as well as partially transformed materials (Figure 8, a, b), are classified as ordered graphite-like crystalline structures.

Polyhedral carbon onions are usually obtained at temperatures of the order of 2073 K and above; however, they can also be obtained by annealing at 1773 K for 5 minutes.

2. Fullerenes

2.1. Properties of fullerenes

The possibility of the existence of *highly symmetrical carbon molecules* resembling a football was first predicted by the Japanese scientists E. Osawa and Z. Yoshida in 1970. In 1973, the Russian scientists D. A. Bochvar and E. G. Galpern performed the first theoretical quantum-chemical calculations of such molecules and proved their stability.

Only years later (1985) did the English scientist H. Kroto and his co-workers succeed in synthesising the C_{60} *fullerene* molecule. **Fullerenes** are closed molecules C_{60} , C_{70} , C_{76} , C_{84} , in which all the carbon atoms lie on a spherical or spheroidal surface.

- It is believed that the fullerene molecule is an organic molecule, and the crystal formed by these molecules (*fullerite*) is a molecular crystal that links organic and inorganic matter.
- Fullerene molecules are not only spherical but may also be ellipsoidal in shape.
- The formation of multilayer spheres and ellipsoids is also possible. In all cases, the size of a fullerene molecule is ≈ 1 nm.

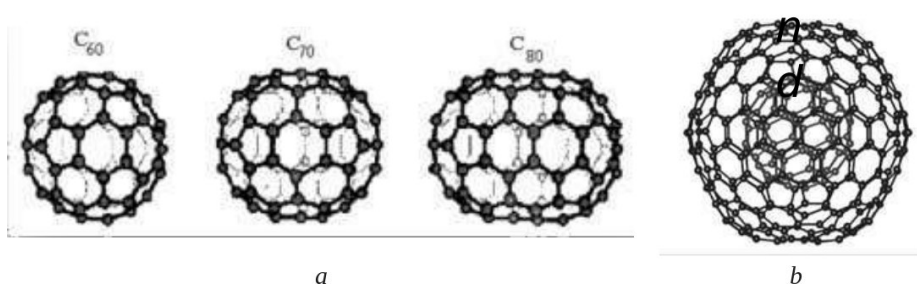


Figure 9. Examples of structures based on carbon clusters: *a* – fullerenes C_{60} , C_{70} , C_{80} ; *b* – multilayer fullerene C_{60}/C_{240}

At present, the concept of a "fullerene" applies to a wide class of polyatomic carbon molecules with the general formula C_n (n is an even number from 20 to 1840 (hyperfullerenes)) that obey certain regularities.

The central place among fullerenes is occupied by the C_{60} molecule, which is characterised by high symmetry and high stability:

- structurally, the C_{60} cluster is a truncated icosahedron with a carbon atom at each vertex; each atom forms three bonds with its neighbours;
- the surface of the molecule consists of 12 regular pentagons and 20 distorted hexagons;
- one type of edge is common to a five- and a six-membered ring, while the other is shared by two six-membered rings; these bonds are called "single" and "double", respectively;
- the entire surface of the fullerene is covered by a system of conjugated bonds, which are strained, since the surface is not flat;
- the length of the "single" bond is 0.144 ± 0.001 nm, and that of the "double" bond is 0.139 ± 0.001 nm.

In the C_{60} cluster, as in the fullerene molecule, there are bonds of two types: r_1 , corresponding to the five-membered rings (length 0.1401 nm), and r_2 , common to five- and six-membered elements (0.1456 nm). The radius of the C_{60} molecule is 0.375 nm.

The structural features of fullerenes determine their unique properties:

- pure fullerite (a crystal of fullerene molecules) is a semiconductor with a band gap of ≈ 1.5 eV;
- C_{60} has high elasticity and strength;
- the fullerenes of alkali metals are superconductors; the maximum superconducting transition temperature for these compounds is slightly above 30 K; however, for fullerenes containing several metals it is 49 K, and copper fullerene becomes superconducting at 120 K.

Fullerenes have high electronegativity; in chemical reactions they act as strong oxidising agents and are capable of attaching up to six free electrons. More than one-third of the elements of the periodic table can be placed inside the C_{60} molecule.

Fullerenes are practically insoluble in polar solvents such as alcohols and acetone, and slightly soluble in ordinary alkanes. They dissolve best in liquids for which the

ratio of the specific enthalpy of evaporation to the specific molecular volume of the solvent is close to the corresponding value for C₆₀ molecules.

The C₆₀ fullerene is black and is the "purest" of the allotropes of carbon. The density of fullerene is 1.7 g/cm³, which is much lower than the density of graphite and diamond (Table 1); this is due to the hollowness of fullerene molecules.

Table 1. Properties of the allotropic forms of carbon

Carbon form	Density, g/cm ³	Specific heat capacity, J/(kg·K)	Thermal conductivity, kW/(m·K)	Electrical resistivity, Ω·m
Graphite	2.3	0.72	0.1	(3–5)·10 ^{–7} (along the layers); (1–5)·10 ^{–2} (perpendicular to the layers)
Diamond	3.5	0.5	1.4	10 ^{–2} –10 ^{–6}
Fullerene	1.7	0.68	0.4	10 ¹⁴

2.2. Structures based on fullerenes

Fullerenes are a "raw material" for creating nanostructures ("fullerene substances") with various properties, such as crystals, coatings and polymers, which are promising for application in electronics, optoelectronics, power engineering, materials science, biotechnology, medicine and other fields. The number of fullerene materials already exceeds 10 000.

One direction is the introduction of atoms (or molecules) of various elements (metals, non-metals) into the fullerene molecule without violating its integrity. Such fullerenes are called *endofullerenes* or *doped fullerenes* (Figure 10).

In addition to endofullerenes, fullerenes are capable of forming *exohedral compounds* (exofullerenes), in which atoms of other elements, ions or molecules are located outside the carbon shell. Partial substitution of carbon atoms by atoms of other elements (*heterofullerenes*), for example C₅₉B, C₅₈B₂, etc., is also possible. When carbon atoms are replaced by other elements, the symmetry of the molecule is distorted, its electronic structure changes and its reactivity increases.

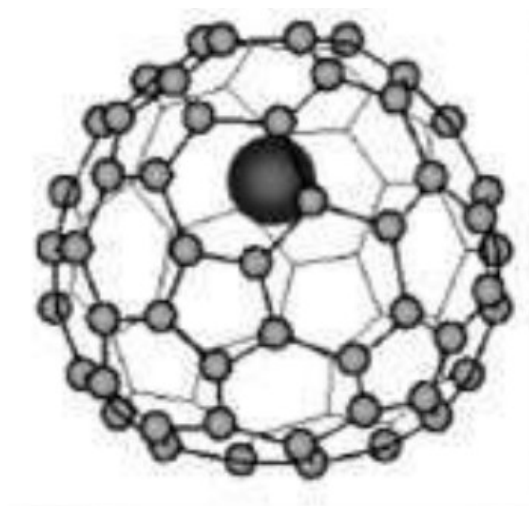


Figure 10. Structure of a doped fullerene

Under the influence of high pressure or laser or electron irradiation, polymerisation of the initial fullerene structures and the formation of polymers based on them can occur (Figure 11). Such polymers are more stable than traditional polymers and can be used in the production of solar cells and polymeric glasses with protective functions.

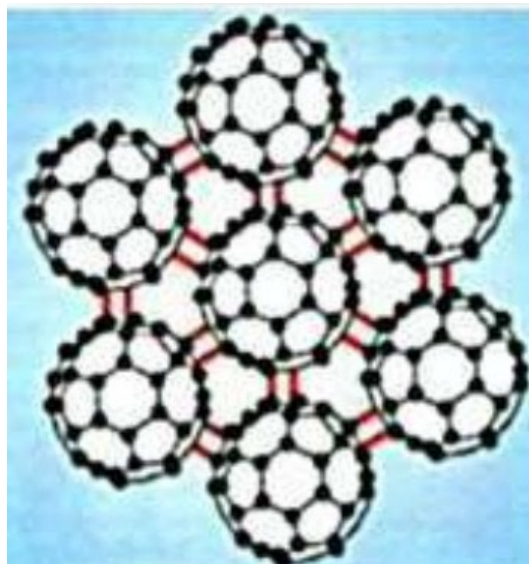


Figure 11. *Polymerised fullerene exhibiting ferromagnetic properties*

Another direction in the use of fullerenes as elementary objects of nanotechnology is the formation of fullerene and metal–fullerene nanocrystalline coatings:

- at low fullerene concentrations in titanium–fullerene coatings deposited in vacuum, the structure-forming particles have a rounded shape and dimensions of 15–40 nm;
- such coatings can be applied as antifriction materials, as electric energy storage devices, etc.

In the future, the addition of fullerenes to alloys is expected for the creation of nanocrystalline bulk materials. Fullerenes can also serve as the basis for the production of unique lubricants.

Yet another way of using fullerenes as elementary nano-objects is associated with the possibility of synthesising crystalline structures based on them. Under certain conditions, spherical C_{60} molecules are arranged in space in the closest packing to form a molecular crystal, *fullerite*:

- the distance between the centres of the nearest fullerene molecules, which are held together by weak van der Waals forces, is ~ 1 nm;
- in a fullerite crystal, C_{60} molecules play the same role as atoms in an ordinary crystal;
- at room temperature ($T \sim 300$ K), a face-centred cubic (FCC) lattice is formed (Figure 12, *a, b*);
- as a result of doping, i.e. filling of the interstitial sites (Figure 12, *c*), new materials (*fullerides*) with a wide range of properties can be formed on the basis of fullerite.

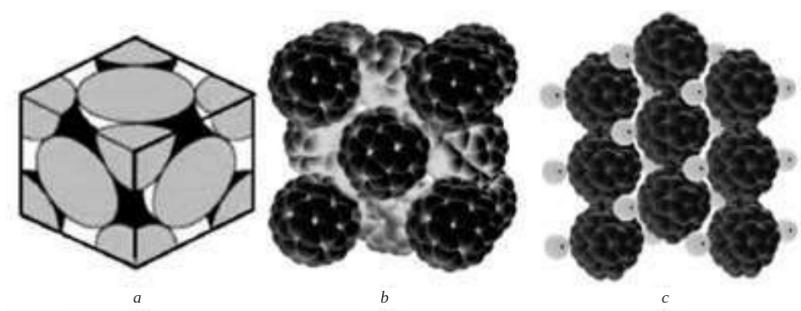


Figure 12. Structure of fullerite: *a* – schematic of the unit cell of the FCC lattice of fullerite; *b* – representation of the unit cell of fullerite by means of C_{60} molecules; *c* – structure of rubidium-doped fullerite

2.3. Electronic structure of fullerenes

The electronic structure of fullerenes is determined by the features of interatomic interaction and chemical bonding associated with the curvature of the surface of these molecules. In C_{60} fullerenes, the chemical bonding is provided by sp^2 -hybrid orbitals:

- sp^2 hybridisation is observed in the bonds between atoms in the hexagons;
- sp^3 hybridisation is observed in the pentagons.

It has been suggested that in C_{60} an intermediate $sp^{2.28}$ hybridisation is realised. It has been shown that the admixture of the sp^3 component to the sp^2 hybridisation is a consequence of the curvature of the fullerene surface.

It was previously believed that fullerenes are formed from flat graphene sheets that have broken away from a graphite layer. When folded, graphene sheets (Figure 13) form halves of C_{60} particles, to which smaller graphite fragments are attached, forming a fullerene.

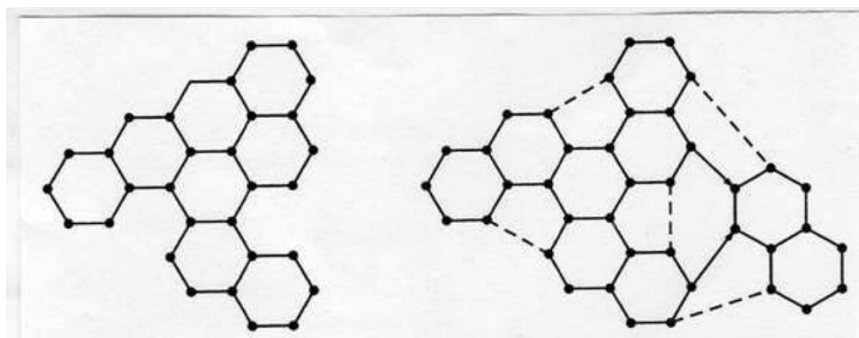


Figure 13. Fragment of graphite that can form half of a fullerene molecule (left), and the scheme of formation of part of a closed cluster from graphite fragments (right)

2.4. Mechanisms of fullerene formation

One of the mechanisms of fullerene formation is the "snail" model.

- According to this model, at the initial stages of fullerene formation the carbon cluster has the form of a curved sheet.
- The bonds between the carbon atoms in such sheets form pentagons and hexagons.

On further growth, the carbon sheet rolls up so as to minimise the number of free bonds. Some of the growing clusters accidentally close into fullerenes (Figure 14), while the rest grow into quasi-helical soot particles.

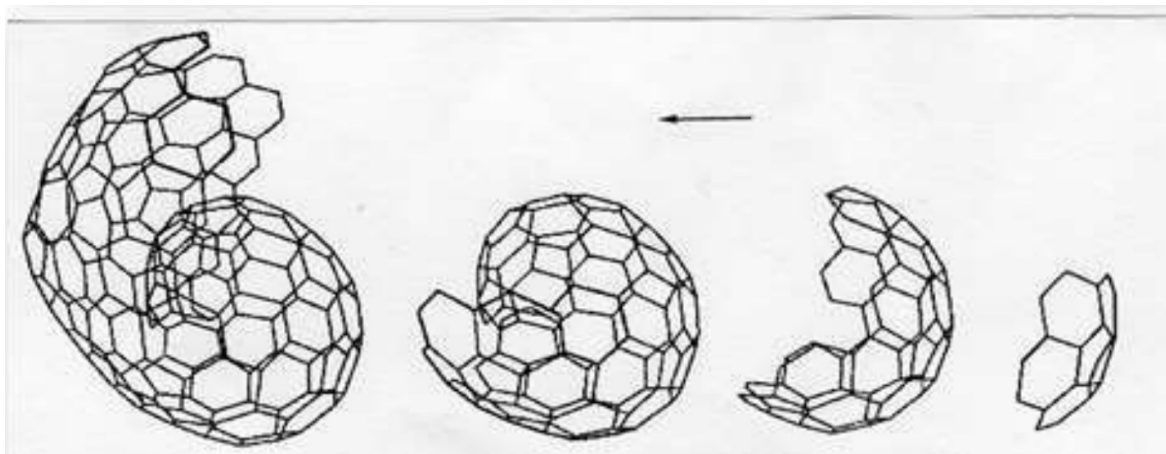


Figure 14. Scheme of fullerene growth according to the "snail" model

R. Smalley and co-authors proposed the "**party line**" mechanism of fullerene formation. According to this model, carbon particles form linear molecules that join and form rings (Figure 15). The addition of small linear chains increases the size of the rings to 25–35 atoms:

- when such domain sizes are reached, polycyclic networks similar to unrolled graphite sheets become the most thermodynamically favourable;
- such graphite sheets have many unsaturated bonds; to minimise them, pentagons are introduced into the carbon network, forming cup-shaped particles;
- from time to time, one of these particles accumulates a sufficient number of pentagons in such a way that the sheet closes, forming a fullerene.

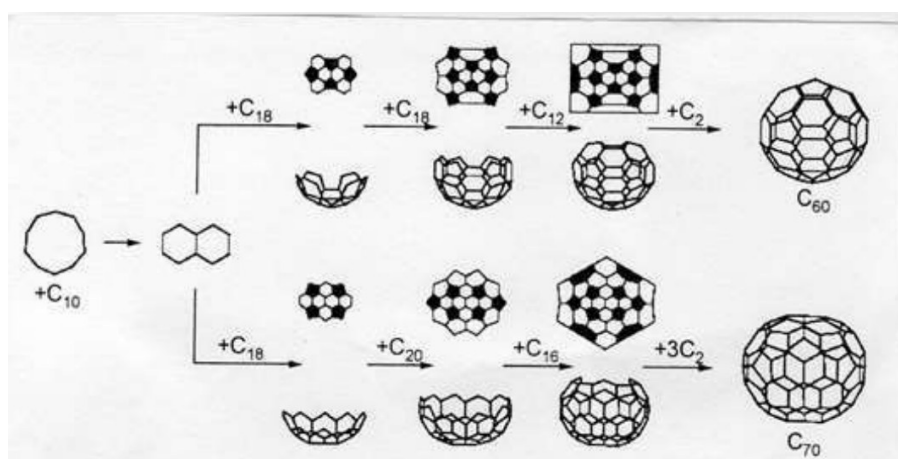


Figure 15. Formation of fullerenes from rings

After the discovery of the method of producing fullerenes in large quantities, R. Smalley and co-authors modified their original theory and developed the "**Pentagon Road**" mechanism.

- According to it, small graphite fragments consist only of five- and six-membered rings, and pentagonal rings cannot be adjacent.

- The basic mechanism of fullerene formation according to the "Pentagon Road" theory consists in the addition of C₂ and other small carbon particles to the edges of growing graphite networks.

The fullerenes formed no longer grow, since all the bonds in them are closed.

The scheme of fullerene formation called the "**Fullerene Road**" differs in that intermediate molecules of 30–58 atoms, like large particles, close into fullerene shells; since small fullerenes cannot satisfy the isolated pentagon rule, they are more active than large molecules with 5–5 bonds.

Some authors explain the formation of fullerenes by annealing of carbon clusters.

2.5. *Non-carbon fullerenes*

There are many calculations of stable closed fullerene-like structures consisting not only of carbon atoms but also of atoms of other elements. In practice, similar structures are obtained on the basis of *silicon* atoms. Potentially, spherical silicon fullerene molecules can be applied in quantum computers, chemical catalysts and superconductors.

The first *metallic analogue of fullerene* was synthesised in 2006 from **gold** atoms:

- only 16 gold atoms were required to form the spherical "golden" fullerene molecule (Figure 16);
- similar molecules of 17 and 18 atoms have also been synthesised.

The molecules obtained are stable at room temperature and can exist independently. Similar gold nanoclusters exhibit fairly strong catalytic properties and can find wide application in various fields.

One of the most promising fields of application of the "golden" fullerene is biotechnology and medicine; a method of delivering DNA into a living cell by means of gold nanoparticles has been developed.



Figure 16. "Golden" fullerene

2.6. Potential fields of application of fullerenes

Fullerenes can be used as *sorbents*, since they have a high sorption capacity, as evidenced by the changes in their properties in various gaseous media.

The effect of non-linear transparency of solutions containing fullerenes and their compounds makes it possible to use them as the basis of optical shutters, i.e. limiters of intense laser radiation in the visible and near-infrared ranges; for C₆₀, the restricted optical range lies in the wavelength interval 400–700 nm.

Promising fields of application of fullerenes are presented in Table 2.

Table 2. Promising fields of application of fullerenes

Main directions and fields of application	Materials and devices based on fullerenes
Structural materials with unique properties	High-strength alloys based on fullerene modifications. Woven materials for special purposes (tapes, fabrics, sails, high-strength threads) based on new polymer molecules modified with fullerenes. Radiation-protective materials based on graphite modified with fullerenes. High-strength concrete polymers. Sealing materials based on graphite modified with fullerenes
Functional coatings and protective technologies	Superhard coatings for tools. Antifriction coatings. Strengthening and stabilisation of paints and varnishes. Improved adhesion and moisture-proof properties of varnishes
Lubricating and cooling materials	Increased efficiency of lubricating and cooling process fluids in metalworking. Effective lubricant additives
Polymers and rubber	Production of polyethylene with extended service and storage life. Production of polyethylene pipe grades with increased strength and elasticity. Protective glass. Production of tyres with improved cross-country ability
Microelectronics	Diamond-like films. Materials for microsensors. Submicron resistors. Ultra-high-density storage media

3. Carbon Nanotubes

3.1. Structure and types of carbon nanotubes

Carbon nanotubes are elongated structures in the form of hollow cylinders consisting of one or several graphite layers rolled into a tube, with a hexagonal arrangement of carbon atoms (Figure 17).

Carbon nanotubes, as a new allotropic form of carbon, were discovered by the Japanese physicist S. Iijima in 1991:

- the diameter of carbon nanotubes is 1–150 nm;
- their length is measured in tens and hundreds of micrometres and is constantly increasing as the technology of their production improves;
- on the surface of the tubes, the carbon atoms are located at the vertices of regular hexagons;
- the ends of the tubes are closed by six pentagons.

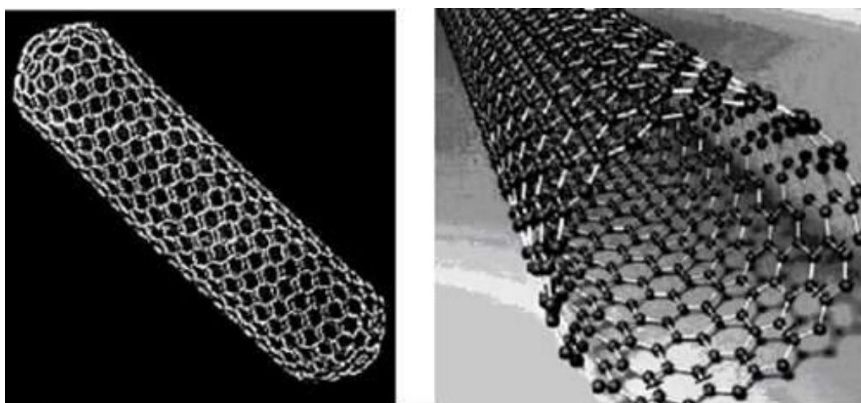


Figure 17. Schematic image of a carbon nanotube (a) and the arrangement of atoms on its surface (b)

Carbon nanotubes can have different atomic structures and, accordingly, different properties (Figure 18).



Figure 18. Examples of some possible structures of carbon nanotubes depending on the way the graphite sheet is rolled: a – armchair structure; b – zigzag structure; c – chiral (helical) structure

Similarly to fullerenes, there are also *multi-walled nanotubes* (Figure 19), which differ from single-walled nanotubes in a much wider variety of shapes and configurations, both in the longitudinal and in the transverse direction.

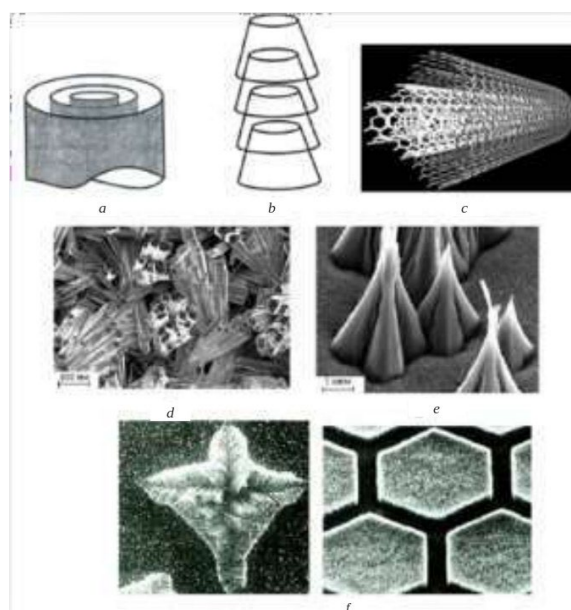


Figure 19. Examples of structures based on carbon nanotubes: a, b – multi-walled cylindrical and conical nanotubes, respectively; c – multi-walled nanotube $C_{60}/C_{240}/C_{540}$; d – "colonies" of carbon nanotubes; e – "bundles" of carbon nanotubes on a silicon surface; f – examples of the diversity of shapes of nanotubes grown artificially (catalytically) in special templates

Multi-walled nanotubes:

- the "Russian doll" structure is a set of coaxially nested single-walled nanotubes (Figure 19, *a*);
- another variety of such structures is a set of nested coaxial prisms (Figure 19, *b*);
- there are also scroll-like structures;
- for all structures, the distance between neighbouring graphite layers is close to 0.34 nm, i.e. the distance between neighbouring planes of crystalline graphite;
- the realisation of one structure or another in a specific experimental situation depends on the conditions of nanotube synthesis.

At present, not only individual nanotubes but also ordered aggregates, namely bundles, colonies (arrays) and ropes, are grown in sufficient quantities; they can be manipulated to create devices and instruments (Figure 19, *d*, *e*). The most promising as the basis of functional materials and devices are homogeneous single-walled nanotubes, which can be practically defect-free.

Along with spheroidal carbon structures, cylindrical structures, so-called nanotubes, which differ in their physicochemical properties, can also form.

3.2. Topological and metric characteristics of nanotubes

The basic element of carbon nanotubes is a graphene sheet rolled into a cylinder, i.e. a monolayer tiled with regular hexagons at whose vertices the carbon atoms are located.

According to the number of layers forming a nanotube, *single-walled* and *multi-walled* (polyhedral) nanotubes are distinguished. Electron microscopy studies show that most nanotubes consist of several graphene layers, either nested one inside another or wound around a common axis.

The distance between neighbouring graphene layers is approximately 0.34 nm, i.e. the distance between neighbouring planes of crystalline graphite. In practice, this distance is distorted by the influence of neighbouring nanotubes; the presence of defects causes distortion of the rectilinear shape of nanotubes into the form of an accordion.

Another type of defect in multi-walled nanotubes is associated with the incorporation of a certain number of pentagons and heptagons into the surface, which consists of regular hexagons; this violates the cylindrical shape. Such defects cause the appearance of bent and helical nanotubes.

The various structural characteristics of carbon nanotubes should lead to differences in the electronic structure of these objects.

3.3. Properties of carbon nanotubes and prospects for their production

The properties of nanotubes depend strongly on their geometry. The electrical properties of nanotubes depend on chirality: they can exhibit metallic conductivity or be semiconductors.

- One-third of nanotubes have metallic conductivity.

- The rest are semiconductors with band gaps from several tenths to 2 eV, which increase as the nanotube diameter decreases.

An *electromechanical effect* has been discovered in individual nanotubes, which consists in a significant change in the electrical conductivity of nanotubes even under slight bending.

Nanotubes have *capillary properties* and can be filled with other elements, including hydrogen, which is important for the development of hydrogen power engineering. Thus, nanotubes can be used as containers for the storage of chemically and biologically active substances: poisonous gases, fuel components and molten metals.

Nanotubes have a high specific surface area and chemical stability, which makes it possible to use them as electrodes of high-capacity, high-power electrochemical capacitors.

Nanotubes are characterised by high catalytic activity and mechanical strength.

- The addition of nanotubes to various alloys makes it possible to increase their strength, wear resistance and crack resistance significantly.
- Nanotubes are also used in the development of new lubricating and cooling mixtures to increase the service life of mechanical friction units of transport systems.

Carbon nanotubes have significant *emission properties* at low electric fields. They have proved themselves as sources of intense field electron emission:

- such properties make it possible to develop high-efficiency low-voltage and low-temperature thermionic emitters based on nanotubes;
- as well as field-emission devices for the creation of economical flat displays, light sources, vacuum pressure sensors, etc.

Superconductivity has been found in nanotubes at temperatures close to 4 K.

The form of carbon under consideration occupies an intermediate position in its structure between graphite and fullerene. However, many properties of nanotubes have nothing in common with these structures.

Owing to the peculiarities of their structure (high bond strength, high packing density of atoms, absence or low density of structural defects), nanotubes have unique physicochemical and mechanical properties.

Modification of carbon nanotubes can be accomplished in several ways:

- filling the inner cavities with substances that change their electronic, magnetic or mechanical properties;
- "grafting" of various functional groups to carbon nanotubes;
- substitution of part of the carbon atoms in carbon nanotubes by atoms of other elements;

- partial or complete "opening" of the double bonds on the lateral surface by means of various reagents.

Among the many unusual properties of carbon nanotubes and their modifications, the most important are the following:

- nanotubes demonstrate high tensile and bending strength;
- the bonds between carbon atoms in a graphite sheet are the strongest known;
- the density of single-walled carbon nanotubes is more than 5 times lower than that of steel, and their strength is more than 20 times higher;
- the specific strength of nanotubes can exceed the corresponding parameter for steel by more than a hundred times.

The Young's modulus of carbon nanotubes ranges from 0.5 to 2 TPa (for steel $E = 0.21$ TPa), which determines their high stiffness.

- At the same time, carbon nanotubes are very elastic in bending owing to the small wall thickness (~ 0.43 nm) and their perfection.
- In addition, the carbon rings of the walls in the form of regular hexagons change their structure on bending but do not break (Figure 20).



Figure 20. Behaviour of carbon nanotubes under extreme deformation

Lightweight composite materials of ultimate strength can be produced from such tubes for the needs of the technology of the new century: load-bearing elements of bridges and buildings, structures of compact aircraft, turbine elements, power units of engines with low specific fuel consumption, etc. One of the ideas under consideration is the creation of *space elevators* capable of transporting loads to space stations; such research is being carried out in NASA laboratories.

Carbon nanotubes are an ideal *reinforcing material* for composite materials with polymer and metal matrices. For example:

- the addition of only 10–12% of multi-walled carbon nanotubes to polypropylene doubles its tensile strength;
- the addition of 5% nanotubes to aluminium doubles its tensile strength.

One of the important tasks of the new carbon materials industry is the creation of nanotubes of "infinite" length. One of the reasons for the high conductivity of carbon nanotubes is the very small number of defects causing electron scattering.

Carbon nanotubes can become ideal connecting wires: it is expected that electric cables made of nanotubes will have a conductivity at room temperature two orders of magnitude higher than that of copper.

A unique feature of nanotubes is that their conductivity depends on their diameter and chirality (the direction of rolling of the tube relative to the graphite sheet). Depending on these factors, nanotubes can show metallic or semiconducting (zigzag structure) properties.

The essence of the *electromechanical effect* in carbon nanotubes consists in a significant change in their electrical conductivity even under slight bending. Examples of the application of this effect are a microphone with an active transducer based on a nanotube that converts sound vibrations into an electromagnetic signal, a subminiature transistor, etc.

Glow of nanotubes is observed when an electric current is passed through them. Nanotubes are unique quantum objects, since their diameter is smaller than the electron wavelength, while their length is macroscopic; this is the basis for their use as quantum rings and nanocoils, cylindrical ultraviolet lasers, resonators, etc.

Similarly to fullerenes, atoms of other substances can be placed in the cavities inside nanotubes. Owing to capillary effects, nanotubes can be used as microscopic containers for the safe transport of chemically and biologically active substances: proteins, poisonous gases, fuel components and molten metals.

The combination of the unusual properties of carbon tubes includes their nanoscale size, high strength, elasticity and the ability to develop resonant mechanical oscillations whose frequency is determined by the geometry of the tube and its elasticity. These "intelligent" properties allow the use of these structures as highly sensitive tools and instruments (Figure 21).

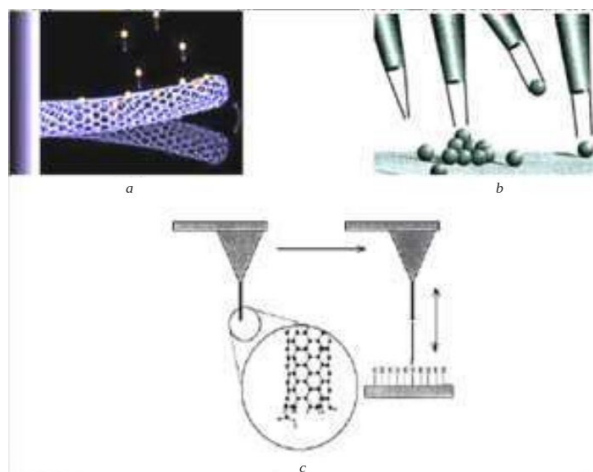


Figure 21. Some examples of the application of the "intelligent" properties of nanotubes: *a* – nanolevers; *b* – nanotweezers, with which particles of nanometre size can be captured and transferred; *c* – chemically modified nanotubes as probes for studying the chemical composition of different surface groups

The unusual properties of nanotubes envisage their wide practical application:

- as an independent material (microelectronics, electrical engineering, the chemical industry, biology and medicine);
- as an elementary object of nanotechnology in the formation of coatings and composite materials of ultimate strength (mechanical engineering, construction, medicine, etc.).

In terms of production volumes, carbon nanotubes occupy second place among nanomaterials.

4. Carbon Nanofibres

Carbon nanofibres are one-dimensional, often hollow formations with a transverse size of 10–100 nm and a length of about 1000 nm.

- Carbon nanofibres can be composed of plane-parallel planes perpendicular to the fibre axis, with graphene-wall cones or truncated cones of small width and height ($\approx 2\text{--}10$ nm).
- There are also "deck-of-cards" type fibres, whose planes are parallel to the fibre axis.
- Nanofibres in the form of spirals can also be created.
- The interplanar distance between graphene planes in nanofibres corresponds to that in graphite: the bond length between hexagons is 0.142 nm, and the interplanar distance is 0.335 nm.

Carbon fibres based on polyacrylonitrile consist of fibrils that form layers oriented mainly along the fibre axis; within a layer, the carbon atoms are arranged similarly to those in graphite and are linked to each other by strong covalent bonds. The bonding between the layers is provided by weak van der Waals interaction.

4.1. Properties of nanofibres

Carbon fibres, unlike the objects considered earlier, are *linear systems* characterised by anisotropy of properties.

Characteristics:

- a high specific surface area;
- conductivity and strength, which make it possible to create on their basis effective catalyst supports for various processes;
- elastic properties and relatively high conductivity make it possible to recommend carbon nanofibres as reinforcing and conductive components in adhesives for joining metallic materials;
- the possibility of using carbon nanofibres for reversible hydrogen storage.

Even a very small amount of carbon nanofibres introduced into a polymer matrix can significantly improve the main mechanical properties of the material and change such properties as electrical conductivity, piezoresistivity, electromagnetic shielding, and heat absorption and dissipation characteristics.

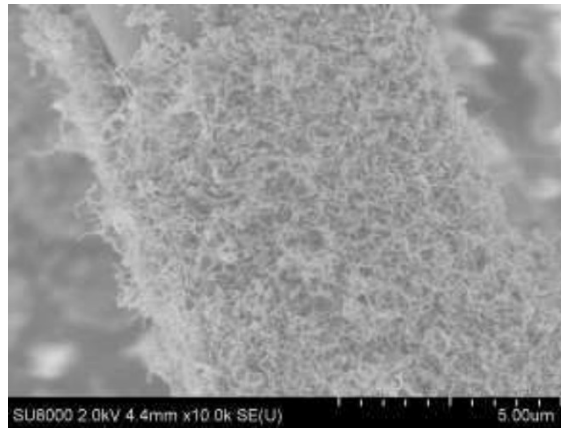


Figure 22. Carbon nanofibres on a fibreglass catalyst containing nickel

4.2. Structural characteristics of carbon fibres

Carbon fibres 18 μm and 30 nm thick obtained from polyacrylonitrile were studied.

- X-ray phase analysis of a sample of large fibres showed that it has a single-phase structure of hexagonal graphite.
- A similar result was obtained in the X-ray phase analysis of nanoscale fibres: in this case too, only the lines of graphite with a hexagonal structure appear on the diffraction pattern.
- The diffraction patterns of the coarse fibre arranged vertically and horizontally do not actually differ, i.e. the diffraction pattern does not change when the shooting geometry changes, since the fibres studied are bundles.

The thickness of the large fibres is 18 μm , and the nanofibres are 3000 times thinner: the thickness of the thin fibres in contact with the bundle is 30 nm.

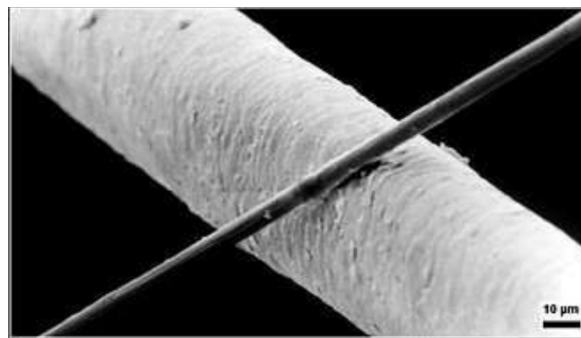


Figure 23. A 6 μm carbon fibre compared with a 50 μm human hair

4.3. Electronic structure of carbon fibres

Owing to the peculiarities of their structure, carbon fibres have high strength and flexibility comparable to those of steel wire, but they are much lighter and more heat-resistant.

Since in composites the layers are located parallel to the fibres, their high longitudinal strength is provided by sp^2 -hybrid bonds. At the same time, in the direction perpendicular to the fibre axes, they readily delaminate owing to weak interplanar interactions.

To determine the parameters of such interatomic interactions, it is necessary to study the electronic structure of these fibres. Taking into account the weak interactions between parallel-oriented graphene layers and their dimensions (layer length 100–200 nm), one can predict that:

- the longitudinal strength is provided by their mechanical interlocking;
- in carbon fibres, the bonds in one graphene strip along the fibre are not broken, whereas broken σ - and π -bonds are present in the transverse sections of the fibres.

Thus, in carbon fibres sp^2 -hybrid bonds are realised along the fibre parallel to the layer axes, while broken σ - and π -bonds are present in the direction perpendicular to the fibres.

Review Questions

1. What properties characterise nanodiamonds?
2. Name the fields of application of nanodiamonds.
3. What is diamond? Describe the structure of nanodiamond particles.
4. Describe the structural components of detonation nanodiamond.
5. How are onions formed?
6. Name the components of the particles. Describe partially transformed diamond.
7. Describe the structure of carbon onions.
8. What are fullerenes? Describe their structure and properties.
9. Describe the structure of the C_{60} molecule.
10. What are endofullerenes? What other compounds can fullerenes form? Describe them.
11. How are fullerenes polymerised? Where are polymerised fullerenes applied?
12. What mechanisms of fullerene formation do you know? Describe them.
13. Name the first metallic analogue of fullerene synthesised in 2006. What properties does it have? In which fields is its application promising?
14. Describe the structure of carbon nanotubes. Name the basic element of carbon nanotubes.
15. Identify the important properties of carbon nanotubes.
16. Name the promising fields of use of carbon nanotubes.
17. Define the term "carbon fibres" and describe them.

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Lecture 14. Physicochemical Foundations of Micro- and Nanotechnology Processes

Outline

1. Self-organisation and self-assembly in nanotechnology: self-organisation in nanotechnology; well-known examples of successful self-organisation; modern examples of self-assembly; self-organisation of nanoparticles on various templates; forms of organisation of polymer systems.
2. Heterostructures and other exotic materials: hybrid nanomaterials; synthesis of nanoparticles in supercritical fluids; nanofluidic systems.

1. Self-Organisation and Self-Assembly in Nanotechnology

1.1. Self-organisation in nanotechnology

The idea of self-organisation (synergetics) already had a place in the classical science of the 18th–19th centuries: the Kant–Laplace cosmogonic hypothesis, Ch. Darwin's theory of evolution, and the Maxwell–Boltzmann theory of the behaviour of thermodynamic systems.

- Modern science has accumulated a large body of experimental observations of the phenomenon of self-assembly. Observations of the self-assembly of biological objects are particularly impressive.
- Hermann Haken, professor at the University of Stuttgart, introduced the concept of self-organisation: "Self-organisation is a process of ordering in an open system owing to the coordinated interaction of the many elements of which it consists."

Thus, **self-assembly** is a term used to describe processes in which disorganised systems come to an ordered state owing to specific, local interactions of the system components.

Two types of this phenomenon are distinguished:

- *dissipative* (the synergetic approach): a process of ordering (spatial, temporal or spatio-temporal) in an open system due to the coordinated interaction of the multitude of its elements;
- *conservative*: phenomena of ordering in high-molecular-weight systems under equilibrium conditions. In the case of static self-assembly, the system approaches a state of equilibrium, decreasing its free energy.

The most striking example of self-organisation is **crystallisation**: chaotically arranged atoms of a substance are transformed into a stable, systematically organised structure; the crystallisation process begins spontaneously and proceeds without any external shaping intervention.

Other examples of the self-organisation of molecules are the processes of building lipid membranes in a living cell:

- these membranes are thin and mobile envelopes that protect the cell organelles from unfavourable external influences (Figure 1);

- the membrane is based on a double layer of molecules having hydrophilic and hydrophobic ends;
- by joining their like ends, the molecules form micelles, i.e. structures with a very high density.

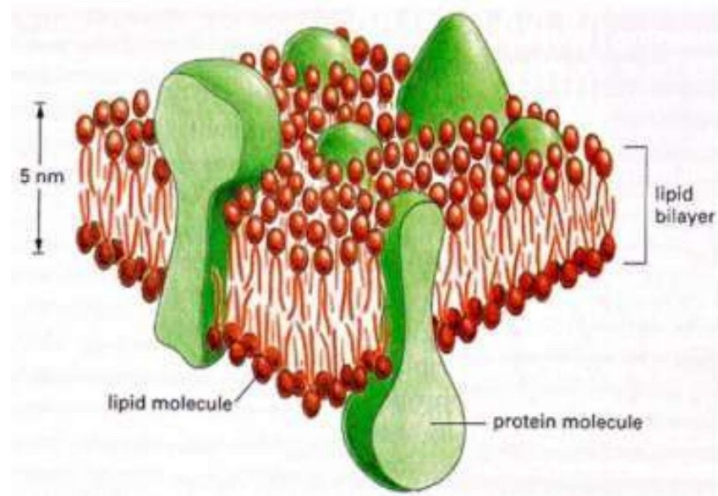


Figure 1. Lipid membrane

Self-organisation processes also manifest themselves in the formation of the DNA double helix by means of hydrogen bonds. Other examples are the association of scattered elementary particles (nucleons and electrons) into atoms, and the formation of gravitational systems of massive bodies rotating around one another (Figures 2 and 3).

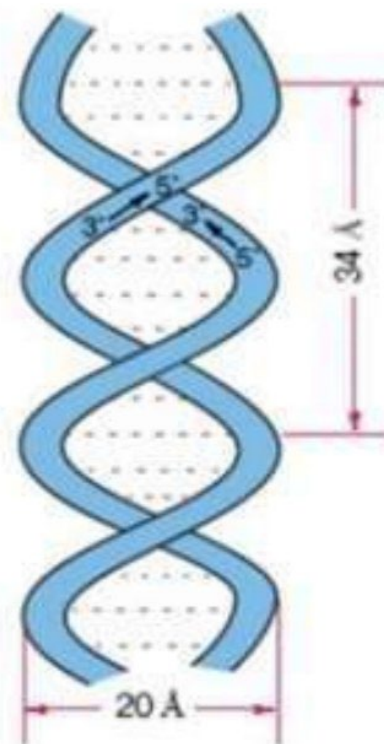


Figure 2. Schematic representation of the DNA double helix (dotted lines indicate hydrogen bonds between the bases)

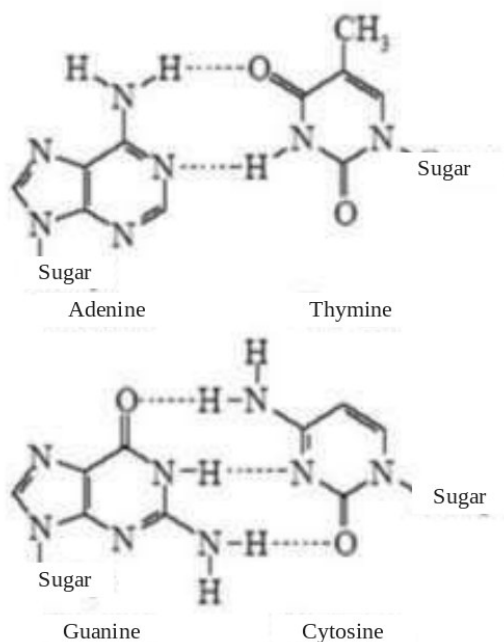


Figure 3. *Hydrogen bonds between complementary pairs of DNA bases (purine–pyrimidine base pairs)*

A **self-assembled monolayer (SAM)** is an ordered layer of amphiphilic molecules in which one end, the "head" group, shows a specific affinity for the substrate.

- The choice of the type of head group depends on the application of the SAM.
- A suitable substrate is selected for interaction with the head group. Substrates can be flat or uneven (nanoparticles). Gold is usually used, since it is inert, compatible with biological materials and easy to obtain.

1.2. Well-known examples of successful self-organisation

Such examples of self-organisation include Liesegang rings, the Marangoni effect, the Belousov–Zhabotinsky reaction and Bénard cells.

Liesegang rings (also Liesegang layers; the general name is Liesegang structures) are concentric rings or rhythmically alternating bands that arise as a result of the periodic precipitation of compounds diffusing in a gel (Figure 4).

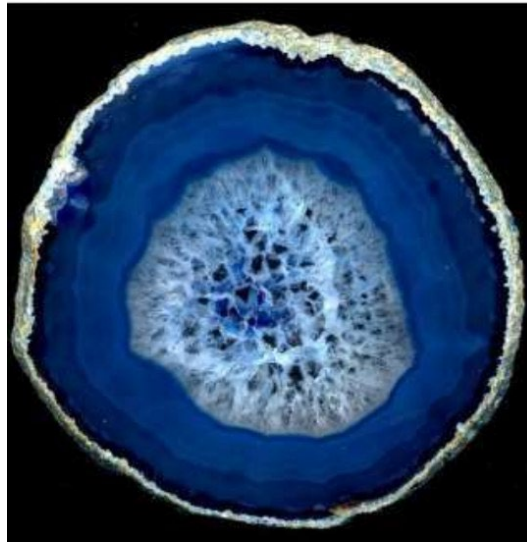


Figure 4. Liesegang rings

The **Marangoni effect** (Marangoni–Gibbs effect) is the phenomenon of mass transfer along the interface between two media, which occurs owing to a surface tension gradient. This type of convection is called capillary or Marangoni convection (a well-known example is the "tears of wine").

The "tears of wine" (Figure 5) are clearly visible on the shadow cast by a glass. The reasons for the appearance of the so-called "tears of wine" were first discovered in 1855 by James Thomson. In 1865, Carlo Marangoni carried out a detailed study of the effect for his doctoral dissertation.



Figure 5. Tears of wine

The **Belousov–Zhabotinsky reaction** is a class of chemical reactions that proceed in an oscillatory mode, in which certain reaction parameters (colour, concentration of components, temperature, etc.) change periodically, forming a complex spatio-temporal structure of the reaction medium (Figure 6).

At present, this name unites a whole class of related chemical systems that are similar in mechanism but differ in the catalysts used (Ce^{3+} , Mn^{2+} and complexes of Fe^{2+} , Ru^{2+}), organic reducing agents (malonic acid, bromomalonic acid, citric acid, malic acid, etc.) and oxidants (bromates, iodates, etc.).

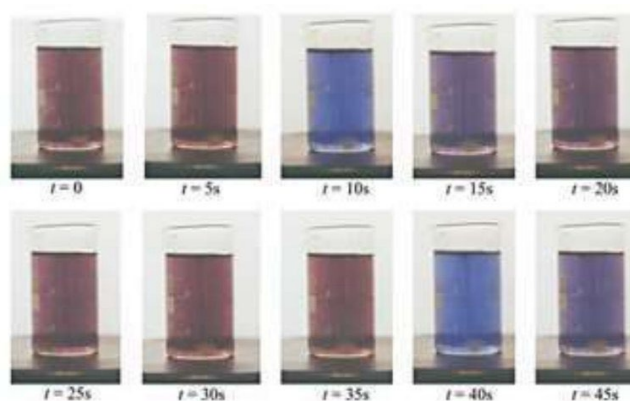


Figure 6. Change in the colour of the reaction mixture in the Belousov–Zhabotinsky reaction with ferroin

Bénard cells (Rayleigh–Bénard cells) are the emergence of order in the form of convective cells shaped as cylindrical rolls or regular hexagonal structures in a layer of viscous liquid with a vertical temperature gradient, i.e. uniformly heated from below (Figure 7). Rayleigh–Bénard cells are one of the three standard examples of self-organisation, along with the laser and the Belousov–Zhabotinsky reaction.

- The control parameter of self-organisation is the temperature gradient (Figures 7 and 8).
- Owing to heating, the initially homogeneous liquid layer begins to develop density inhomogeneities as a result of diffusion.
- When a certain critical value of the gradient is exceeded, diffusion does not manage to bring the temperature distribution in the volume to a homogeneous state.

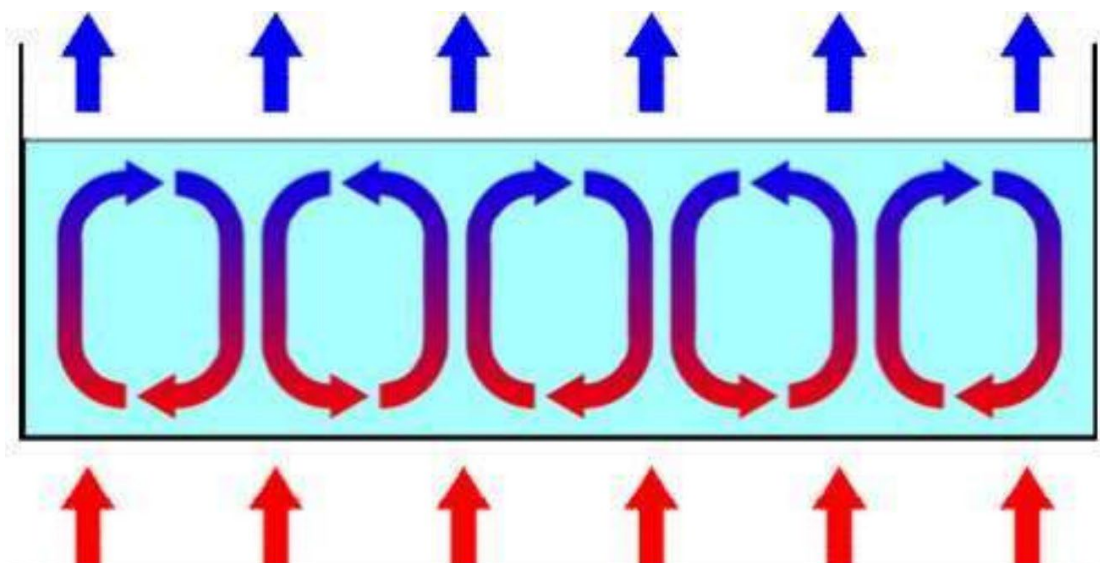


Figure 7. Scheme of the emergence of Bénard cells (heating from below, cooling from above)

- Cylindrical rolls arise that rotate towards each other (like meshing gears).
- As the temperature gradient increases, a second critical transition appears.
- To accelerate diffusion, each roll disintegrates into two smaller rolls.
- With a further increase in the control parameter, the rolls are fragmented and turbulent chaos arises, which is clearly visible in the bifurcation diagram, or Feigenbaum tree.

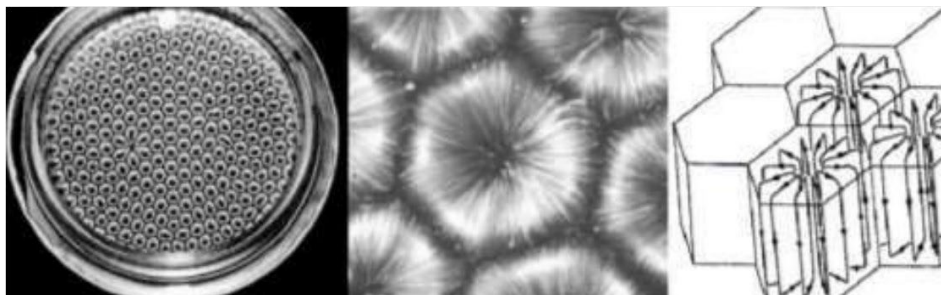


Figure 8. Bénard cells and their emergence

In thin layers heated from below, cells of regular hexagonal shape are formed, inside which the liquid rises at the centre and falls at the edges of the cells. This setting of the experiment was historically the first, but here Marangoni convection was actually observed, which occurs because of the action of surface tension forces and their dependence on the temperature of the liquid.

1.3. Modern examples of self-assembly

Creation of organic nanofilms. Principle of operation:

- a well-cleaned solid substrate is immersed in a dilute solution of a positively charged polyelectrolyte for a time optimal for the adsorption of one monolayer (≈ 1 nm thick);
- it is then washed and dried (usually in a gas jet);
- next, the plate with the positively charged layer is immersed in a solution of a negatively charged polyelectrolyte or of nanoparticles for the time necessary for the adsorption of a monolayer;
- the disc is again washed and dried;
- in this way one bilayer "sandwich" is obtained. Proceeding in a similar way, a film of the desired thickness can be obtained.

In the formation of multilayers, the effective adsorption of one layer takes place at the stage of immersing the plate in the polyelectrolyte solution, while desorption of the nanoparticles that form the second and subsequent layers takes place during washing of the plate. Experience has shown that a 1–2-minute intermediate washing of the sample removes $\approx 10\%$ of the particles weakly bound to the deposited layer, thereby providing more homogeneous and controllable films.

Layer-by-layer assembly using organic solvents.

- To prove the influence of hydrophobic interactions on film assembly, studies were carried out using modified polysaccharides, carboxymethylpullulan (CMP), with different degrees of hydrophobicity. Alkyl chains were grafted onto the carboxymethyl groups.
- It was found that the modified molecules form films equally well with different polycations. Conversely, the use of unmodified CMP and the same polycations showed that film growth depends on the nature of the polycation.
- An important factor in the assembly process is intermediate drying of the films: polyvinyl chloride (PVC) adsorbed on the surface of the plates becomes insoluble in aqueous solution.
- When the polycation polylysine was used, film growth based on unmodified CMP stopped after the formation of several bilayers, whereas the film based on modified CMP grew without limit.

This indicates the importance of hydrophobic interactions in the creation of thin polymer films by layer-by-layer assembly. Fields of application include microchips, new-generation organic films, DNA nanotechnology and medicine.

DNA nanotechnology. In this case, DNA is used as a structural material rather than as a carrier of biological information; for example, for the production of two-dimensional periodic lattices (by the method called "DNA origami") or three-dimensional structures in the form of polyhedra (Figure 9).

Several years ago, a group of Russian, German and Dutch scientists announced that they had implemented one of the most promising directions in the field of self-assembly: the development of self-assembling microcircuits. The scientists developing the project succeeded in making molecules assemble themselves according to a given template into a working device a few nanometres thick.

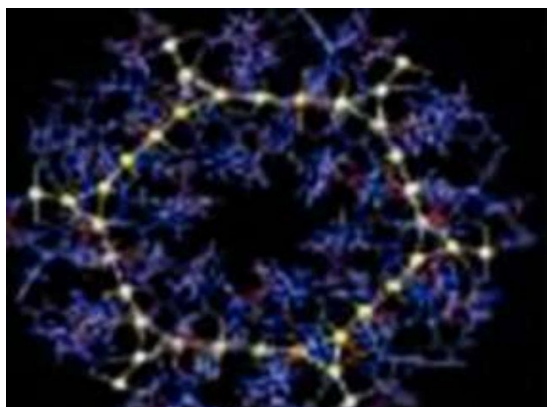


Figure 9. Example of self-assembly: gold nanoclusters on a single-crystal surface

Single-walled nanotubes rolled into rings can be obtained as follows:

- a suspension of single-walled nanotubes in water is treated with ultrasound, as a result of which 50% of them roll up into rings with a characteristic diameter of 100 to 800 nm;
- the nanotubes (hydrophobic particles) act as centres for the formation of cavitation bubbles, around which they coil;
- in the rolled-up state, such objects are held by van der Waals forces.

Molecular dynamics modelling has shown that van der Waals forces keep a ring 20 nm in diameter in the closed state at 300 K (Figures 10 and 11).



Figure 10. Ring 20 nm in diameter and 0.7 nm thick; the chemical bonds at the open ends are terminated with hydrogen atoms. The structure was optimised in the AMBER force field

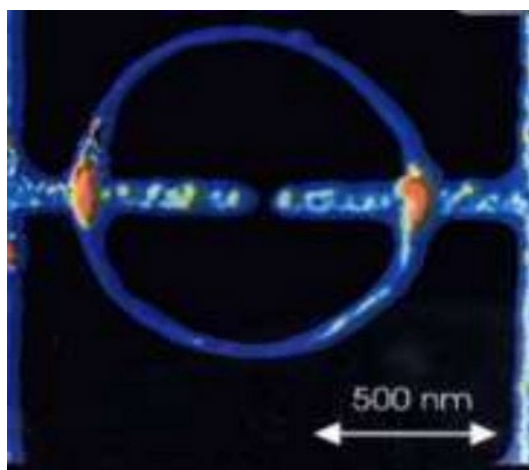


Figure 11. Single-walled nanotube rolled into a ring 600 nm in diameter and placed on a gold electrode

Self-assembled monolayers can also be used for coating nanoparticles. For example:

- gold nanoparticles can be passivated with a self-assembled layer of octadecanethiol ($\text{C}_{18}\text{H}_{37}\text{S}-\text{Au}$);
- here a long hydrocarbon chain is bound at one end by the thiol group SH to the gold nanoparticle with the formation of a strong S–Au bond;
- the attraction between the molecules leads to their symmetrically ordered arrangement around the particle;
- such a symmetrical arrangement of molecules around particles is characteristic of self-assembled monolayers (Figure 12).

Thus, for a system to self-organise, it must have three main properties: openness, non-linearity and dissipativity.

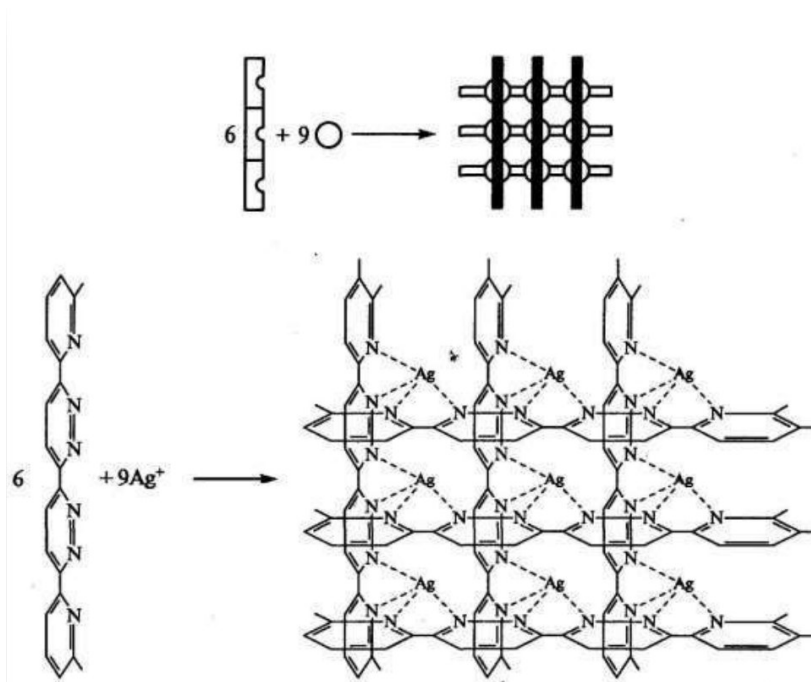


Figure 12. Scheme of the self-assembly of a lattice from six linear molecules and nine silver ions

Examples of dissipative self-organisation in nature are shown in Figures 13 and 14.



Figure 13. Honeycomb as an example of dissipative organisation in nature



Figure 14. Bees in a hive

1.4. Self-organisation of nanoparticles on various templates

Self-assembly is a process of formation of ordered supramolecular structures or media in which only the components (elements) of the initial structures participate in practically unchanged form; they combine additively, like the parts of a whole, which results in a complex structure.

- Therefore, carbon nanotubes, block copolymers, DNA molecules and viruses can be used as templates for the organisation of nanoparticles.
- A strong interaction between the template and the nanoparticles leads to the formation of structures whose form is determined by the template (Figure 15).

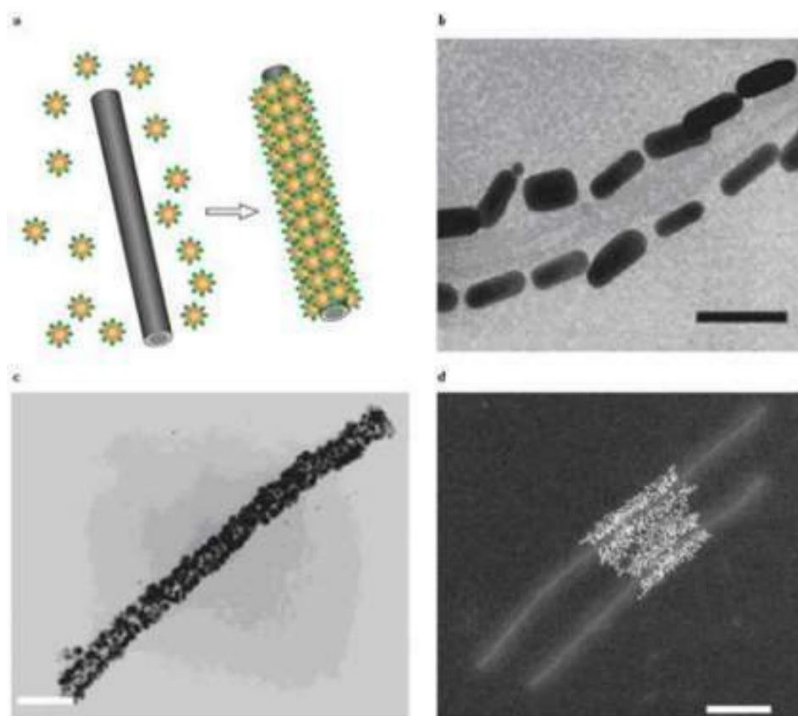


Figure 15. Strong interaction between the template and nanoparticles

The process of self-organisation can be controlled by means of external fields or influences (Figure 16):

- ferromagnetic nanoparticles line up along magnetic field lines;
- particles that have a dipole moment line up along electric field lines;

- the self-organisation of nanoparticles with photoactive ligands can be controlled by light.

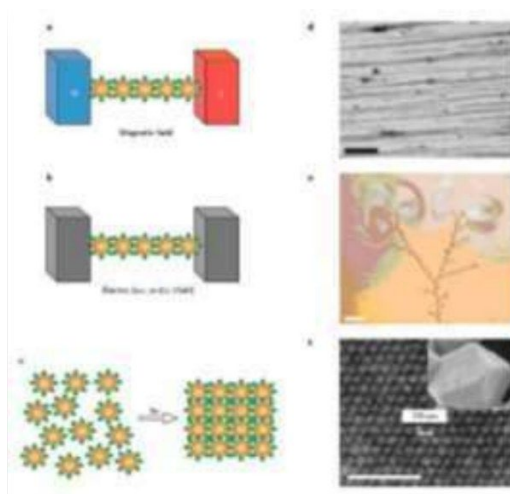


Figure 16. Self-organisation of nanoparticles into a lattice structure under the influence of external fields

A combined hexadentate ligand (8) undergoes self-organisation in the presence of silver ions with the formation of a 3×3 lattice structure; six ligand molecules and nine silver ions are involved in the formation of the lattice (the self-organisation proceeds owing to the coordination bonds between them, Figure 17).

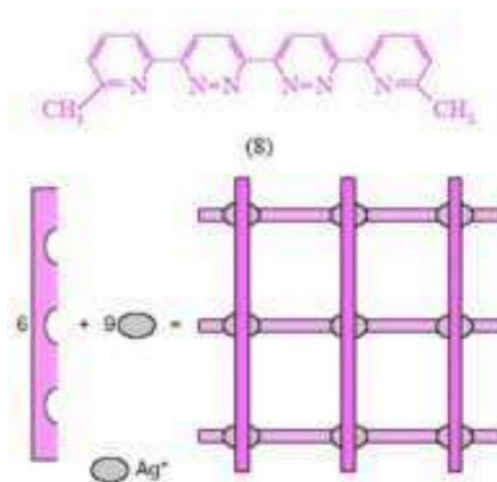


Figure 17. Self-assembly of ligand (8) with silver ions

1.5. Forms of organisation of polymer systems

For polymer systems, the structural variety (polymorphism) is even wider than in the case of low-molecular-weight amphiphiles. This is determined by:

- the great chemical diversity of macromolecules;
- the higher stability of the superstructures formed, which is due to entropic reasons.

In this case, blocks of one type form spherical micellar domains about 10 nm in size, which constitute the framework of the structure, while blocks of the other type fill the inter-domain space. Such a nanometre morphology is characteristic of melts of block copolymers with neutral blocks (Figure 18).

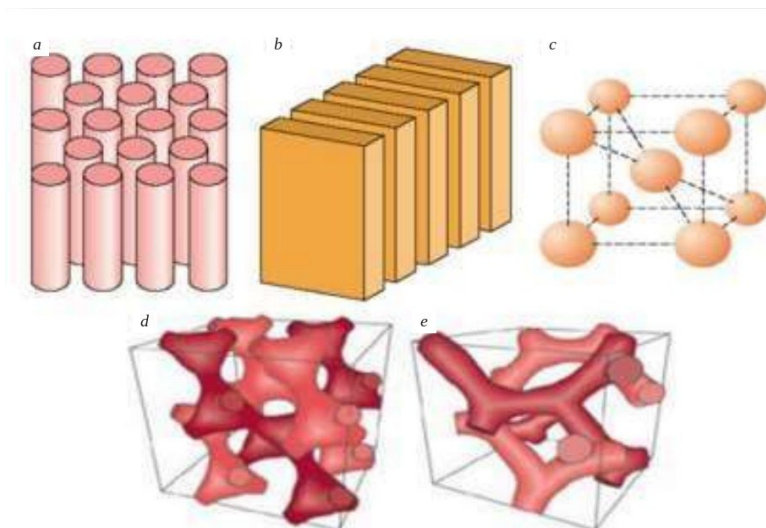


Figure 18. Schematic images of some regular superstructures: *a* – hexagonal mesophase; *b* – lamellar mesophase; *c* – cubic mesophase; *d* – bicontinuous double-diamond structure; *e* – bicontinuous gyroid structure

- At temperatures below 100 °C, molecular self-assembly leads to the formation of a hierarchical lamellar morphology with alternating layers built of the two types of blocks (Figure 19, *a*).
- A small increase in temperature destroys the microstructure of the first type (Figure 19, *b*); the conductivity of the system increases sharply.
- Above 150 °C, the blocks organise into cylinders (Figure 19, *c*), and the electrical conductivity drops abruptly.

Thus, within a narrow temperature interval, this system can operate as a molecular electronic device. A supramolecular ensemble with a reconfigurable microarchitecture is shown in Figure 19.

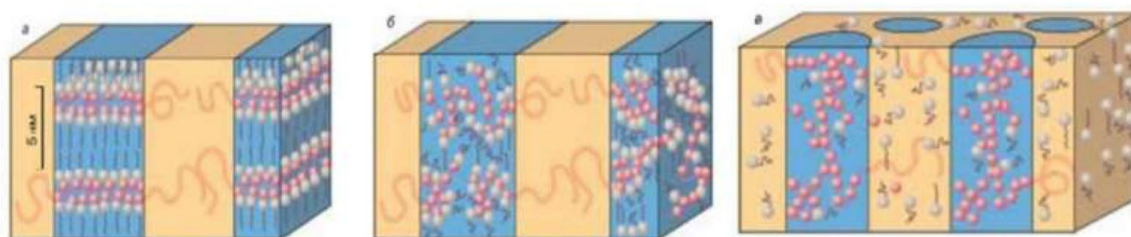


Figure 19. Supramolecular ensemble with a microarchitecture that is rebuilt at temperatures $T \leq 100$ °C (*a*), 100 °C $< T < 150$ °C (*b*) and $T \geq 150$ °C (*c*)

Application of self-organising polymers. This includes:

- the traditional task of creating new structural materials;
- a relatively recent task aimed at creating macromolecular devices for optoelectronics, ordered molecular media for functional purposes (for example, for controlled catalysis of chemical reactions or the transport of ions and molecules), etc.

In all cases, interest in self-organising polymers is determined by their ability, on the one hand, to form stable and often highly ordered nanostructures and, on the other hand, to change their form of self-organisation easily under small changes in external parameters. Self-organising molecules and polymers will be able to play a decisive role in the development of nanotechnology.

In most cases, traditional chemical synthesis can serve only as:

- the first stage, i.e. the initial stage of obtaining the necessary molecular blanks (building blocks);
- the next stage is the self-organisation of such blocks into three-dimensional supramolecular ensembles with a particular hierarchy of structural levels (Figure 20).

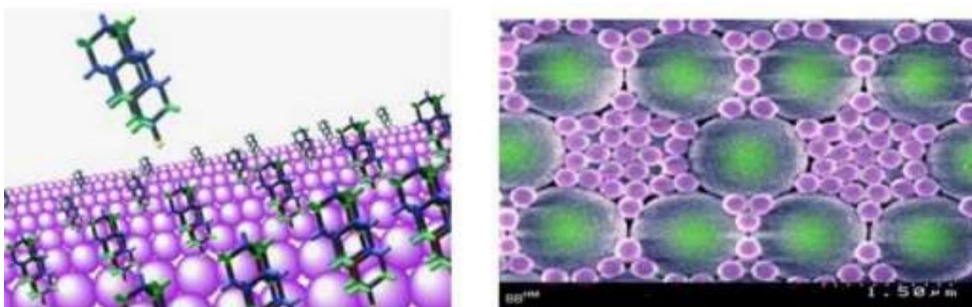


Figure 20. Example of self-organisation

Therefore, **self-organisation** is a process of ordering of the elements of one level of a system owing to internal factors, without a specific external influence (a change in external conditions may have a stimulating or suppressing effect). Under certain conditions, micro- or nano-objects themselves begin to line up in the form of ordered structures.

There is nothing contradicting the fundamental laws of nature here: the system in this case is not isolated, and a certain external influence is exerted on the nano-objects. However, this influence is directed not at a specific particle, as happens in "top-down" assembly, but at all of them at once.

- There is no need to build the required structure manually, placing nano-objects one by one at the necessary points in space; the conditions created are such that the nano-objects do it themselves and simultaneously.
- Processes that use the creation of such special conditions are called *self-assembly processes*, and they already play a very important role in many fields of science and technology.

Returning again to the concept of self-assembly, it should be emphasised that this term is used to describe processes in which disorganised systems come to an ordered state owing to specific, local interactions of the system components. For self-assembling components, all that is required of a human is to put a sufficient number of them into a test tube and allow them to assemble automatically into the required configurations according to their natural properties. The property of self-organisation belongs to the system as a whole, but not to its individual elements.

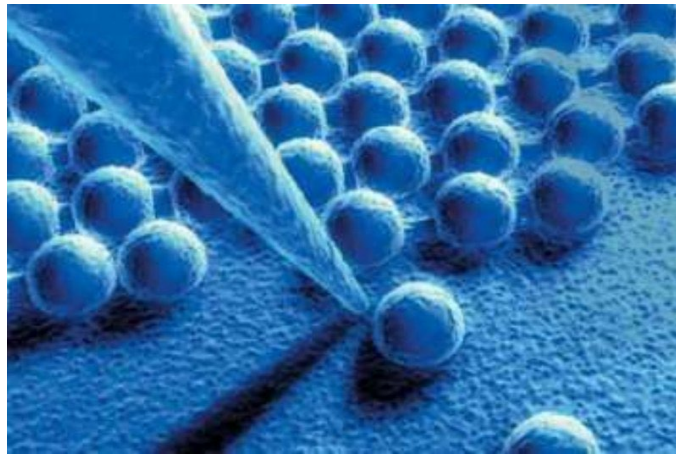


Figure 21. *Cantilever over the surface under study*

The **formation of droplets from vapour** is self-organisation of the first type:

- it is the formation of structures from initially uniformly distributed substances (Figure 22);
- self-organisation of the first type produces static structures.



Figure 22. *Self-organisation of vapour droplets*

Self-organisation of the second type is the formation of qualitatively new structures. These are temporal and spatio-temporal structures, *patterns*, which require a constant supply of energy and matter. Examples are the transition from laminar to turbulent flow, the magnetisation or demagnetisation of substances, changes in the state of aggregation, electrification and changes in crystal symmetry. In all these cases, self-organisation takes place.

For the process of self-organisation to proceed, the following conditions are necessary:

1. The open system must be in a strongly non-equilibrium state.
2. There must be a strong non-linear coupling between the elements of the system, which determines the collectivity, cooperativity and coherence of motion.
3. The system must have a sufficiently high level of fluctuations prone to growth.
4. The system must be prone to bifurcations, i.e. the energy influx into the system must ensure that the system reaches a critical state (bifurcation point), followed by an abrupt exit from this state in the manner of a phase transition.

2. Heterostructures and Other Exotic Materials

2.1. Hybrid nanomaterials

Most of the well-known and well-studied materials, such as metals, ceramics and plastics, cannot always fully satisfy human needs. However, scientists and engineers have long noticed that various combinations of materials often exhibit improved properties compared with the individual substances.

One of the most successful examples of such mixtures is *composite materials*, which are formed from a base substance distributed in one way or another in the volume of a second substance called the *matrix* (Figure 23).

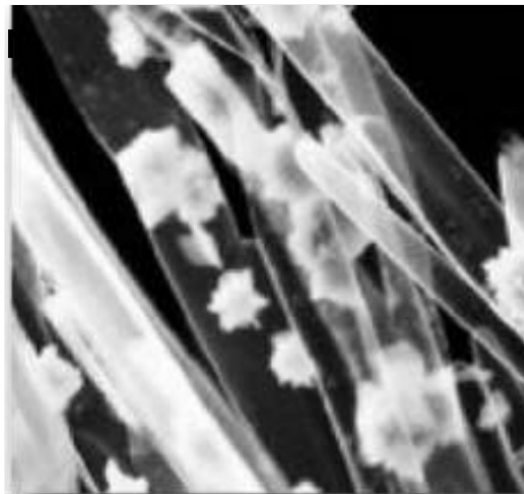


Figure 23. *Structure of a composite material*

- Natural composites built simultaneously from organic and inorganic components, for example nacre (mother-of-pearl) and bone, are of special interest.
- However, in natural composites the size of the inorganic particles lies within the range from several micrometres to several millimetres; therefore, the material is heterogeneous, which can sometimes be noticed even with the naked eye (Figure 24).



Figure 24. *Composite materials based on nacre*

If the size of the inorganic particles of a hybrid material is reduced to the molecular size of the organic part (several nanometres), the homogeneity of the composite can be increased and materials with improved or even entirely new properties can be obtained. They are called **hybrid nanomaterials**.

As an example, one can consider a material in which inorganic fibres are distributed in a polymer matrix:

- the inorganic component provides the mechanical strength of the material;
- the organic component is the binder between the inorganic parts and provides flexibility and a certain softness of the material.

The inorganic building blocks of such materials can be nanoparticles, macromolecules, nanotubes or layered substances (Figure 25).

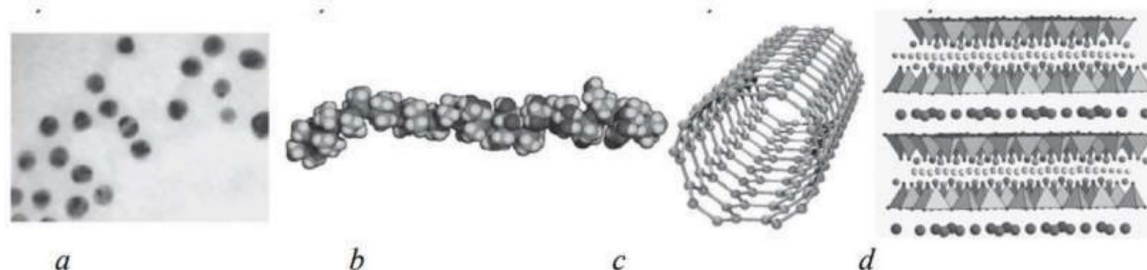


Figure 25. Building blocks of hybrid nanomaterials: *a – nanoparticles; b – macromolecules; c – nanotubes; d – layered substances*

Depending on their purpose, hybrid materials are conventionally divided into three groups: *structural*, *functional* and *multifunctional*.

Structural composites are used to create building and technological structures (cement, concrete) and are, as a rule, products of large-tonnage production.

Functional and multifunctional composites have specific optical, magnetic, electrical, chemical or biological properties and are produced on various scales, from large-tonnage quantities to batches of several grams.

Substances consisting of inorganic matrices formed by silicates with inclusions of organic molecules are used as *photochromic* materials (which change colour when irradiated with light) and *electrochromic* materials (which change colour when an electric charge is passed). By changing the organic component, the optical properties can be controlled, which is associated with the creation of various coatings based on hybrid materials.

Fields of application:

- medicine: the mechanical strength of materials is provided by the inorganic parts, and biocompatibility by the organic molecules;
- solid electrolytes: a combination of the ionic and electrical conductivity of various organic molecules with the heat resistance and strength of inorganic matrices.

2.2. Synthesis of nanoparticles in supercritical fluids

A **supercritical fluid** is a state of matter in which the difference between the liquid and gas phases disappears. Any substance at a temperature and pressure above its critical point is a supercritical fluid (Figures 26 and 27).

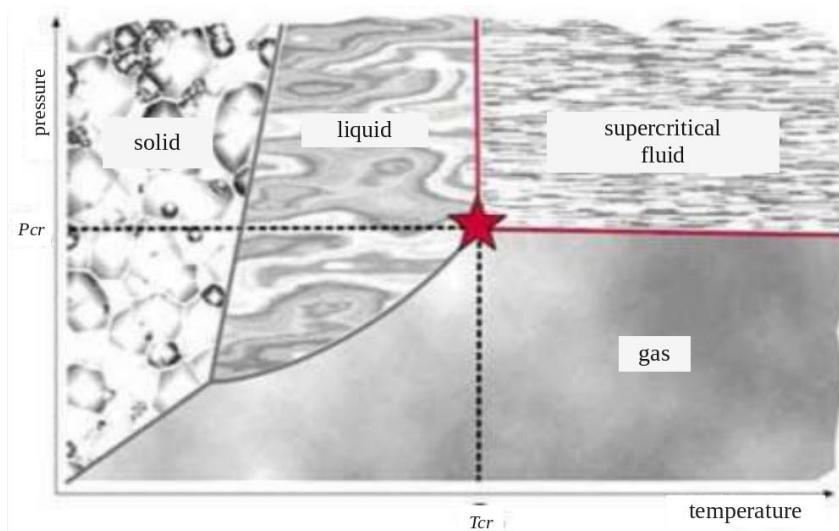


Figure 26. Scheme of the phase states of matter

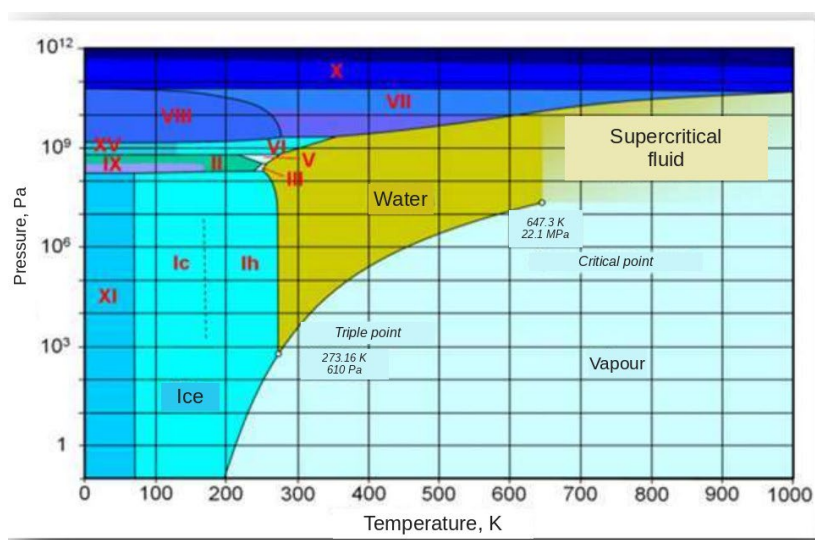


Figure 27. Phase states of water

The main properties of supercritical fluids are:

- low viscosity;
- a high diffusion rate of the components;
- high solubility of substances;
- absence of a liquid–vapour interface;
- ease of removal after the process.

The low viscosity and high diffusion rate of the components make it possible to synthesise nanoparticles of various structures and compositions in them.

As the pressure increases, the solubility of the components increases. Therefore, a higher supersaturation of the solution can be achieved (Figure 28):

- the region of existence of a supersaturated solution is wider at pressure $P_2 > P_1$;
- however, at very high pressure the structure of the material being synthesised may change.

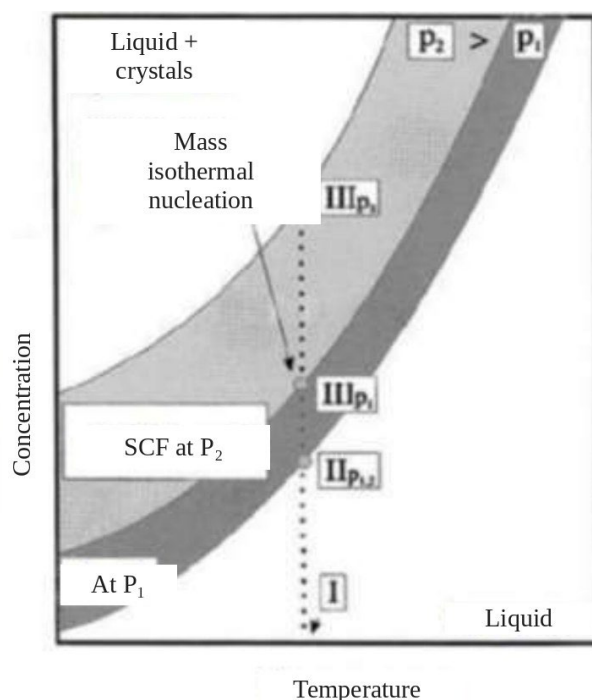


Figure 28. Influence of temperature and pressure on the phase state of the fluid

The main parameters affecting the morphology of the nanomaterials synthesised are the *temperature* and *pressure* in the reaction medium.

- The rate of formation and the stability of the crystallising material, as well as the convection regime within the reaction vessel, depend on temperature.
- As the pressure increases, the solubility of the components increases; therefore, a higher supersaturation of the solution can be achieved (Figure 28). The region of existence of a supersaturated solution is wider at pressure $P_2 > P_1$.

Depending on the stability of the precursor and the compounds synthesised, the process duration is selected:

- for unstable compounds, the synthesis time must be minimised;
- thermodynamically stable phases are synthesised over a long time (Table 1).

Table 1. Parameters of the transition of water and carbon dioxide to the supercritical state

Substance	Critical temperature, °C	Critical pressure, atm
Carbon dioxide	31.1	72.8
Water	374.2	217.6

Methods of synthesising nanoparticles and nanomaterials in supercritical fluids can be classified depending on the role of the supercritical fluid in the synthesis process: the supercritical fluid as a solvent; as an antisolvent; or as a solute.

The RESS method (rapid expansion of supercritical solutions):

- the target component is dissolved in supercritical CO₂ at a certain temperature and pressure;
- this solution is then sprayed at high velocity through a nozzle or capillary into a collector at atmospheric pressure (Figure 29);
- as a result, a high supersaturation is created, which leads to the formation of many crystallisation centres;
- rapid expansion of the supercritical solution into a liquid solvent is also possible;
- when scaling up, a sintered or porous disc is used for spraying.

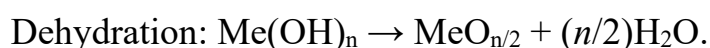


Figure 29. The RESS method

Advantages of the method: relatively simple hardware design; the possibility of synthesising nanoparticles with a narrow size distribution; absence of contamination by organic solvents. *Drawbacks:* a large consumption of solvent is required; therefore, the cost of the product increases.

Hydrothermal synthesis is a method of producing various chemical compounds and materials using physicochemical processes in closed systems, which are carried out in aqueous solutions at temperatures above 100 °C and pressures above 1 atm.

Hydrothermal synthesis of metal oxide nanoparticles from their salts in supercritical H₂O is carried out as a result of a two-stage reaction of hydrolysis and dehydration:



Let us describe the principle of synthesis in supercritical CO₂:

- the target component is dissolved in supercritical CO₂ at a certain temperature and pressure;
- this solution is then sprayed at high velocity through a nozzle or capillary into a collector at atmospheric pressure (Figure 30);
- as a result, a high supersaturation is created, which leads to the formation of many crystallisation centres;
- rapid expansion of the supercritical solution into a liquid solvent is possible.

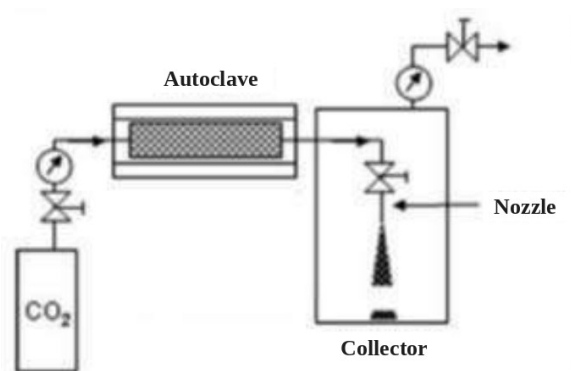


Figure 30. Scheme of a nanoparticle synthesis unit

Examples of hydrothermal synthesis products are presented in Figures 31 and 32.

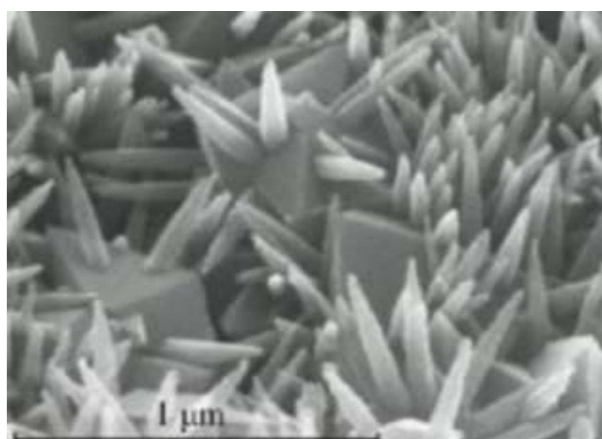


Figure 31. Nanocrystalline TiO_2 obtained by the hydrothermal method

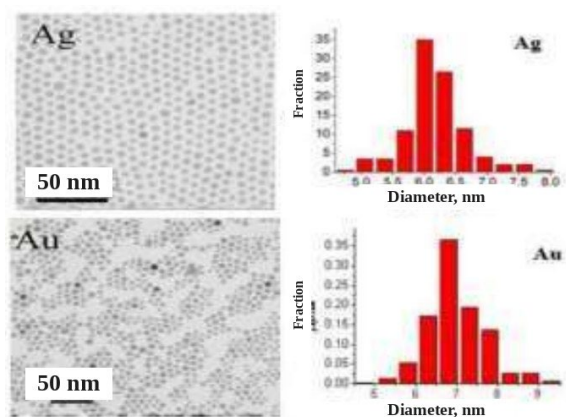


Figure 32. Micrographs and size distributions of Ag and Au nanoparticles synthesised under hydrothermal conditions

Under hydrothermal conditions, both spherical semiconductor nanoparticles and branched structures can be synthesised (Figures 33 and 34).

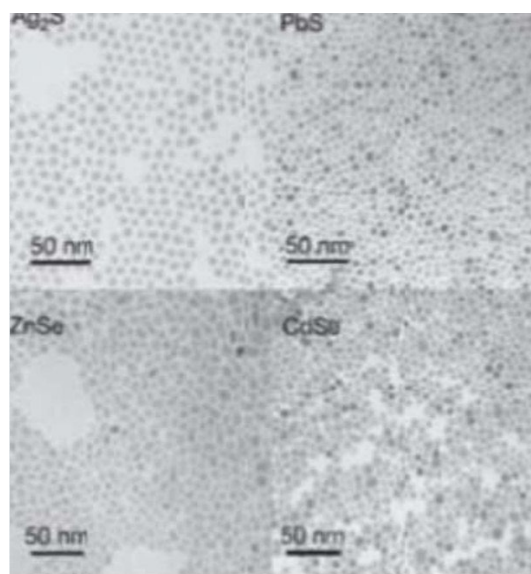


Figure 33. Spherical semiconductor nanoparticles (Ag_2S , PbS , ZnSe , CdSe) synthesised under hydrothermal conditions

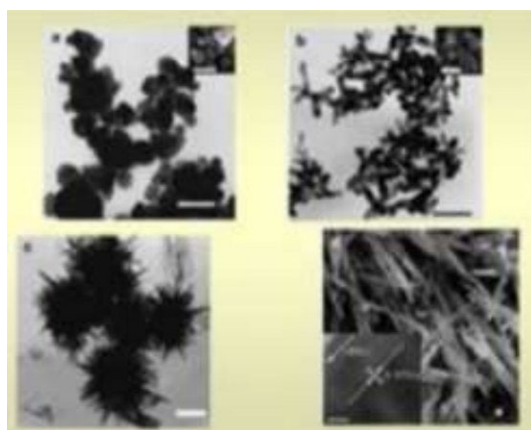


Figure 34. Non-spherical and branched CdS nanoparticles synthesised under hydrothermal conditions

A method of hydrothermal synthesis of particles of complex metal oxides, for example LiCoO_2 , is known, in which nanoparticles are synthesised continuously in supercritical water. The method involves a separate supply to the reactor of salt solutions of $\text{Co}(\text{NO}_3)_2$, lithium hydroxide LiOH and hydrogen peroxide H_2O_2 . In the prototype, hydrogen peroxide is used to obtain oxygen by decomposition of H_2O_2 and its subsequent participation in the oxidation of Co^{2+} .

Synthesis of LiCuO_2 :

- the mother solution (0.1 M) is prepared by dissolving the salts lithium nitrate LiNO_3 and copper acetate $\text{Cu}(\text{CH}_3\text{COO})_2$ in water;
- the hydrothermal synthesis temperature was varied in the range 380–390 °C, and the pressure 226–230 atm;
- according to scanning electron microscopy data, the sample synthesised is a polycrystalline mixture of crystals with a high degree of faceting, corresponding to cubic symmetry and fairly uniform in habit;

- their shape and dimensions are: isometric (cubes) 50 nm; elongated (parallelepipeds) 50×150 nm; flattened (plates) 50×100 nm;
- dendritic growths of these crystals are characteristic;
- on the surface of the crystals, under the electron beam, an amorphous molecular layer with a thickness of the order of molecular dimensions is formed, which is inherent in crystalline lithium compounds.

Advantages of this method: relatively simple hardware design; the possibility of synthesising nanoparticles with a relatively narrow size distribution; absence of contamination by organic solvents.

This method makes it possible to synthesise metal oxide nanoparticles of the required size and properties. In terms of the parameters of the transition to the supercritical state, availability, cost and environmental safety, it is most appropriate to use supercritical water and carbon dioxide.

2.3. Nanofluidic systems

The term **nanofluidics** means that a device controls the motion of liquids and certain ions through channels of submicrometre diameter. Microfluidic systems, long known in the scientific arena, have acquired a new embodiment by means of nanotechnology:

- nanofluidic systems are already used in hybrid nanoelectronic devices that make it possible to obtain electricity from biochemical processes taking place in living cells located in vitro (inside) the chip.

Engineers predict that, just as electronic semiconductor transistors served as the building blocks of microcircuits, the nanofluidic transistor will become the basis for miniature "lab-on-a-chip" chemical factories operating without any moving parts.

The principle of operation of the transistor is similar to that of its "electronic" counterpart, but instead of a flow of electrons, ions of certain substances in the liquid move. A nanofluidic analogue of the transistor has been built using nanotubes as conducting channels (Figure 35).

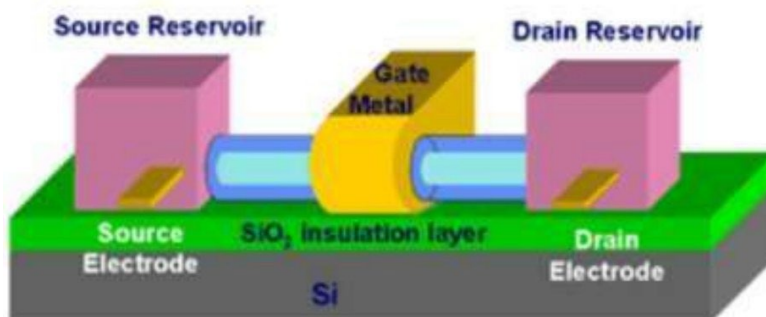


Figure 35. Scheme of a nanofluidic transistor. The flow of ions in the liquid within the nanotubes (blue) stops when a voltage is applied to the gate (yellow)

The main part of the nanotransistor capable of controlling the liquid flow is a microchannel 35 nm in diameter located in silicon between two layers of silicon dioxide:

- it is filled with water with dissolved salts that form hydrogen ions;
- when a voltage is applied to the gate, similarly to the gate of a field-effect MOSFET transistor, the liquid flow stops.

As is clear, the principle of operation of the nanofluidic transistor is fully similar to that of electronic transistors.

The appearance of such a transistor will apparently play an important role in oncology: a nanofluidic processor will be able to analyse at least ten cancer cells simultaneously, extracting protein markers from them, the analysis of which will help doctors find the best ways to fight the disease.

Organising the production of such processors will not require the creation of new industries: the technologies currently used in microelectronics are quite suitable for this.

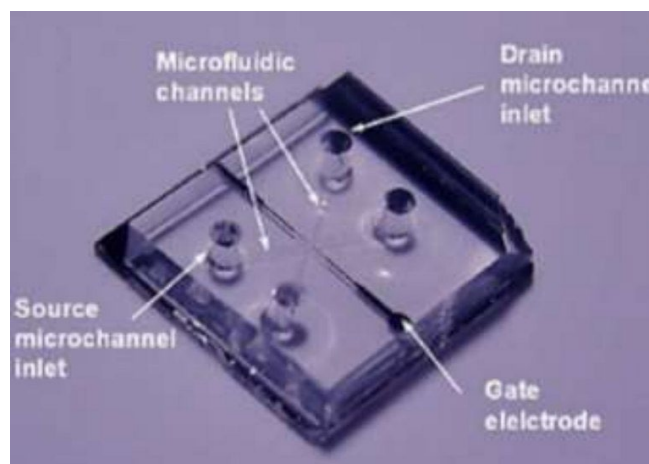


Figure 36. Nanofluidic transistor, too small to be seen with the naked eye

Review Questions

1. What is the idea of self-organisation? Give a definition and describe it.
2. Give examples of self-organisation and justify them.
3. The Marangoni effect: name a well-known example of capillary convection. What does it consist in?
4. Describe the principle of creating organic nanofilms.
5. How can single-walled nanotubes rolled into rings be obtained?
6. What is self-assembly?
7. Name the main functions and tasks of self-organising polymers.
8. Name the main conditions for the process of self-organisation to proceed.
9. What are hybrid nanomaterials?
10. Into what groups are hybrid nanomaterials divided according to their purpose? Describe them.
11. What is a supercritical fluid? Name its main properties.

12. Identify the advantages and drawbacks of the synthesis of nanoparticles and nanomaterials in supercritical fluids.

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Lecture 15. Nanostructured Materials in Nuclear Power Engineering

Outline

1. Nanomaterials in nuclear power engineering.
2. Nuclear fuel with nanometric additives.
3. Oxide-dispersion-strengthened (ODS) ferritic–martensitic steels. Nanodispersed ODS steels.
4. Nanomembranes and nanofilters.
5. Ultra-strong and highly conductive materials.
6. Superconducting nanostructured materials for thermonuclear power engineering.
7. Magnetic nanocomposites.
8. Nanomaterials in security systems.

1. Nanomaterials in Nuclear Power Engineering

The fields of application of nanotechnology in nuclear power engineering are very diverse and cover practically the entire range of problems of the nuclear fuel cycle and the thermonuclear cycle. Work is being carried out on:

- the creation of new high-density nuclear fuel with nanoadditives and of fuel compositions for the fuel assemblies of the core of nuclear power plants (NPPs);
- the creation of a new class of mixed uranium–plutonium oxide fuel, MOX fuel (from "mixed oxides");
- mastering the thorium–uranium cycle, a science-intensive task requiring the application of high technologies;
- the creation of nanodispersed structural and functional materials;
- zirconium alloys for fuel elements;
- oxide-dispersion-strengthened (ODS) ferritic–martensitic steels, or nanodispersed ODS steels;
- studies of the stability of systems with nanoscale features, in particular the stability of ODS nanoclusters in steels;
- research and development of materials for fast reactors and future Generation IV reactors;
- studies of radiation-induced microstructures and microstructural prediction of the possibilities of extending the service life of reactors: reactor vessels (embrittlement) and in-core steels (swelling).

Further fields of application of nanotechnology in nuclear power engineering are:

- the development and production of rapidly solidified brazing alloys for fluxless high-temperature (vacuum) brazing of steels, zirconium alloys, corrosion-resistant steel–zirconium and steel–titanium adapters and other dissimilar materials, providing a specified level of radiation and corrosion resistance of the brazed joints;

- nanomembranes and nanofilters for spent nuclear fuel and radioactive waste handling technologies, and ceramic materials for the afterburning of radiolytic hydrogen;
- structural, functional and metrological devices based on nanomaterials for nuclear installations;
- multiscale modelling of nanostructures, materials and processes;
- nanosensors for the physical protection systems and automated process control systems of NPPs, providing new opportunities for improving the safety and security characteristics of NPPs;
- research and development of materials for future thermonuclear reactors;
- nanostructured (low- and high-temperature) superconductors for the ITER magnets.

In addressing these problems, experimental and industrial technologies are being developed for producing functional substances and products using nanotechnology and nanomaterials for nuclear, thermonuclear, hydrogen and conventional power engineering, as well as medical preparations.

2. Nuclear Fuel with Nanometric Additives

Energy strategy envisages the gradual introduction of new fast-neutron nuclear power technologies with closure of the nuclear fuel cycle using MOX fuel. Further development of nuclear power requires the inclusion of fast reactors in the structure of NPP capacities.

Of all types of fast reactors, those developed industrially today are reactors with a sodium coolant (BN):

- for example, the BN-600 reactor at the Beloyarsk NPP, which has been operating since 1980;
- a power unit with the BN-800 reactor has been built at the Beloyarsk NPP, with the organisation of MOX fuel production and the implementation of a closed fuel cycle based on this reactor.

One of the conditions for improving the efficiency of NPPs is an increase in the *burn-up depth of nuclear fuel*: for deep fuel burn-up, it is necessary to create coarse-crystalline structures of nuclear fuel with controlled porosity.

Coarse-crystalline structures of nuclear fuel retain gaseous and volatile fission products and hinder the transport of fission fragments along grain boundaries to the fuel cladding, owing to which the damage to the fuel element cladding is significantly reduced.

Such directions include:

- nuclear fuel modification, i.e. the creation of complex UZrCN carbonitride doped with nanodiamond;

- completion and modernisation of a pilot plant project for the production of MOX fuel for the BN-800;
- model development of the structural boundaries of solid reactor melt formation;
- study of the interaction of molten prototype core materials with the reactor vessel;
- the mechanism of explosion of liquid-metal droplets;
- large-scale modelling of core materials.

The paradox of using ultradispersed additives in the manufacture of fuel ceramics consists in the use of nanoadditives to obtain structures close to single-crystalline (Figure 1).

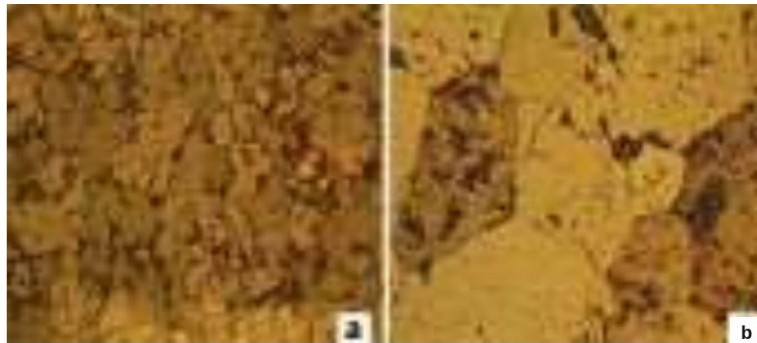


Figure 1. Microstructure of nuclear fuel: *a* – standard microstructure; *b* – microstructure obtained using nanoadditives

3. Oxide-Dispersion-Strengthened (ODS) Ferritic–Martensitic Steels. Nanodispersed ODS Steels

Increasing the efficiency and service life of advanced fast-neutron reactors requires, first of all, an increase in fuel burn-up to 18–20% without reducing the coolant parameters.

The main factors determining the radiation resistance of the structural materials of fast-neutron reactors are:

- radiation swelling;
- radiation creep;
- high- and low-temperature radiation embrittlement;
- the radiation stability of the structure and properties of the material in the neutron irradiation field.

Similar problems arise in the creation of radiation-resistant structural materials for the first wall and blanket of the international thermonuclear experimental reactor, ITER.

Solving this problem requires the creation of a new class of radiation-resistant metallic materials *strengthened by metal oxide nanoparticles*. These materials must meet the following requirements:

- low creep up to 970 K and dimensional stability over a service life of ~9 years;
- high resistance to neutron irradiation (irradiation dose ~250 dpa);

- radiation resistance of the cladding material combined with increased heat resistance;
- high mechanical properties: ultimate strength > 300 MPa at 970 K, long-term strength > 120 MPa for 10⁴ h at 970 K, elongation > 1%;
- high corrosion resistance with respect to coolants at elevated temperatures and chemical compatibility with the fuel;
- high chemical compatibility in contact with the fuel and sodium flow.

One of the ways of solving this problem is the creation and use of a new class of *ferritic–martensitic radiation-resistant steels strengthened by nanometre-sized oxide particles* (ODS steels), which at the same time have high strength and mechanical properties.

The global trend is the creation of structural materials strengthened by highly dispersed non-metallic particles (nanoparticles) intended for core elements of advanced nuclear reactors.

In recent years, a series of ODS ferritic–martensitic steels for fast-neutron reactors has been developed, including one based on EP-450 steel (Fe–13Cr–2Mo–Nb–V–B–0.12C), which is used as the standard fuel assembly material of the BN-600 reactor.

A new technology for producing ODS steel has been developed, which includes:

- production of rapidly solidified powders of spherical or flake shape by centrifugal atomisation of the melt;
- solid-phase alloying of the matrix material with nanodispersed yttrium oxides in a high-energy attritor;
- compaction of the powders and thermomechanical treatment of the product.

To obtain rapidly solidified powders by centrifugal atomisation of the melt, a process scheme for producing ODS ferritic–martensitic steel based on EP-450 steel was selected. Two types of powder were obtained. These procedures promote the formation of nanoscale yttrium oxide precipitates in the steel matrix.

- Powder with spherical particles is formed on crystallisation in free flight in the chamber atmosphere (Figure 2, *a*). The structure of the spherical powder material is fine-grained and homogeneous (Figure 2, *b*).
- Powder with flake-shaped particles is obtained on crystallisation on a copper screen (Figure 3, *c*). The surface of the flake powder shows granularity and elongation of the grains along the direction of heat removal (Figure 3, *d*).

In both cases, the chemical composition of the steel does not change during atomisation.

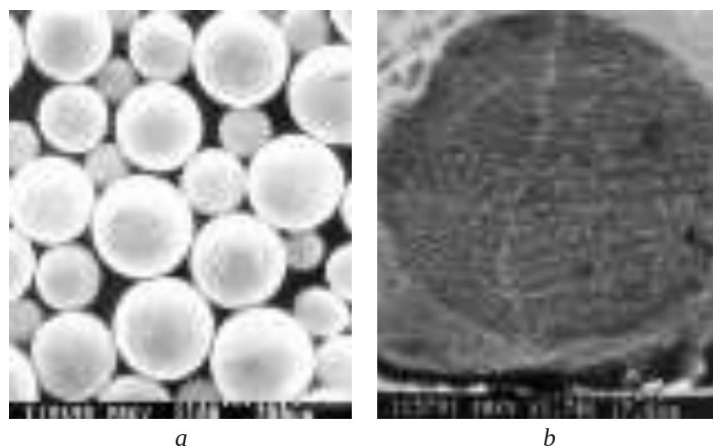


Figure 2. Micrographs of powder with spherical particles (a) and of the surface of spherical particles (b)

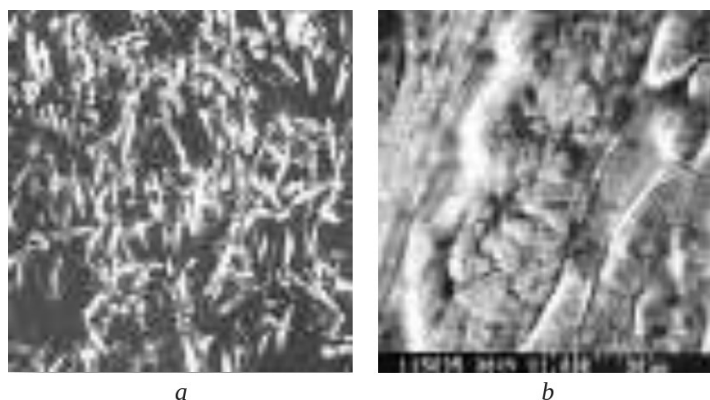


Figure 3. Micrographs of powder with flake-shaped particles (c) and of the surface of a flake-shaped particle (d)

The yttrium oxides used were, in the initial state, agglomerates several micrometres in size (Figure 4, a). Figure 4, b shows the structure of an individual agglomerate, which consists of individual crystallites in the size range 40...80 nm.

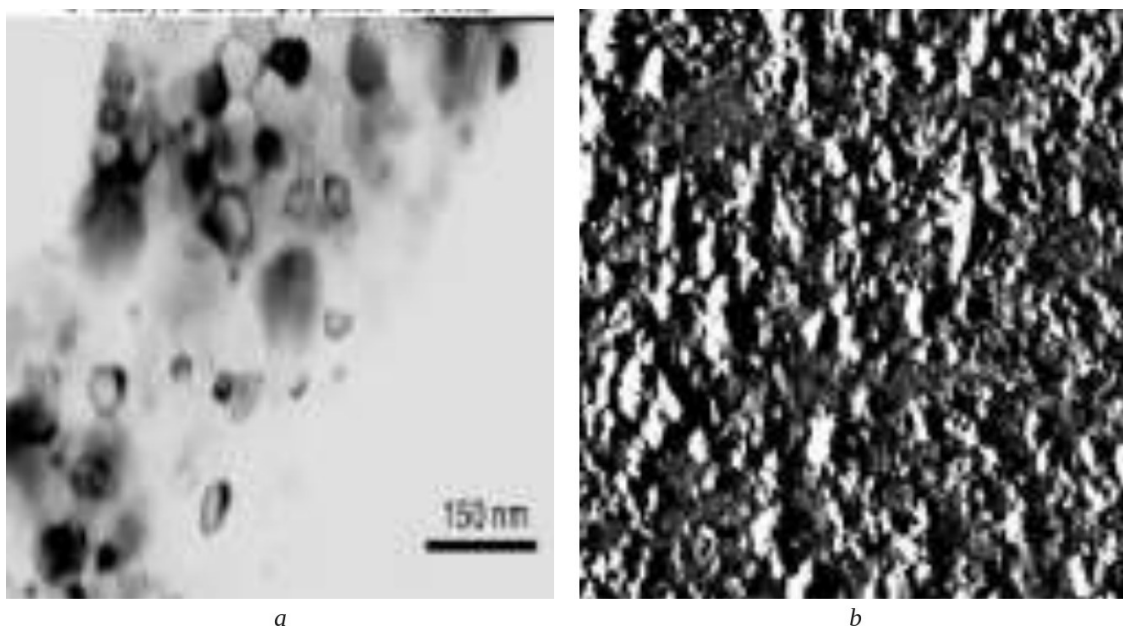


Figure 4. Micrograph of yttrium oxide agglomerates (a) and structure of an individual yttrium oxide agglomerate (b)

It has been shown that nanostructured steel retains high residual elongation after cold deformation by 60%.

Extrusion resulted, on the one hand, in the formation of a polygonised structure with a grain size of $\sim 3\text{--}5\text{ }\mu\text{m}$ (Figure 5, *b*) and, on the other hand, in the refinement of yttrium oxides (Figure 5, *a*): the yttrium oxides are located in the grain volume, and the size of the oxides inside the grains is $5\text{--}10\text{ nm}$.

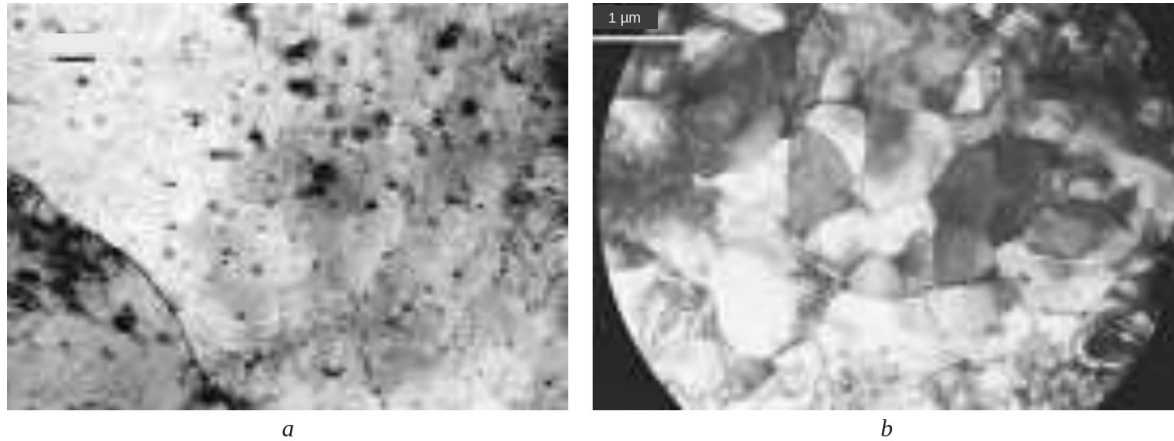


Figure 5. Structure of ODS steel: *a* – nanostructure; *b* – macrostructure

Some results of high-temperature tests of EP-450 and EP-450 ODS steels are presented in Table 1.

Table 1. Results of tests of EP-450 and EP-450 ODS steels

$T, ^\circ\text{C}$	σ, MPa	Material type	Time to failure, h
650	140	Steel to specification	392
		ODS steel	No failure of specimens; tests stopped after 3000 h
700	120	Steel to specification	2.3
		ODS steel	187

EP-450 ODS steel has a ferritic structure with regions elongated along the extrusion direction (Figure 6), consisting of large ($30\text{--}50\text{ }\mu\text{m}$) and small ($0.5\text{--}2\text{ }\mu\text{m}$) grains. The thermal creep of EP-450 ODS steel at $650\text{--}700\text{ }^\circ\text{C}$ is much lower than that of the ordinary steel (Figure 7).

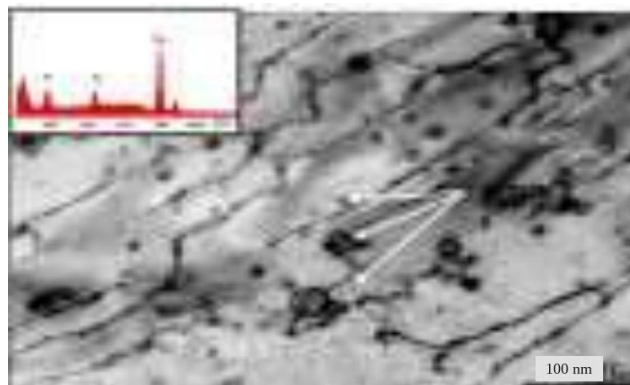


Figure 6. Structure of an extruded specimen of EP-450 ODS steel

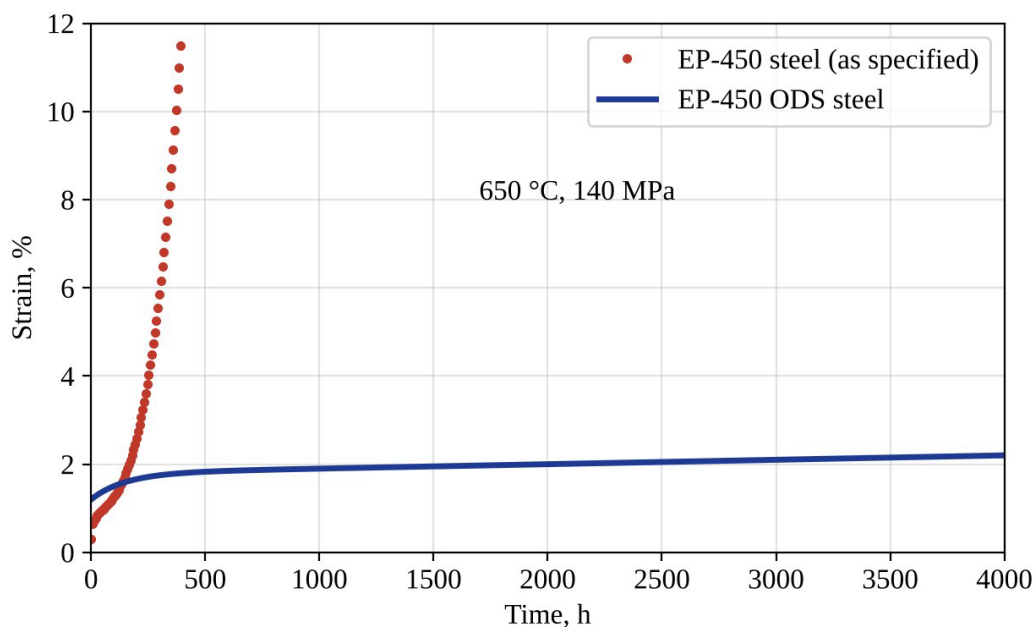


Figure 7. Thermal creep of the initial steel and ODS steel

Products (tube billets, thin-walled tubes and plate specimens) have been manufactured under research and industrial conditions (Figure 8); their pre-reactor tests showed a multiple (8–10-fold) increase in the time-dependent heat resistance characteristics and high radiation resistance in comparison with the standard steel. Trial production of the product technology under factory conditions has begun.



Figure 8. Stages of the production of products from dispersion-strengthened steel

The best creep resistance characteristics are achieved when the maximum number of uniformly distributed nanoclusters 1–2 nm in size is formed. These particles are distributed with a high density in the volume of the steel.

The role of nano-oxide particles in the corrosion processes of steel and the main mechanisms of their influence on the properties of ODS steel are characterised by the following important factors: as a result, the corrosion resistance, high-temperature strength and radiation resistance of the steels increase.

An example of a successful development is *boron-containing stainless steel*: to obtain a uniform distribution of borides in the steel, the method of ultrafast cooling of the melt was used to obtain particles with an X-ray-amorphous structure. On subsequent annealing, nanometre-scale borides are formed.

The transition to nanostructured boride precipitates (from 5 to 100 nm) makes it possible to increase the boron content 3–4 times while preserving the plasticity and weldability of stainless steels.

Thin-walled tubes of boron-containing stainless steel with a wall thickness of a few tenths of a millimetre have been manufactured (Figure 9). Boron-containing stainless steel is promising for:

- use in the control systems of nuclear reactors;
- the creation of nuclear-safe equipment for handling spent nuclear fuel and its reprocessing.

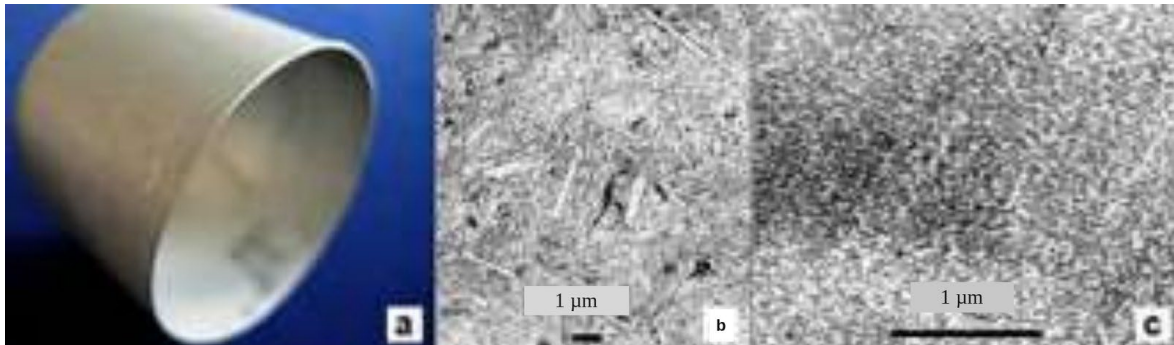


Figure 9. Boron-containing stainless nanocomposites: *a* – extra-thin-walled product of boron steel; *b* – ordinary steel; *c* – nanocomposite steel

A new direction in the nanotechnology of structural materials for nuclear power engineering is the newly developed technology of high-temperature brazing with *rapidly solidified brazing alloys* (RSBA). It allows the use of RSBA in the production of structural core elements of nuclear reactors from dispersion-strengthened alloys and dissimilar material compositions.

The justification for introducing brazing is based on the well-known problems of welded joints:

- in the welding zones, grain growth, nodular and crevice corrosion, incomplete penetration, burn-through and low rigidity are possible;
- welding requires a certain contact area, which limits the possibility of changing shape, and annealing is necessary to relieve welding stresses, which leads to recrystallisation and fracture.

Brazing with rapidly solidified alloys is diffusion joining through a layer of material that reduces the temperature and time of joint formation. Brazing technology using RSBA makes it possible to increase the service life of core structures owing to the following advantages: a narrow melting temperature range; uniform melting of the brazing alloy throughout its volume; good spreading and wetting of surfaces; high capillary activity of the brazing alloy; and high diffusion activity of its components.

On the basis of nanotechnological ideas, a methodology of *liquid-phase surface alloying* of materials by means of concentrated energy fluxes (CEF) has been developed (Figure 10).

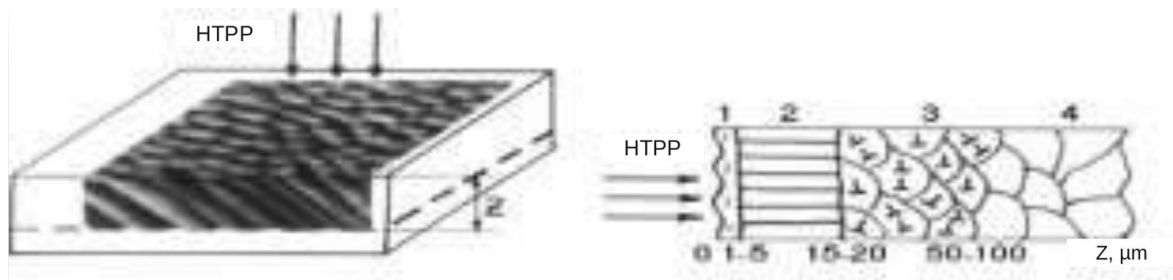


Figure 10. Treatment with high-temperature pulsed plasma (HTPP) flows leads to the formation of a gradient composite material

It has been shown that, in the development of new corrosion-resistant steels with protective coatings, surface layers modified by concentrated energy fluxes (pulsed electron beams, plasma flows) are effective. This method is used for surface alloying of fuel element tube fragments with pulsed plasma flows (Figure 11).

Advantages of treatment with pulsed plasma flows:

- simultaneous use of the plasma substance as a means of heating and alloying;
- the possibility of treating large surface areas or finished products in a short time (multiple pulses 10–60 μ s long);
- the possibility of simultaneous all-round surface treatment of shaped cylindrical products.

Drawbacks:

- insufficient study of the processes occurring during the interaction of a pulsed plasma flow with a solid body;
- problems in controlling the plasma flow in the accelerators existing at present.

The scheme of surface alloying of fuel element tubes is given in Figure 11.

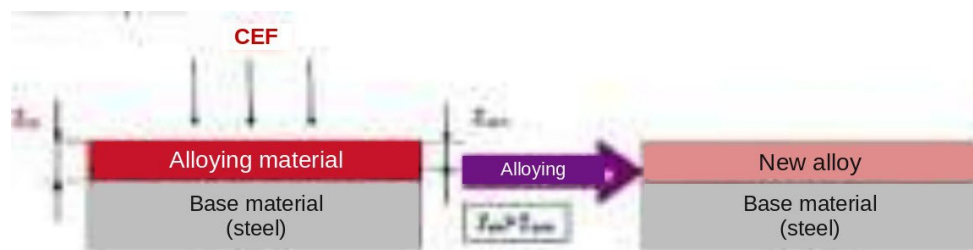


Figure 11. Scheme of surface alloying of fuel element tubes using a concentrated energy flux (CEF)

Surface alloying of steel includes:

- deposition of the alloying coating, followed by intermediate vacuum annealing for diffusion bonding of the coating and the substrate;
- liquid-phase mixing of the coating with the tube surface material under the action of pulsed plasma flows.

The results of surface alloying are given in Table 2. The surface layer after treatment is close to nanocrystalline.

Table 2. *Results of surface alloying of steel tubes*

Alloying element	Coating thickness before treatment, μm	Maximum concentration of the alloying element, wt. %	Penetration depth of the alloying element, μm
Nickel	1.7–4.3	10.0–20.0	47.5–28.0
Chromium	0.2–0.65	1.0–6.0	18.0–34.0
Titanium	0.2–0.3	0.5–2.0	8.5–24.3
Vanadium	0.8–0.9	2.0–4.0	28.0–34.0

Treatment with pulsed plasma flows increases the corrosion resistance of steel 3–10 times in tests for intergranular corrosion, in liquid lead flows and in interaction with vapours of simulated nuclear fuel fission products.

To date, the use of austenitic steel ChS68 (06Kh16N15M2G2TFR) for fuel rod claddings and ferritic–martensitic steel EP-450 (1Kh13M2BFR) for wrappers has ensured the operability of fuel elements in the BN-600 reactor up to a damage dose of 83 dpa and a fuel burn-up of 11% h.a.

At present, the limitation of the maximum fuel burn-up is associated with the relatively low radiation resistance of austenitic steels and the low heat resistance of ferritic–martensitic steels. The heat resistance of high-strength ageing steels is determined by the stability of the strengthening particles of the steel matrix at elevated temperatures and loads.

At present, structural materials of practically all classes (austenitic, ferritic and ferritic–martensitic steels) are being considered for reactors of the BN type to increase burn-up (Figure 12). Similar steels may also be used in fusion power engineering as materials for the first wall and blanket of a thermonuclear reactor.

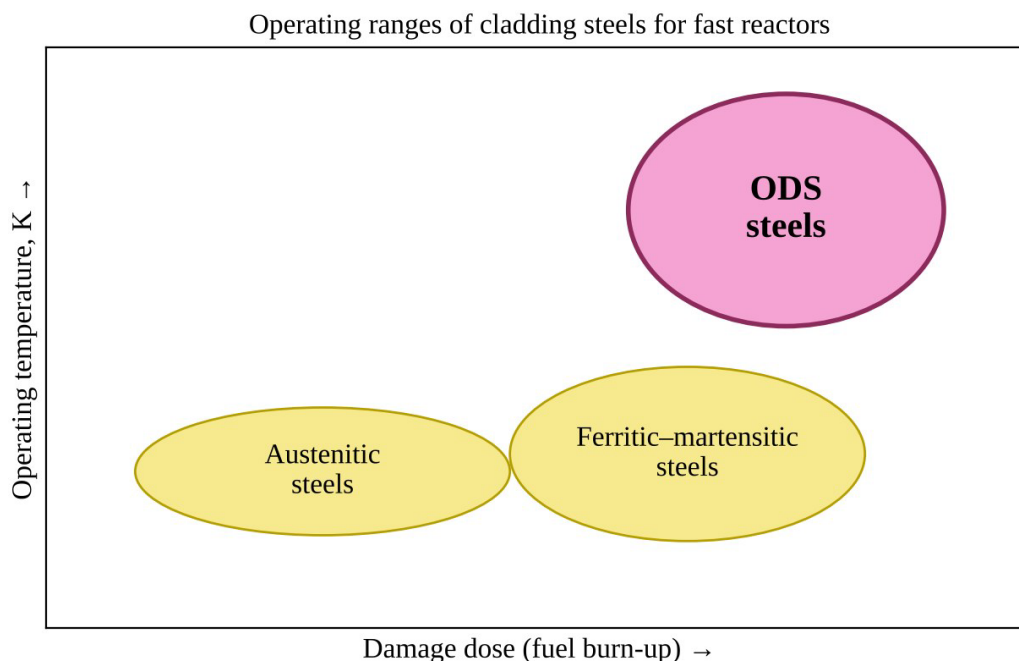


Figure 12. Scheme illustrating the loss of the dispersion-hardening effect in ferritic–martensitic steels at temperatures above 920 K and the effectiveness of dispersed oxide particles in ODS steels at temperatures above 970 K

4. Nanomembranes and Nanofilters

Bulk metallic nanofilters are promising for use in water treatment systems and for cleaning the coolant of NPP reactors.

Nanomembranes, nanofilters and nanocatalysts are used in:

- technologies for handling spent nuclear fuel and radioactive waste;
- water treatment and coolant purification systems;
- afterburning of radiolytic hydrogen;
- purification of air and process gases, etc.

Research and industrial installations using nanofiltration are used for:

- afterburning of hydrogen in the hydrogen safety systems of NPPs;
- processing of liquid radioactive waste;
- cleaning gases of radioactive aerosols;
- fine purification of air and process gases.

The ability of a nanotube to change its conductance with its dimensions makes it an ideal element of new-generation electronics, molecular electronics. Nanotubes can also be used to reinforce the binder in the production of uranium centrifuge rotors.

An important property of carbon nanotubes (CNTs) is that, since a CNT is a surface structure, its entire mass is concentrated on the surfaces of its layers. Since the diameter of the inner channel of a CNT is only 2–3 times larger than the dimensions of molecules, capillary properties of nanotubes manifest themselves on the nanometre scale.

5. Ultra-Strong and Highly Conductive Materials

Thermonuclear reactors require conductive materials with high conductivity and strength, capable of operating in strong magnetic fields and withstanding high mechanical loads. For research equipment and household use, ultra-strong and elastic highly electrically conductive materials are also needed.

Such materials are, for example, *nanocomposite conductors based on Cu–Nb alloys*, which have high strength and a conductivity close to that of copper.

A technology has been developed for a new class of high-strength Cu–Nb winding wires of rectangular cross-section with the following properties:

- ultimate strength 1100–1250 MPa;
- conductivity about 70% of that of copper.

High-strength Cu–Nb fine wires with diameters from 0.4 to 0.05 mm have been developed with the following properties:

- ultimate strength 1300–1600 MPa;
- conductivity 70–80% of that of copper;
- the nanocomposite has the strength of steel with an electrical conductivity close to that of copper.

The fundamental possibility of creating new-generation contact wires with a much higher set of properties by using nanostructured components has been shown.

6. Superconducting Nanostructured Materials for Thermonuclear Power Engineering

The development of superconducting materials such as nanostructured superconductors is an example of developments whose initial purpose was the production of bulk nanostructured materials.

As a result of the transition to nanometric structures, it has been possible to increase the current-carrying capacity of superconductors several times, which has made it possible to create powerful magnet systems and save up to 30% of electricity. The powerful magnetic fields that confine the plasma in thermonuclear reactors are created by superconducting systems. Examples of the structures of superconducting nanocomposites are shown in Figure 13.

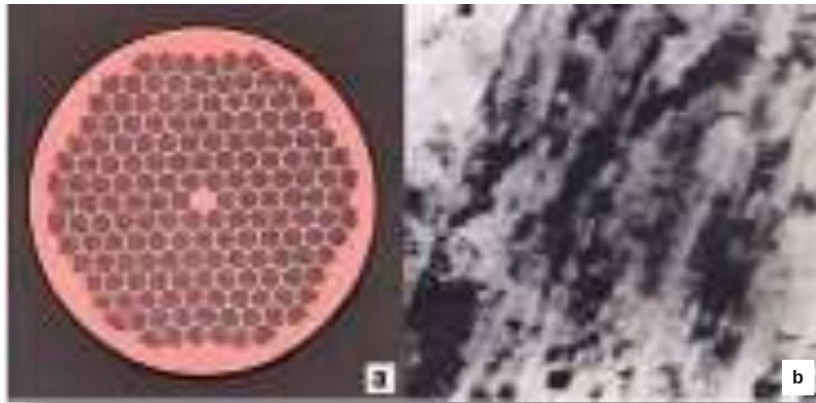


Figure 13. Superconducting nanostructured materials for thermonuclear power engineering: *a* – Nb–Ti superconductor wire 0.85 mm in diameter; *b* – titanium precipitates 10–50 nm in size in the fibres

The realisation of the transport superconducting characteristics of high-temperature superconductors (HTSC) is difficult. Let us illustrate the possibilities of applying nanotechnology with examples related to the introduction of nanoscale TiO_2 additives (Figure 14, *a*) and the use of the principle of property inheritance in thin films (Figure 14, *b*).

Staining of the structural components, both precipitates and grains of the HTSC matrix, makes it possible to identify them and evaluate their texture (Figure 14). The origin of the bands on the crystal surface is associated with the formation of twin defects.

- The presence of twins confirms that the crystals have passed the oxidation stage and have superconducting properties.
- They are oriented in a quite definite way: the *c* axis is directed strictly upwards, and the *a* and *b* axes are parallel to the corresponding faces of the crystal.

Precisely such an artificially achieved arrangement of the crystals is most favourable from the point of view of realising the transport superconducting characteristics, since HTSC phases have a high crystallographic anisotropy of properties.



Figure 14. *a* – micrograph of the surface of a superconducting composite tape based on Bi-2223 with nanosized TiO_2 additives (900 °C); *b* – superconducting yttrium barium cuprate $\text{YBa}_2\text{Cu}_3\text{O}_7$ on a silver–palladium alloy substrate with a striped surface relief

7. Magnetic Nanocomposites

At present, manufacturers show increased interest in *composite magnets*, which provide an increase in the technical parameters of magnetic systems with a simultaneous reduction in their dimensions.

New magnetic materials are used, first of all, in small-sized ultra-high-speed electric motors and generators for the aerospace, automotive and instrument-making industries. For example, magnetic microcomposite materials based on Co–Fe–Nb and Fe–Ni alloys have been created on the basis of the *Wiegand effect*.

During the magnetisation reversal of bistable magnetic wires by an external field, a pulse of electromotive force is induced in a coil placed over the wire, which corresponds to the main or additional magnetisation jump.

A technology for producing nanocrystalline magnetic materials by centrifugal atomisation of the melt has been developed and patented. Nanocrystalline magnetic materials surpass the known barium and strontium ferrites in magnetic energy by 6–8 times.

8. Nanomaterials in Security Systems

The most promising directions for the use of nanotechnology in security systems in the coming years are reflected in the following examples of the creation of technical security means based on nanotechnology and nanomaterials:

- nanosensors of various physical principles, tunnel pressure sensors, "smart dust" intelligent sensors, distributed arrays of "smart dust" nanosensors for the protection of borders and perimeters of facilities, and sensors for very early fire detection;
- nanosensors based on the tunnelling effect have ultra-high sensitivity in the range from 0.1 Hz to 200 kHz and can be used in seismic and acoustic location systems and for monitoring the strength of materials;
- the sensitive element of the sensor is a nanosystem consisting of a guide needle made using silicon micromechanics, ultra-thin corrugated layered membranes and tunnelling current maintenance systems;
- anti-terrorist means, in particular spectral nanoanalysers of ultra-low concentrations of prohibited substances, and multifunctional "electronic nose" sensors for the detection and identification of very small quantities of hazardous substances.

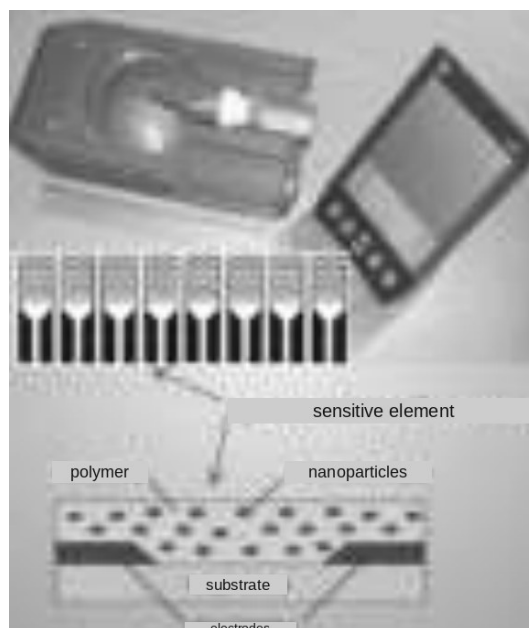


Figure 15. *Nanosensor neural system "electronic nose"*

Figure 15 shows the "electronic nose" nanosensor neural system, which includes a nanosensor unit, a signal recording system and olfactory recognition software. The principle of operation of the device is as follows:

- the electrical conductivity of chemical sensors is measured during interaction with vapours of substances;
- as a result of the adsorption of molecules of the substance under study, the electrical conductivity of the sensitive materials of the sensors increases;
- mathematical processing of the data of the sensor array makes it possible to form a chemical image of the substance analysed.

Access control and management systems include:

- identification documents and access control and management systems based on nanotags and nanomemory;
- locking devices for restricted premises with unique electronic keys, i.e. nanotags;
- new means and methods of inspecting and protecting documents against counterfeiting, for example based on nanomaterials, microprinting, thin electronic circuits, paper with added nanoparticles, and compact data readers.

Further directions include:

- more compact and informative portable and stationary metal detectors and nanosensor motion detectors;
- technologies for producing heteromagnetic structures on the nanoscale with increased resistance to mechanical and climatic influences and to special factors;
- technologies for producing and applying nanocomposite multifunctional protective coatings on structural elements of technical means and security systems.

The main characteristics of such coatings are:

- a 2–4-fold increase in the service life of structural elements of security systems under aggressive chemical acid–base environments, increased humidity and salt fog;
- an increase of up to 20 dB in the noise immunity of security systems under increased electromagnetic interference and radiation background.

From the above results, it is clear that nanostructured materials are acquiring an important role in nuclear power engineering as structural and functional materials at practically all stages of the nuclear fuel cycle.

Review Questions

1. Name the fields of application of nanotechnology in nuclear power engineering.
2. Give examples of the most advanced fast reactors at present. What conditions for increasing the efficiency of NPPs can you name?
3. Name the requirements that a new class of radiation-resistant metallic materials must meet.
4. Describe ODS ferritic–martensitic steels and give examples.
5. What influence do nano-oxide particles have on the properties of ODS steels?
6. Characterise boron-containing stainless steels and name the fields of their use.
7. Describe the methodology of liquid-phase surface alloying of materials. Name the advantages and drawbacks of the method.
8. In which industries are magnetic nanocrystalline materials applied?
9. Name the most promising directions for the use of nanotechnology in security systems.

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Lecture 16. Nanostructured Alloys and Nanomaterials in the Automotive Industry

Outline

1. Relevance of the topic. Nanostructured steels.
2. Main fields of application of nanotechnology in the automotive industry.
3. New materials.
4. Improving engine efficiency and fuel consumption.
5. Improvement and miniaturisation of electronic systems.
6. Reduction of friction.
7. "Smart" self-repairing materials.
8. Transition to hydrogen fuel.

1. Relevance of the Topic. Nanostructured Steels

In the very near future, nanotechnology will play one of the main roles in the automotive industry. In recent years, **nanostructured steels** have been actively developed. A nanostructured steel is a steel whose properties depend to a significant extent on the presence of nanoscale components in its structure: block structures, which lead to a substantial increase in strength without a noticeable loss of plasticity and toughness of the metal; nanoscale dispersed precipitates, which make it possible to use immiscible materials together; etc. Nanostructured steels have improved physical and mechanical properties: the strength of such steels increases 3–4 times and the hardness by an order of magnitude, with improved cold resistance and a multiple increase in corrosion resistance. High-nitrogen stainless steels, which can also be nanostructured, may also become promising structural materials for the automotive industry.

Today, stainless steel is an extremely popular material. Its key feature is a thin passivating self-healing film on the surface (owing to a chromium content of 12–20%). The thickness of this film is about 1–5 nm. This solid film is chemically stable even under conditions in which the surface layers have absorbed a significant amount of oxygen. If there is enough oxygen, the protective layer can self-repair: if there are scratches or pits on the steel surface, the protective layer is restored as a result of the interaction of atmospheric oxygen with chromium. Besides high service properties, steels of this class can also carry an aesthetic load; for example, chrome-plated parts make a car attractive to certain categories of car enthusiasts.

In 2004, a special programme (NanoMobile) was created in Germany by the Federal Ministry of Education and Research (BMBF). It envisages separate funding for nanotechnology in this sector.

Competition in the automotive industry is very high; therefore, nanomaterials and developments in the field of nanotechnology are used both to improve the performance of units and parts of mechanisms and for aesthetic and functional reasons. It is no secret that high-quality materials make the interior of a car a second home, and if, thanks to

nanotechnology, these materials also have additional properties, the convenience of using such a car will only increase.

The range of applications of nanotechnology and nanomaterials varies from those already existing (high-quality paints, fuel cells, batteries, wear-resistant tyres, lighter and stronger materials, ultra-thin anti-glare nanocoatings for glass and mirrors) to futuristic ones (energy-harvesting bodywork, self-repair, coatings with variable colour and shape).

The largest steel company, ArcelorMittal, announced a new technology that will make it possible to reduce the weight of cars. The new steel, made using nanotechnology, is somewhat lighter and much stronger than ordinary steel. Thanks to this innovation, the weight of the car body alone can be reduced by about 85 kg (which means lower fuel consumption), and the overall reduction in vehicle weight, including the engine, transmission, brakes, etc., may be even greater. The new steel itself is not much lighter than ordinary steel; its advantage lies in its greater strength. Parts made of it can be thinner without loss of consumer properties, which is where the main weight saving comes from. Another component of this saving is the elimination of auxiliary fasteners and parts used to reinforce the body structure. As a result, for example, the front pillars can become thinner while meeting safety requirements, and have less effect on visibility. Although aluminium, magnesium and composites pose a certain competitive threat to steel, they are much more expensive and more difficult to repair; moreover, their processing requires much more energy.

2. Main Fields of Application of Nanotechnology in the Automotive Industry

The main fields of application of nanotechnology in the automotive industry are:

1. Lightweight but strong materials (to reduce fuel consumption and increase safety).
2. Increasing engine efficiency and reducing fuel consumption for cars with petrol engines (catalysts, fuel additives, nanoadditives, lubricants).
3. Reducing the harmful environmental impact of cars (hydrogen batteries).
4. Improvement and miniaturisation of electronic systems.
5. Significant savings (service life, low failure rate of mechanisms; "smart" materials for self-repair).

Figure 1 presents generalised data on the use of nanotechnology in the automotive industry.

		Already in use				May be used in future	
Applica- tion	Function	Exterior protection	Body frame	Interior	Chassis and tyres	Equipment and electronics	Steering and engine
Effect							
Mechanical function	Hardness, friction, properties	Nano-lacquer			Carbon black in tyres		Low-friction units
		Polymer glazing	Nanosteel		Nanosteel		
Geometric effects	Very small size			Nanofilter		Super-coatings	
			Gecko effect	Gecko effect		Power batteries	
Electronic/magnetic function	Size-dependent electr. & magn. properties		Bonding on command			GMR sensors	Piezo injectors
					Switchable materials	Solar cells	
Optical function	Colour, transparency	Ultra-thin layers		Anti-reflective coatings			
		Electro-chromic layers					
Chemical function	Reactive, selective properties	Care and "repair" systems	High-strength steel formation	Dirt protection			Catalysts
			Corrosion protection	Interior fragrance			Fuel additives

Figure 1. Applications of nanotechnology in the automotive industry

Let us analyse the main directions of application of nanotechnology in the automotive industry in more detail.

3. New Materials

The use of nanosteels and nanostructured alloys makes it possible to increase the strength of parts and reduce the weight of car structures, which will improve safety and fuel economy.

In Izhevsk, the production of a nanospring is being mastered which, according to the manufacturer, will last forever. The springs are made by a high-temperature thermomechanical treatment technology that creates nanoscale structures in the metal. As a result, the strength characteristics of the springs produced are significantly improved.

The **MuCell** technology developed by Ford engineers helps to solve the problem of reducing the weight of a car without loss of quality and functionality of structural materials. Whereas previously all possible excess weight was squeezed out of metal parts, it is now the turn of automotive plastics.

According to company representatives, the new type of plastic is not inferior to its predecessors in strength and cost, although it weighs 20% less (Figure 2). This is achieved by air-filled cavities about 25 μm in diameter each. Moreover, casting the new material requires less pressure, and the process itself is a third faster. In the next few years, the material will replace conventional plastic in the engine covers of such models as the Focus, C-MAX, S-MAX, Mondeo and Galaxy. This development is part of the company's commitment to reduce the weight of its vehicles by 2020 by 100 kg

for small cars and by 300 kg for ordinary passenger cars, which in turn will help reduce fuel consumption and hence harmful emissions.

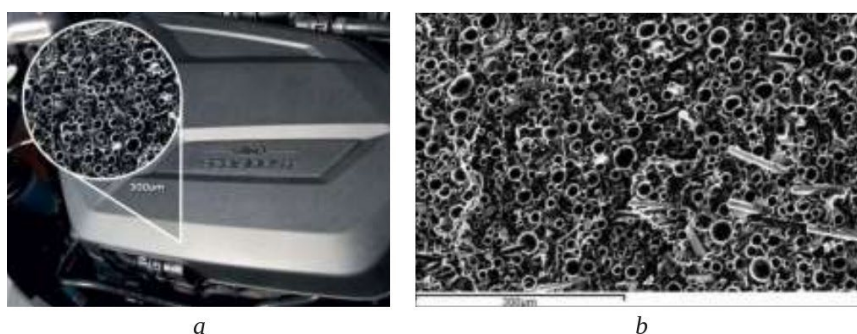


Figure 2. *New nanostructured material for Ford cars: an engine cover (a) and the microstructure of the material (b)*

4. Improving Engine Efficiency and Fuel Consumption

This direction concerns cars with petrol engines (catalysts, fuel additives, nanoadditives, lubricants). A catalyst based on nanoparticles developed at Rice University will help automotive engines become even more powerful.

Researchers from Michael Wong's group report that subnanometre clusters of tungsten oxide deposited on a zirconium oxide support are effective catalysts for the isomerisation of *n*-pentane, which leads to the formation of branched C₅ isomers. Although the catalytic capabilities of tungsten oxide have long been known, Wong believes that nanoparticles based on this substance can substantially increase the catalytic activity of WO₃. Wong's research group worked for several years on the most effective composition of a catalyst consisting of catalytically active tungsten oxide and catalytically inert zirconium oxide.

The key to the performance of the new catalyst was the correct distribution of tungsten oxide nanoparticles on the zirconium oxide surface. Wong notes that the "golden mean" principle had to be followed: the amount of tungsten oxide had to be neither too large nor too small. The researchers sought to place the nanoparticles on the support so that they did not touch one another, believing that this approach would increase the catalyst efficiency about fivefold.

The researchers succeeded in achieving such a placement of tungsten oxide nanoparticles on the support and obtained an *n*-pentane isomerisation catalyst five times more effective than existing ones (Figure 3).

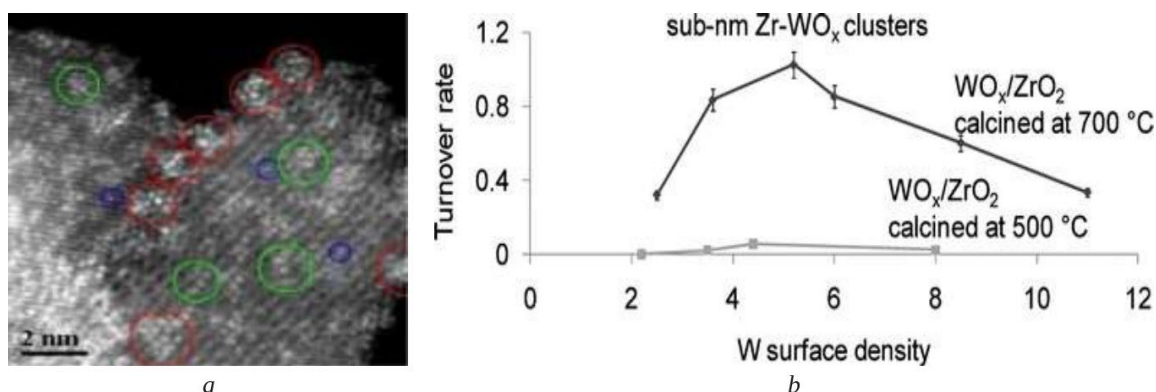


Figure 3. *a* – image of the atomic structure of tungsten oxide nanoparticles (green circles) on the zirconium oxide surface; other circles mark other, less active forms of tungsten oxide; *b* – catalytic activity as a function of the tungsten surface density

5. Improvement and Miniaturisation of Electronic Systems

Microelectronics is one of the most dynamically developing fields of science. At present, about 90% of all innovations in solid-state physics originate to some extent from the microelectronics industry. One of the best-known scientific problems in microelectronics was that, using the visible radiation range, the minimum transistor size could not be achieved; lithography (i.e. the chip production process) would have to be carried out by means of X-rays, synchrotron radiation or ion beams, which would substantially increase production costs. The concern was that the radiation wavelength cannot be greater than the topological size of the transistor. Research on the use of other types of radiation (shorter-wavelength and higher-energy) for lithography is being conducted; however, optical-range microelectronics has not reached a dead end: with the help of new technologies, transistors with a linear size of 22 nm are produced using radiation with a wavelength of 193 nm, i.e. almost an order of magnitude larger.

There are plans to create transistors of 16 nm and 14 nm using the same radiation. In parallel, research is being conducted on the use of other types of radiation, in particular the so-called extreme ultraviolet radiation with a wavelength of 13.5 nm and even 5 nm, but these are not yet in use.

Another problem is the preparation of dielectrics. The concern was that, as the topological size of the transistor decreases, dielectrics would cease to perform their function and hot electrons would pass through them. This problem has now been solved: new types of dielectrics have been developed that function even at such small topological sizes.

Scientific problems are still associated with the behaviour of materials as the topological size of the transistor decreases. For example, the copper used has a peculiarity: the material is heterogeneous and forms grains, and its conductance depends on the grain size. As the transistor size decreases at a fixed grain size, the resistance increases greatly; therefore, to continue reducing transistor size, the grain size must be reduced, otherwise the resistance becomes too high.

Another problem is preserving the high dielectric permittivity of dielectrics as the thickness of their layer decreases. Modern transistors contain 10–12 dielectric layers

whose thickness is already measured in ångströms, i.e. tenths of a nanometre. To preserve the dielectric properties, new materials are being created, for example hafnium-based ones.

Yet another problem is the growing need to take quantum effects into account as topological sizes decrease. In effect, all the frontier problems of solid-state physics and plasma chemistry confront microelectronics; however, there is both an understanding of them and plans for their solution.

Although the discovery of graphene was awarded the Nobel Prize and a great future is predicted for it, it is unlikely to replace silicon completely. Most likely, graphene will find a niche in the production of certain types of devices while silicon generally retains its dominant role.

Application of nanoelectronics (spintronics) in cars. Specialists from the microsensor division of Northrop Grumman have begun work on a DARPA defence research agency project to create a miniature gyroscope for "smart" ships, cars and aircraft. The main goal of the MRIG programme is to develop a vibration gyroscope capable of measuring the rotation angle directly, which will eliminate the need to integrate angular velocity data and the accumulation of errors.

The rapidly growing hybrid car sector uses batteries to store the energy needed to drive the car. During motion, energy is converted by a generator into electric current and, after the car stops, stored in batteries or supercapacitors. Nanotechnology is expected to make a great contribution to the development of ultra-light, flexible, thin batteries and capacitors no thicker than an ordinary newspaper. Microstructured solar cells can already be installed in sunroofs and are offered as an option on some cars. The use of flexible nanostructured plastic solar cells less than 1 μm thick will make it possible to cover the outer surface of a car with an energy-absorbing film.

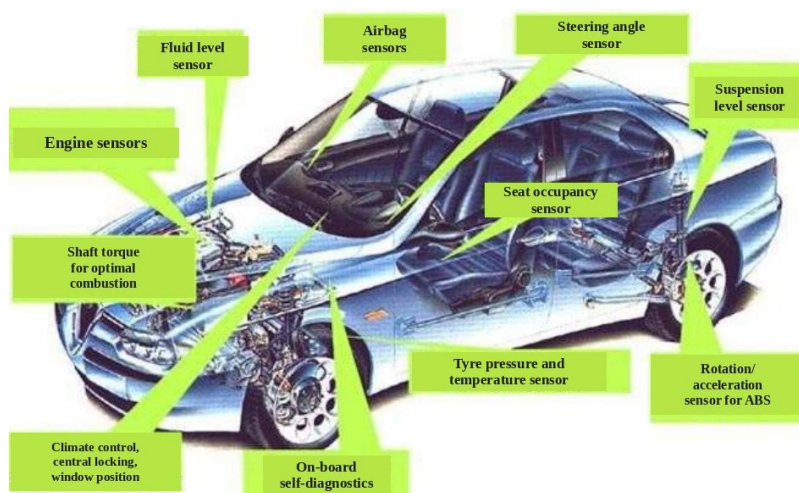


Figure 4. Sensors used in a modern car

6. Reduction of Friction

In modern cars, 10–15% of fuel consumption is accounted for by friction in the engine (losses in rubbing moving mechanical parts: pistons, crankshaft, camshaft).

Nanocoatings for mechanical components and units and nanostructured lubricants reduce friction and wear, thereby reducing fuel consumption.

A group of researchers from the Department of Chemistry of Queen's University, led by Professor Gang-yu Liu, discovered a method of using nanotechnology to reduce friction in car engines and other mechanisms. The nanotechnological additive for creating improved lubricants is based on very small polymer particles several tens of nanometres in size. In tests, these particles were added to automotive engine oil.

During oil degradation, *atomic hydrogen* is released and penetrates into the surface and subsurface layers of the metal. Atomic hydrogen reacts chemically with the metal, forming brittle compounds (hydrides) between the metal crystals, which reduces the strength of the metal crystal lattice. Accumulating in metal microcavities (micropores, casting defects, incipient microcracks), hydrogen atoms combine into molecules, forming gas (H_2), which creates excess pressure inside the microcavity.

As a result, the metal, having lost strength, readily fails under the pressure of hydrogen from inside and the friction forces from outside, i.e. the upper layer of metal gradually separates from its surface. Technological clearances increase, which leads to wear of the unit. Most developers of anti-wear compositions do not take the process of hydrogen wear into account. Therefore, an attempt to prevent wear of the metal by protecting it only from friction, which is how most additives work, gives only a temporary effect, slightly increasing engine life.

Coatings with the property of self-regulation have been developed, patented and certified. When added to engine oil, the "Reagent 2000" protective composition, under the action of friction forces and pressure, is transformed from the liquid state into a very hard, elastic coating capable of withstanding long-term loads with practically no destruction. Along with its high strength, the coating also has an ultra-low friction coefficient. The coating is self-regulating: its thickness is not uniform, being greater in the places of greatest wear.

7. "Smart" Self-Repairing Materials

Today, the product ranges of all leading paint and varnish brands include nanopaints (enamels and varnishes), nanocosmetics and other nanocoatings, which, in comparison with other paint and varnish products, are distinguished by resistance to mechanical, thermal and light-induced destructive factors, reliable adhesion to the surface, durability and convenience in use.

Nanomaterials have a feature that determines all their phenomenal properties: the nanoparticles they contain are about one billionth of a metre in size, which is 50 000 times smaller than the thickness of a human hair and hundreds of times smaller than bacteria; they are densely packed globules containing from ten to thousands of atoms of a chemical element. As a result, nanoparticles have an enormous specific surface area and can interact at the atomic and submolecular levels with various materials, forming thin films with extraordinary chemical stability and mechanical strength.

Another useful property of nanoparticles is their ability to fill the pores and defects of surfaces perfectly, the structure formed exactly reproducing the structure of the substrate. Today, car paints based on nanotechnology (nanocosmetics) include coatings for practically all units and assemblies of a car: bodywork, wheels, windows, leather, ceramics, etc.

Nanocoatings are not, as a rule, intended to perform the functions of traditional car paint; they are applied as a very thin protective layer over the painted surface in the form of a varnish. Such a layer has a number of interesting protective characteristics:

- the formation of a perfectly smooth glossy surface capable of protecting the base paint coating from fading, cracking and chipping on contact with small stones and sand, as well as during car washing and steam cleaning;
- protection against aggressive chemical compounds, in particular acids, alkalis, solvents and snow–salt mixtures;
- dirt-repellent properties: adhering small particles (insects, dirt, bitumen drops) are easily removed with a damp cloth;
- the nanocoating exhibits a "self-healing" property in the case of minor defects (shallow small scratches, cavities from impacts of small pebbles and sand).

Leading manufacturers of such paints include Nissan Motor (Scratch Guard Coat), CeramiClear, XADO and some others.

Nanocosmetics are usually applied at specialised car service stations, although, owing to the relative simplicity of the process, nanocoatings from aerosol cans can also be applied independently. One set of professional mid-price car cosmetics is designed for 2–3 cars and costs about 100–150 dollars.

8. Transition to Hydrogen Fuel

Today almost all car companies have announced their intention to produce electric vehicles. Most electric car motors use electricity from a battery charged from the mains, as well as current generated by energy recovery. However, there is another source of electricity, *fuel cells*, whose use is still more often written about in the future tense.

In fact, work on launching such units into series production is in full swing, for example at the Daimler concern. Fuel cells are complex and expensive devices in which oxygen taken from the air combines with hydrogen stored in a cylinder. An uncontrolled combination of these two gases results in an explosion, whereas in controlled fuel cells electricity is generated. They are controlled by electronics, which fit under the driver's seat. In future Mercedes-Benz models, the hydrogen cylinders are placed under the rear seats.

The stack in which the gases combine and current is generated is located in the boot, and the electric motor on the front axle. One hydrogen refuelling is enough for a Mercedes-Benz B-Class F-Cell to travel 400 km. Moreover, as explained by Peter Froeschle, who is responsible for fuel cell development at Daimler, the range can be increased further if other cylinders are used or they are arranged differently.

Under the bonnet of the Tucson ix Fuel Cell Electric Vehicle (FCEV) there is a completely new highly efficient 100 kW power system based on hydrogen fuel cells. Two hydrogen tanks contain enough hydrogen for the car to travel 650 km. For comparison, the second-generation Tucson FCEV could travel 370 km on the same amount of hydrogen.

The start-up company QuantumSphere proposed its own solution to the problem of converting cars to alternative hydrogen fuel. It developed a technology for creating nanocoatings of nickel–cobalt, iron–cobalt, iron–nickel or silver–copper alloys by vacuum deposition of vapours of these materials. A layer of spherical formations 16–25 nm in diameter is formed on the treated surface, which increases many times the area of the electrode taking part in the reactions.

The nanocoatings developed by QuantumSphere can find application not only for efficient electrolytic production of hydrogen but also for other applications based on electrochemical processes. For example, according to the company, the energy density of alkaline batteries with a nanocoated cathode increases fivefold, and their power by 320%. The new technology also yields significant improvements in nickel–metal hydride batteries, which are potentially less hazardous to the environment than the lithium-ion batteries popular today.

Review Questions

1. What is a nanostructured steel, and what properties does it have?
2. Why are stainless steels able to self-repair their protective film?
3. Name the main fields of application of nanotechnology in the automotive industry.
4. What advantages do nanostructured steels and the MuCell technology give in car design?
5. How do tungsten oxide nanoparticles on zirconium oxide improve catalytic activity?
6. What problems arise in microelectronics as the topological size of transistors decreases?
7. Explain the mechanism of hydrogen wear and how nanotechnological lubricant additives reduce friction.
8. What protective characteristics do automotive nanocoatings provide?
9. How can nanotechnology help in the transition to hydrogen fuel?

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