NANOMATERIALS I.

Selected chapters

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Ostrava 2015
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## LITERATURE
INTRODUCTION

At the present time, micro-miniaturization has reached such a level that properties of solid matters start to depend on their dimensions as small as nanometers. The manufacture of new types of components with high integration is more and more demanding from the point of view of technologies and represents hundreds of operations with high accuracy and reproducibility.

Nanocrystalline materials are single- or multi-phase polycrystalline substances with a grain size of several nanometers, mostly less than 100 nm.

All materials and systems have their “base” in small dimensions. A water molecule has a diameter of c. 1 nm, a single-wall carbon nanotube has a diameter of c. 1.2 nm, bio-molecular devices have sizes about several nanometers, a quantum dot of germanium on a silicon wafer is approximately 10 nm wide and 1.5 nm high, the smallest transistors today have sizes of only c. 20 nm. A DNA molecule is about 2.5 nm wide, a typical protein has a size of 1 to 20 nm and a biochemical motor has a diameter of c. 10 nm.

At present the nanotechnology field is very vast and includes: nanomanufacture, nanometrology, functional nanotechnology, nanomechanical equipments and devices, molecular nanotechnology, nanoparticles, nanostructural materials and extreme nanotechnologies.

Nanotechnology is a technical field dealing with creation and usage of technologies on a scale that spans orders-of-magnitude usually from approximately 1 ÷ 100 nm. There is also a study of a possibility of manipulation with a matter on an atomic and molecular scale, where quantum-mechanical phenomena differing diametrically from the macroscopic scale apply. Thanks to those phenomena new perspectives open in fields of magnetic recording media, computer technology, electronics, optics and other scientific fields.

Nanostructures, i.e. the scope of particles and structures of dimensions ranging from 1 to 100 nm, are considered the basic structural units of nanomaterials. Nanoscience deals with investigating their properties. It covers fields of physics of solid matters, chemistry, engineering and also molecular biology.

The application of nanotechnologies and nanomaterials is very extensive. Nowadays they have found application in many spheres of a common life such as electronics (memory media, spintronics, bioelectronics, quantum electronics), public health (targeted transport of medicaments), machine engineering (superhard surfaces with low friction, self-cleaning scratch resistant paints), chemical industry (nanotubes, nanocomposites, selective catalysis, aerogels), electrotechnics industry (high-capacity recording media, photomaterials, fuel cells), optics industry (optical filters, photonic crystals and photonic fibers, integrated optics), automotive industry, cosmic industry (catalyzers, resistant surfaces of satellites), military industry (nanosensors, structural components of space shuttles), living environment (biodegradation) etc.

In this publication we will describe the state of the art of research and development in the field of nanostructured typical metal, alloy, ceramic and intermetallic materials. The field of materials based on carbon and based on clay minerals is described in details in specialist literature satisfactorily [1, 2]. At first we classify the nanostructured materials. Then we describe the methods of their synthesis, discuss their formation, nanostructural and other properties. The significant progressive and non-traditional technologies used for obtaining various types of metal and ceramic nanomaterials are the subject of the 1st part of the lecture notes “Nanomaterials I” by Jaromír Drápala from the Department of Non-ferrous metals, refining and recycling. The second independent part called “Nanomaterials II” covers particularly the methods for obtaining ultra-fine grained and nanometric materials through the severe plastic deformation methods known under the abbreviation SPD. This part has been elaborated by Miroslav Greger from the Department of Materials forming.
1. **NANOTECHNOLOGY**

Quantum mechanics and standard models of atoms are scientific fields describing behaviour of elementary particles and individual atoms in molecules.

Classical physics describes properties of mass in large volumes. There is a nanoworld between the world of atoms and the actual real world, the field of particles and structures in dimensional range from 1 nm to c. 100 nm. Nanostructures, which are the basic elements of nanomaterials, are small enough for quantum phenomena to apply in them. Today we understand individual properties of atoms, however, so far we have learned only little about the behaviour of their clusters and how their many times unexpected properties originate. Investigating these phenomena is the object of nanoscience, the scientific field crossing the solid phase physics, chemistry, engineering and molecular biology.

However, nowadays the most important thing is not mere observing and characterizing the phenomena showing in the nanoworld, but also the practical use of new and unusual properties of nanomaterials, nanosystems and nanodevices, which we try purposely to create and combine with objects of larger dimensions.

Nanochemistry deals with creation and modification of chemical systems, the functionality of which is based on their nanodimensions. Supramolecular functional systems represent a material base for new matters.

Nanoanalytics ensures analytical methods and tools for learning essential phenomena and for characterization of products.

**A definition of nanotechnology**

Nanochemistry is a scientific discipline involving classical scientific fields, such as physics, quantum mechanics, chemistry, biochemistry, electronics etc., in development of materials, equipment and functional systems with exceptional properties, ensuing from the quantum principle and ability of self-organizing of mass in nanometer dimensions. At present there are many definitions of nanotechnology which differ more or less.

Nanochemistry involves research and technological development on atomic, molecular or macromolecular levels, on a dimensional scale approximately from 1 to 100 nm. This also involves the creation and use of structures, devices and systems, which have new properties and functions due to their small or intermediary dimensions. And this also covers an ability to manipulate objects on the atomic level.

**Nanotechnology** is the study of mass on the atomic and molecular level (usually from 0.1 to 100 nm), where properties differ dramatically from the properties at larger dimensions.

Nanotechnology is application of this knowledge for creating useful materials, structures and devices. It is a science and art of creating complex and practical devices with atomic accuracy.

In Table 1 relative sizes of atoms, biomolecules, bacteria and cells are shown.

**Table 1** The relative sizes of atoms, biomolecules, bacteria and cells

<table>
<thead>
<tr>
<th>Matter</th>
<th>Bond C–C</th>
<th>Glucose</th>
<th>Haemoglobin</th>
<th>Viruses</th>
<th>Bacteria</th>
<th>Red blood corpuscle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size [nm]</td>
<td>0.145</td>
<td>0.9</td>
<td>6.5</td>
<td>10 ÷ 200</td>
<td>1000 ÷ 10000</td>
<td>7000</td>
</tr>
</tbody>
</table>

As shown in Table 1, many biological materials can be classified as nanoparticles. Bacteria, the size of which ranges between 1 to 10 μm, belong to the mezzoscopic regions of the dimensional scale, while viruses with dimensions from 10 to 200 nm belong to the upper zone of nanoparticle sizes. Proteins, which usually occur in dimensions between 4 to 50 nm, belong to the lower zone of the nanometric scale. The structural
blocks of proteins consist of amino-acids; each has a dimension about 0.6 nm. There are more than 100 amino-acids in nature, but only 20 of them are involved in the synthesis of proteins.

Nanotechnology is an interdisciplinary field based above all on findings of chemistry, physics, materials engineering, electronics and biology. Especially electronics is a driving force of development of nanotechnology. The needed structures can be created by manipulation with atoms and molecules, possibly various chemical processes can be used.

2. BASIC METHODS OF PREPARATION OF METAL NANOPARTICLES

Time needed to study: 120 minutes

Aim: After studying this chapter you will:

Define the basic methods of preparation of metal nanoparticles, namely chemical and physical methods.

Describe the methods of reduction of salts of transition metals, electrochemical methods, photochemical and hydrothermal synthesis, methods for preparation of colloids.

Specify applicable methods for stabilization of nanoparticles.

Reading:

Metal nanoparticles can be prepared by two basic methods (Fig. 1):

- mechanical separation of metal aggregates (physical methods)
- nucleation and growth of a “nucleus” (chemical methods)

The physical methods lead to particles the diameters of which have a large variability. The colloid particles prepared this way have usually diameters larger than 10 nm and they cannot be prepared reproducibly. The particles can be prepared e.g. by mechanical milling of lumpy materials and stabilization of the created nanoparticles by adding colloid protective agents. Metal evaporation methods have provided a versatile opportunity for the production of a wide range of metal colloids on a preparative laboratory level. However, the use of the metal evaporation method is limited, because it is difficult to obtain particles of the demanded sizes.

The “bottom-up” method is much more usual for the preparation of nanoparticles, enabling to control their size. At present, these requirements are imposed on nanoparticles:

- A diameter ranging from units to tens of nanometers,
- well defined composition of a surface,
- reproducible synthesis and properties,
- a possibility of isolation and re-dissolving.

For the preparation of nanoparticles by the “bottom-up” method the chemical or electrochemical reduction of metal salts is used and the controlled decomposition of metastable organo-metal compounds. To control the growth of nanoparticles and for their protection against aggregation a large amount of stabilizers,
such as donor ligands, polymers and detergents are used. The nanoparticle formation mechanism is based on nucleation, growth and aggregation. In the initial state of nucleation the salt of metal is reduced, leading to origination of metal atoms. These coagulate with other ions, atoms of metals or clusters and irreversibly create “nuclei” of a stable metal core. A nucleus diameter should be below 1 nm depending on the force of metal bonds and the magnitude of a redox potential of the metal salt and on the used reducing agent.

The separation methods include e.g. chromatography and ultra-centrifugation and provide monodisperse particles, however, only in an amount of milligrams. In a selective synthesis, an important factor affecting sizes of particles is the force of metal bonding, a molar ratio of the metal salt, of the stabilizing and reducing agent, a conversion degree, the reaction time, temperature and possibly even pressure. In addition, newer methods of the selective preparation of nanoparticles, such as electrochemical reduction, thermic decomposition or ultrasonic decomposition, can be used.

2.1 Chemical methods

Chemical methods belong among the most widely used methods for preparation of nanoparticles. Nanoparticles of the demanded shapes and sizes can be prepared using appropriate conditions.

Reduction of salts of transition metals in a solution is the most widely used method for the preparation of colloid suspensions of metals. Monodisperse nanoparticles in amounts in order-of-magnitude of grams originate. Various reducing agents are used for the preparation of colloid matters, such as hydrides and salts or even oxidizable agents, e.g. alcohols.

The classical Faraday method represents reduction of gold tetrachloride by potassium citrate; this way, nanoparticles of diameters about 20 nm used for histological applications were prepared. This procedure was used for creation and observation of gold nanoparticles. For its simplicity it became favourite even in other branches of nanotechnology. However, the citrate anion has a disadvantage, that during reduction the acetonicarboxylic acid occurs, which partly disables formation of well-defined particles.

The most widely used hydrides for creation of metal nanoparticles are NaBH₄ and KBH₄. Other reducing agents include diborane, silanes, hydrazine and its derivates, organo-alumino compounds, potassium tartrate, ascorbic acid and others. As stabilizing agents, detergents or polymers soluble in water are used. This way, metal nanoparticles can be prepared (such as Cu, Pt, Pd, Ag and Au). Recently dendrimers have been used for stabilization, enabling to stabilize all the above mentioned nanoparticles and leading to formation of almost monodisperse particles.

Some salts of transition metals can be reduced in boiling ethanol, in which stabilization substances are present. In this process, alcohol is both the dissolving and reducing agent. Primary or secondary alcohols are mostly used. During reduction the alcohol is oxidized to the corresponding carbonyl compound.

Another method of preparation of nanoparticles is removing ligands from organometallic compounds. Some zero-valent organometallic compounds can be changed to a colloid suspension of metals by reduction or removing of ligands. For example reduction of some organic compounds of platinum (Pt(dba)₂) and palladium (Pd(dba)₂) allows preparing nanoparticles of these metals of sizes of several nanometers. Nickel, cobalt, copper and gold nanoparticles were prepared, too.

Another electrochemical method enables to obtain size-controlled nanoparticles in a large scale. The mechanism involves:
- dissolution of the anode to form metal ions (such as oxidation of Pd to Pd²⁺),
- migration of the metal ions to the cathode,
- reduction of the metal ions at the surface of the cathode,
- aggregation of the particles stabilized by ammonium ions around the metal cores,
- precipitation of the nanoparticles.

This process presents several advantages, such as preventing formation of undesirable side products, easy isolation of the nanoparticles out of the solvent and mainly a possibility to control the formed nanoparticle size. The electrochemical methods were applied successfully for preparation of metal nanoparticles of Pd, Ni, Co, Fe, Ti, Ag and Au in the amount of hundreds of milligrams.

Polymer micelles used as nanoreactors for preparation of nanoparticles can have varied shapes, e.g. a spherical (Fig. 2) or a rod shape.
H₂, NaBH₄, LiAlH₄ and hydrazine are mostly used as reducing agents. They can be used for preparation of metal nanoparticles of Au, Co, Cu, Ni, Pb, Pd, Pt, Rh and Zn as well as nanoparticles of oxides and sulphides of metals.

2.2 Physical methods

Many organometallic compounds are thermally decomposable to their zero-valent components. Photochemical synthesis of nanoparticles can be carried out either by the transition metal salt reduction by radiolytically produced reducing agent or through degradation of an organometallic complex by radiolysis. This way, nanoparticles of Ag, Au, Ir, Pt, Pd and Cu metals were prepared.

By the latter method nanoparticles of Au, Ag, Pt and Pd were prepared, whereas it was found out that UV-Vis irradiation provides smaller nanoparticles with a low relative standard deviation of diameters.

The very high temperature (> 5000 K), the pressure (> 20 MPa) and the cooling rate (> 10⁷ K·s⁻¹) reached by ultrasound gave unique properties to the solution. These extreme conditions were used to obtain gold, iron and other nanoparticles. By warming some metal compounds by microwave radiation Ag, Au and Pt nanoparticles with a low relative standard deviation of particle diameters can be obtained.

Hydrothermal synthesis is carried out in a supercritical liquid environment, which serves as a solvent. Ni, Co and Fe nanoparticles were prepared this way.

2.3 Preparation of bimetallic colloids

Besides usual nanoparticles, bimetallic colloids consisting of two various metals can be also prepared. These colloids often feature better activity and selectivity in comparison with monometallic particles, which is probably caused by synergism between two metals creating the nanoparticle.

One of the options of preparation of bimetallic colloids is co-reduction of metal precursors. The principle of this synthetic method is the same as with the preparation of monometallic nanoparticles. Metal precursors are reduced in the presence of a stabilizing agent in order to prevent aggregation, while the particles are originating. For preparation of Fe/Pt, Pd/Pt, Au/Pd, Pt/Rh, Pt/Ru, Pd/Ru and Ag/Pd bimetallic nanoparticles a number of methods were tested.

Another possibility is a gradual reduction of salts of transition metals for synthesis of bimetallic colloids. This way various bimetallic nanoparticles were prepared (e.g. Au/Ag, Au/Cu, Au/Pt and Au/Pd).

To prepare bimetallic nanoparticles by electrochemical reduction a cell with two metal anodes is needed. This way, among others, bimetallic nanoparticles of the following metals can be prepared: Pd/Ni, Fe/Co and Fe/Ni. In the case of Cu, Pt, Rh, Ru and Mo, which are less soluble anodically, the respective salts are reduced at the cathode.

Ultrasound reduction is the most frequently used physical method. Au/Pd nanoparticles were prepared in the same way as monometallic particles.

Nucleation and growth of nanoparticles

The method of nucleation and growth can be used to obtain nanoparticles with diameters ranging between 5 to 40 nm (the relative standard deviation of diameters of particles is usually from 10 to 15 %). Growing the nanoparticles step by step is more efficient than the one-step method of nucleation and growth of nanoparticles, because secondary nucleation can be avoided.
Synthesis of oxide nanoparticles

Besides metal nanoparticles, nanoparticles of their oxides can be obtained as well, but their application is not as wide as in the case of the metals themselves. Synthesis can be performed in water solutions, in which hydrazine or hydroxylamine is used as a reducing agent. Under these conditions nanoparticles of some oxides were prepared (e.g. VO$_2$, Cr$_2$O$_3$, Mn$_2$O$_3$, NiO and Fe$_3$O$_4$). Another possibility is reduction in an anhydrous environment.

2.4 Stabilization of nanoparticles

One of the main characteristics of colloid particles is their small size. These metal nanoparticles are unstable as a result of aggregation, which leads to formation of clusters. In most cases the aggregation results in a loss of properties related to the colloidal state of these nanoparticles. For example, coagulation during catalysis leads to a significant loss of the catalytic activity. Stabilization of a nanocluster is usually divided into electrostatic and steric stabilization (Fig. 3).

![Fig. 3 a) electrostatic stabilization, b) steric stabilization of metal colloids](image)

Four types of stabilization mechanisms:
- Electrostatic stabilization by surface adsorbed anions,
- Steric stabilization by the presence of large functional groups,
- Combination of these two mechanisms with electrosteric stabilization,
- Stabilization by a ligand or a solvent.

Electrostatic stabilization

Ion compounds, such as halogenides, carboxylates or polyoxoanions dissolved in a solution (mostly aqueous), can lead to electrostatic stabilization. Adsorption of these compounds and their corresponding anions on the metal surface create electric double-layer around particles, which results in the electrostatic repulsion between particles. If the electric potential of the double-layer is large enough, the electrostatic repulsion can prevent aggregation of particles. Colloid suspensions stabilized by electrostatic repulsion are very sensitive to any influences disturbing the double-layer, such as the ion force or temperature, so the control of these parameters is necessary to ensure the effective stabilization of colloids.

The electrostatic stabilization effect can be easily found out by a change of the solution ion force, which can be achieved by adding salt. When creating such a solution ion force, which destroys the electrostatic repulsion, aggregation of nanoparticles occurs, accompanied by a plasmon resonance wavelength change. This test is widely used and, except for others, it serves for confirmation of the electrostatic stabilization change after modification of nanoparticles.

Steric stabilization

Another method to protect colloid metal particles against aggregation is to use macromolecules, such as dendrimers, polymers, block copolymers or oligomers, which create a protective layer around the nanoparticles. Steric stabilization can be used both in organic and in aqueous phase.
Electrosteric stabilization

Electrostatic and steric stabilization were combined in order to maintain metal nanoparticles in the solution. The above mentioned ion detergents or organo-metals are used as stabilizers. These compounds carry both the polar functional group enabling to generate electric double-layer and lipophilic chain providing steric repulsion.

Stabilization by a ligand or a solvent

This is application of conventional ligands for stabilization of transition metal colloids. This stabilization is enabled by coordination of metal nanoparticles with ligands, such as phosphines, thiols and their derivatives and amines.

Nanoparticles can be stabilized by solvent molecules themselves. The advantages of stabilization by a solvent are as follows:

- The method is generally applicable for salts of metals of 4th to 11th group in the periodic table.
- The method provides high yields of colloids of metals, which are easily isolatable as powders.
- The particles are almost monodisperse.
- The synthesis is advisable for preparation of several grams and it can be easily performed even on a larger scale.

### Summary of terms:

- Basic chemical and physical methods of preparation of metal nanoparticles.
- Reduction of transition metal salts, electrochemical methods, removing ligands from organometallic compounds.
- Photochemical and hydrothermal synthesis, preparation of bimetallic colloid solutions.
- Methods of stabilization of nanoparticles – electrostatic, steric, electrosteric, stabilization by a ligand or a solvent.
3. PROGRESSIVE METHODS OF A SYNTHESIS OF NANOMATERIALS

Time needed to study: 240 minutes

Aim: After studying this chapter you will:

- Define the basic types of modern methods of a synthesis of nanomaterials from the gaseous, liquid and solid phase.
- Describe the basic types of mills for the manufacture of powders and nanopowders.

Reading:

Nanocrystalline materials can be prepared by combining small clusters or destruction (breaking-up) of larger material to smaller and smaller particles. There is a variety of methods for preparation of nanostructural materials from the gaseous, liquid or solid phase. In recent years, nanostructured materials have been prepared mainly using the following methods [1]:

- Condensation from the inert gaseous phase.
- Milling and mechanical alloying.
- Plastic deformation.
- Electro-deposition.
- Rapid precipitation from the melt.
- Epitaxy – Solid Phase Epitaxy (SPE), Vapor Phase Epitaxy (VPE), Liquid Phase Epitaxy (LPE), Molecular Beam Epitaxy (MBE), Metal Organic Vapor Phase Epitaxy (MOVPE), Laser Epitaxy.
- Physical Vapor Deposition (PVD).
- Chemical Vapor Deposition (CVD).
- Lithography – nanolithography, Extreme Ultraviolet Lithography (EUV), X-ray photolithography, electron and ion projection lithography.
- Chemical reactions.
- Sol-gel methods.
- Plasma application.
- Laser ablation.
- Hydrothermal pyrolysis.
- Ultrasound synthesis.

<p>| Table 2 Overview of the methods to synthesize nanocrystalline metallic materials [3] |
|---------------------------------|---------------------------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Starting phase</th>
<th>Technique</th>
<th>Dimensionality of product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor</td>
<td>Inert gas condensation</td>
<td>3-D</td>
</tr>
<tr>
<td></td>
<td>Physical vapor deposition (PVD)</td>
<td>1-D</td>
</tr>
<tr>
<td></td>
<td>Evaporation and sputtering</td>
<td>3-D</td>
</tr>
<tr>
<td></td>
<td>Plasma processing</td>
<td>3-D, 2-D</td>
</tr>
<tr>
<td></td>
<td>Chemical vapor deposition (CVD)</td>
<td>3-D</td>
</tr>
<tr>
<td></td>
<td>Chemical reactions</td>
<td>3-D</td>
</tr>
<tr>
<td>Liquid</td>
<td>Rapid solidification</td>
<td>3-D</td>
</tr>
<tr>
<td></td>
<td>Electro-deposition</td>
<td>1-D, 3-D</td>
</tr>
<tr>
<td></td>
<td>Chemical reactions</td>
<td>3-D</td>
</tr>
<tr>
<td>Solid</td>
<td>Mechanical alloying/milling</td>
<td>3-D</td>
</tr>
<tr>
<td></td>
<td>Devitrification of amorphous phases</td>
<td>3-D</td>
</tr>
<tr>
<td></td>
<td>Spark erosion</td>
<td>3-D</td>
</tr>
<tr>
<td></td>
<td>Sliding wear</td>
<td>3-D</td>
</tr>
</tbody>
</table>
The choice of the method depends upon the ability to control the most important feature of the nanocrystalline materials, the microstructural features (grain size, layer spacing, etc.). Other aspects of importance are the chemical composition and surface chemistry or cleanliness of the interfaces. Extremely clean interfaces can be produced and retained during processing and subsequent consolidation by conducting the experiments under UHV conditions.

Inert gas condensation, mechanical alloying/milling, spray conversion processing, electrodeposition, and devitrification of amorphous phases are some of the most popular techniques used to produce nanocrystalline intermetallics.

### 3.1 Inert-Gas Condensation method

Vapor condensation has been known to produce very fine-grained or amorphous alloys depending on the substrate temperature and other processing conditions. This technique was originally used to synthesize small quantities of nanostructured pure metals. A number of variants have also been subsequently developed.

The inert gas condensation technique (Figure 4) consists of evaporating a metal (by resistive heating, radio-frequency heating, sputtering, electron beam heating, laser/plasma heating, or ion sputtering) inside a chamber that was evacuated to a very high vacuum of about $10^{-4}$ Pa.

Isolated nanoparticles are usually produced by evaporation of metal, alloy or semiconductor at a controlled temperature in the atmosphere of a low-pressure inert gas. Next follows the subsequent condensation of the vapour in the vicinity or on the cold surface. This is the simplest method of producing nano-crystalline powders. In contrast to vacuum evaporation, the atoms of the substance, evaporated in a rarefied inert atmosphere, lose their kinetic energy more rapidly as a result of collisions with gas atoms and form segregations (clusters).

A method of the condensation of metal vapours in a gas atmosphere is the process of dispersion of a metal by means of an electric arc in a liquid with subsequent condensation of metallic vapours in liquid vapours. The group of researchers evaporated gold from a heated tungsten filament at a nitrogen pressure of 40 Pa, and produced in the condensates spherical particles with a diameter of $1.5 \div 10$ nm (the mean diameter approximately 4 nm). They found that the particle size depends on the gas pressure and, to a lesser degree, on the rate of evaporation. The condensation of vapours of aluminum in H$_2$, He and Ar at different gas pressures made it possible to produce particles with a size of $20 \div 100$ nm. Later, the method of combined condensation of metal vapours in Ar and He was used to produce Au-Cu and Fe-Cu highly dispersed alloys, formed by spherical particles with a diameter of $16 \div 50$ nm [4].

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Fig. 4 Schema of the inert-gas condensation chamber for synthesis of nanocrystalline materials [3]
Nanomaterials I.

The method for production of nanomaterials is based on the method of input of evaporated material, the method of supplying energy for evaporation, the working medium, setup of the condensation process, the system for collecting the produced powder.

Evaporation of a metal may take place from a crucible or the metal may be fed into the zone of heating and evaporation in the form of wire, injected metallic powder or a liquid jet. The metal may also be dispersed with a beam of argon ions. Energy may be supplied directly by heating, the passage of electric current through a wire, electric arc discharge in plasma, induction heating with high- and super-high frequency currents, laser radiation, and electron-beam heating.

Evaporation and condensation may take place in vacuum, in a stationary inert gas, or in a gas flow, including in a plasma jet. Condensation of the vapour-gas mixture with a temperature of 5000 °C to 10000 K may take place during its travel into the chamber with a large section and the volume filled with a cold inert gas. There are systems in which two jets travel coaxially into the condensation chamber: the vapour-gas mixture is supplied along the axis, and a circumferential jet of a cold inert gas travels along its periphery. As a result of turbulent mixing, the temperature of metal vapours decreases, super-saturation increases and rapid condensation takes place. Favourable conditions for the condensation of metallic vapours are generated in adiabatic expansion in a Laval nozzle, when rapid expansion results in the formation of a steep temperature gradient and almost instantaneous vapour condensation takes place.

An independent task is the collection of the nanocrystalline powder produced by condensation, because the individual particles of this powder are so small that they are in constant Brownian motion and remain suspended in the gas, not settling under the effect of the forces of gravity. The produced powders are collected using special filters and centrifugal deposition; in some cases, the particles are trapped by a liquid film.

Depending on the evaporation conditions of the metal (gas pressure, the position and temperature of the substrate), its condensation may take place either in the volume or on the surface of the reaction chamber. Volume condensates are characterised by the presence of spherical particles, whereas the particles of the surface condensate are faceted. In the same evaporation and condensation conditions, metals with high melting points form smaller particles.

If the gas pressure is lower than approximately 50 Pa, spherical particles of metal with a mean diameter of $D < 30$ nm settle on the walls of relatively large reaction chambers (diameter greater than 0.25 m). When the pressure is increased by several hundreds of Pa, the formation of highly dispersed metallic particles is completed in convective flows of the gas in the vicinity of the evaporator.

Gas-phase synthesis can be used to produce particles with a size from 2 nm to several hundreds of nanometers. Metal vapours are passed through a cell with helium with a pressure of $\sim 1000$ to $1500$ Pa, and are then transferred into a vacuum chamber ($\sim 10^{-5}$ Pa), where the mass of the cluster is stabilised during the time of flight of a specific distance in the mass spectrometer. This method is used to produce clusters of antimony, bismuth and lead.

Recently, the gas-phase synthesis of nanoparticles has been developed extensively as a result of the application of different methods of heating the evaporated substance. Highly dispersed deposits of silver and copper on glass were produced by evaporation of metals in an inert atmosphere at a pressure of 0.01 to 0.13 Pa. The same method was used to produce clusters of Li. Evaporation of lithium in high vacuum was accompanied by the formation of only separate atoms of lithium. Nanocrystalline powders of the oxides $\text{Al}_2\text{O}_3$, $\text{ZrO}_2$ and $\text{Y}_2\text{O}_3$ were produced by evaporating oxide targets in a helium atmosphere, magnetron sputtering of zirconium in a mixture of argon and oxygen, and by the controlled evaporation of yttrium nanocrystals. To produce highly dispersed powders of transition metal nitrides, the electron-beam heating of targets of appropriate metals, with evaporation carried out in the atmosphere of nitrogen or ammonia at a pressure of 130 Pa, was used.

Nanocrystalline powders have also been produced by plasma, laser and arc heating methods. Some authors produced nanoparticles of carbides, oxides and nitrides by the pulsed laser heating of metals in a rarefied atmosphere of methane (in the case of carbides), oxygen (in the case of oxides), nitrogen or ammonia (in the case of nitrides). The pulsed laser evaporation of metals in the atmosphere of an inert gas (He or Ar) or a reagent gas ($\text{O}_2$, $\text{N}_2$, $\text{NH}_3$, $\text{CH}_4$) makes it possible to produce mixtures of nanocrystalline oxides of different metals, oxide-nitride or carbide-nitride.
mixtures. The composition and size of nanoparticles may be controlled by the variation of the pressure and composition of the atmosphere (inert gas or reagent gas), the power of the laser pulse, the temperature gradient between the evaporated target and the surface on which condensation takes place.

The method of condensation of vapors in an inert gas is used most frequently for producing small amounts of nanopowders. The powders synthesised are not agglomerated efficiently and are sintered at a relatively low temperature.

The inert gas condensation technique (Figs. 4 and 5) consists (as you can see above) of evaporating a metal (by resistive heating, radio-frequency heating, sputtering, electron beam heating, laser/plasma heating, or ion sputtering) inside a chamber that was evacuated to a very high vacuum of about $10^{-4}$ Pa and then back-filled with a low pressure inert gas, typically a few hundred Pascals of helium. The evaporated atoms collide with the gas atoms inside the chamber, lose their kinetic energy, and condense in the form of small, discrete crystals of loose powder. Convection currents, generated due to the heating of the inert gas by the evaporation source and cooled by the liquid-nitrogen-filled collection device (cold finger), carry the condensed fine powders to the collector device, from where they can be stripped off by moving an annular teflon ring down the length of the tube to carry the powder product into a compaction device. Compaction is carried out in a two-stage piston-and-anvil device initially in the upper chamber at low pressures to produce a loosely compacted pellet, which is then transferred in the vacuum system to a high-pressure unit where final compaction takes place. The scraping and compaction processes also are carried out under UHV conditions to maintain cleanliness of the particle surfaces (and subsequent interfaces) and also to minimize the amount of any trapped gases.

The crystal size of the powder is typically a few nanometers and the size distribution is narrow. The crystal size is dependent upon the inert-gas pressure, the evaporation rate, and the gas composition. Extremely fine particles can be produced by decreasing either the gas pressure in the chamber or the evaporation rate and by using light gases such as He rather than heavy inert gases such as Xe.

 Nanostructured intermetallics could also be synthesized using this method – see Fig. 4. Different metals could be evaporated from more than one source and the cold finger could be rotated to help in achieving a better mixing of the vapor. But achievement of correct stoichiometry may not be easy. Therefore, magnetron sputter deposition, which provides excellent control of the alloy composition, has been used instead of thermal evaporation to produce nanocrystalline TiAl.

Characteristics (distribution and sizes of particles, agglomeration capacity, agglomeration temperature) of nanopowders obtained by this method do not differ from nanopowders synthetized by standard and evapora-
tion condensation methods. However, the surface reactivity of nanocrystalline particles makes the preparation of these nanopowders considerably difficult.

### 3.2 Milling and Mechanical Alloying (MA)

Generally, mechanical milling is meant as milling powders of the same composition, such as pure metals or intermetallic compounds. In this case the transfer of materials is not needed for homogenization. Conventional milling in a ball mill provides low mechanical energy, which adequately disintegrates large particles, however, their crystalline structure does not change. When milling in a high-energy ball mill the impact energy is 1000-fold higher, so it induces rapid changes of phases and chemical reactions just at ambient temperature. Therefore the disintegrating process and reduction of particle sizes in a conventional ball mill is usually designated as the first step of high-energy milling, which forgoes mechanical alloying.

During mechanical alloying a mixture of powders comprising various metals, alloys or compounds is milled. A transfer of materials is applied in order to obtain homogenous alloys. This way, nanostructured and metastable materials and a wide variety of new materials, which usually cannot be synthetized or their manufacture is considerably difficult, can be obtained. Various types of mills with a high-energy milling ability are used for the manufacture of mechanically alloyed powders. The mills differ in capacity, milling effectiveness and a need for additional equipment for cooling or heating.

The mills of SpeX „shaker“ type can pulverize about 10 to 20 g of powder at the same time. This is the most frequently used mill for the laboratory research. The typical arrangement of this mill incorporates a container (Fig. 6) containing a sample and a grinding ball secured in a special clamp, shaking in a fast back-and-forth motion more than a thousand times per minute. The shaking motion is combined with lateral movements at the end of the container. With each swing the grinding balls impact the sample and the front of the container, so that the sample is milled and mixed at the same time. As the amplitude and the velocity of the clamp movement contribute to the speed of the balls, the resulting ball impact force is unusually high.

**Fig. 6 Milling set comprising the container, cover, seal and grinding balls of tungsten carbide**

**Planetary ball mill**

Another mill suitable for mechanical alloying is a planetary ball mill. In mills of this type several hundreds of grams of powder can be milled. Containers in the mill move like planets. They are positioned on a supporting disc and a special driving mechanism causes their rotation around their own axes. Centrifugal forces generated by the rotation of the containers around their own axes and the rotation of the supporting disc affect the content of the containers consisting of the milled material and grinding balls.

**Fig. 7 a) Planetary ball mill: 1) a base plate, 2) a motor with a changing direction of rotating and rotations, 3) a drive transmission, 4) a supporting disc, 5) grinding containers (rotating direction opposite towards the supporting disc) b) Schematic depiction of grinding in a container**

As the containers and the disc rotate in the opposite direction, the centrifugal forces alternately act in like and opposite directions. The grinding balls fall down onto the inner wall of the containers – the impact effect (see Fig. 7).
Attritors (Fig. 8) are ball mills able to generate higher energies. An attritor incorporates a vertical drum containing a number of rotating impellers inside. These stirring impellers “enhance” the balls, because a strong motor rotates the impellers and they gradually stir the steel balls in the drum. In attritors a large amount of powders can be processed at the same time – from 0.5 up to 40 kg.

Commercial mills used for mechanical alloying are much larger than the above described mills and they can process several hundreds of kilograms of materials at the same time. For commercial purposes of mechanical alloying, ball mills up to a capacity about 1250 kg are used. Mechanical alloying is a complex process involving many variable parameters influencing obtaining a demanded phase of a product or microstructure. A type of a mill, a milling drum material, milling speed and time of milling, a type, size and size distribution of the grinding medium, mass ratio of grinding balls towards powder, a rate of filling of the milling containers, temperature during milling, belong among important parameters.

The main problem is a possible contamination of material during the manufacturing process. Contamination can originate in a grinding medium or atmosphere. If alloyed steels are used as grinding media, contamination with iron may occur. Heavy materials, such as Fe, can cause a contamination degree > 5 % in high-energy ball mills. As many intermetallic phases belong among heavy materials, dangerous contamination threatens here, too. A decrease of the contamination degree can be achieved by the use of a low-energy mill with a grinding medium of tungsten carbide or transformation hardened zirconium, by a highly pure inert atmosphere (e.g. argon) or by milling in vacuum. It is evident that also further processing of the powder must be carried out under a protective atmosphere.

Intermetallic phases can be directly synthetized by MA technology, because the most of them just have a nanostructural character. In recent years, SPD (severe plastic deformation) processes are often used, such as ECAP methods (equal-channel-angular pressing), torsion straining and ARB (accumulative roll bonding) techniques, through which ultra-fine grained structures could be made. A grain size is usually ranging between 0.3 ÷ 0.5 μm.

The grain sizes were found to decrease with milling time down to nanometer levels, as shown in Figure 9 for a series of α2 – titanium aluminide compositions. The smallest attainable grain-size scales inversely with the melting temperature. Powder contamination (from the milling tools and/or the atmosphere) is usually a matter of concern with this process, especially when reactive metals and/or long milling times are involved.

3.3 Spray Conversion Processing

This is a commercial process employed to produce nanocrystalline WC-Co composite powders. This process starts with aqueous solution precursors such as ammonium metatungstate [(NH₄)₆(H₂W₁₂O₄₃).4H₂O] and
cobalt chloride \([\text{CoCl}_2]\), cobalt acetate \([\text{Co(CH}_3\text{COO})_2]\), or cobalt nitrate \([\text{Co(NO}_3)_2]\). The solution mixture is aerosolized and rapidly spray dried to give extremely fine mixtures of tungsten and cobalt complex compounds. This precursor powder is then reduced with hydrogen and reacted with carbon monoxide in a fluidized-bed reactor to yield nanophase cobalt/tungsten carbide powder. The tungsten particles are \(2 \div 40\) nm in size. A typical powder particle consists of a hollow, porous \(75\ \mu\text{m}\) sphere containing hundreds of millions of WC grains in a cobalt matrix. To prevent grain growth of tungsten, additions of inhibitors such as VC and Cr\(_2\)C\(_2\) are made as binders during sintering steps. Recently, vanadium is introduced into the starting solution itself to achieve a more uniform distribution in the powder mixture.

3.4 Devitrification of amorphous phases

Many non-equilibrium processing techniques such as rapid solidification from the liquid state, mechanical alloying/milling, electrodeposition, and vapor deposition can produce amorphous (glassy) alloys [3]. Controlled crystallization of these amorphous alloys leads to the synthesis of nanostructured materials (by increasing the nucleation rate and decreasing the growth rate). The most common method to produce nanocrystalline magnetic materials has been to obtain an amorphous phase by rapidly solidifying a melt of appropriate composition and then crystallizing the glassy phase at a relatively low temperature. The microstructure in this condition consists of nanometer-sized grains in an amorphous matrix.

The simple devitrification methods have been commonly employed to study the magnetic properties of nanocrystalline materials because it can produce:

(a) porosity-free samples,
(b) samples with different grain sizes by controlling the crystallization parameters,
(c) large quantities of material.

The interfaces are clean and the product is dense. Samples with different grain sizes can be synthesized by controlling the crystallization process, affording a way of comparing the properties of amorphous, nanocrystalline, and coarse-grained materials of the same composition.

In recent times there have been several basic investigations to define the conditions under which very fine (nanocrystalline) microstructures form, starting from the glassy phases. A recent development in this area is the study of nanocrystalline materials produced by crystallization of amorphous powders or ribbons when they are subjected to mechanical milling. Even though the exact mechanism of the process is presently not known, mechanical milling offers a useful route to the preparation of high-purity nanocrystalline materials in bulk quantities since metallic glassy ribbons are commercially available.

The most commonly used method for the manufacture of nanocrystalline magnetic materials, through which amorphous phases were obtained by rapid solidification, is RSP - Rapid Solidification Process (extreme solidification velocity as high as \(10^5\ \text{K/s}\)) for a melt of a proper composition with a following formation of the glassy phase at relatively low temperature.

### Summary of terms:

- Basic methods of synthesis on nanomaterials from gaseous, liquid and solid phases.
- Inert-Gas Condensation method.
- Mechanical milling and mechanical alloying.
- Mills for production of nanopowders, SPEX shaker, planetary ball mill, attritors.
- High- and low energy milling
- Spray conversion processing.
- Devitrification of amorphous phases

4. CHEMICAL METHODS OF THE PRODUCTION OF NANOMATERIALS
**Aim:** After studying this chapter you will:
- describe chemical methods of the manufacture of nanomaterials from the liquid phase,
- precipitation from colloid solutions,
- synthesis of dispersed oxides,
- electrolytic segregation.

**Reading:**

### 4.1 Chemical methods (in the liquid phase)

The most significant methods for preparation of nanomaterials from the point of view of controlled growth and increasing the amount of prepared materials are chemical methods. For example molybdenum nanoparticles can be reduced in the toluene solution by a reducing agent at room temperature. In this reaction a large amount of molybdenum nanoparticles with dimensions of 1 to 5 nm are formed. Chemical equation of the reaction:

\[
\text{MoCl}_3 + 3\text{NaBEt}_3\text{H} \rightarrow \text{Mo} + 3\text{NaCl} + 3\text{BEt}_3 + 3/2 \text{H}_2
\]

Aluminum nanoparticles can be prepared by the decomposition of the reducing agent Me₂EtNAlH₃ (Me = methyl) in toluene by heating the solution to 105 °C for a period of 2 hours.

**Precipitation from colloid solutions**

Precipitation from colloid solutions is evidently the first method of producing nanoparticles. The conventional method of producing nanoparticles from colloid solutions is based on a chemical reaction between the components of the solution and interrupting the reaction at a specific moment in time. Subsequently, the dispersed system is transferred from the liquid colloidal state to the nanocrystalline solid state. For example, nanocrystalline powders of sulfides are produced by reaction of hydrosulfuric acid H₂S or sulfide Na₂S with the water-soluble salt of a metal: Nanocrystalline cadmium sulfide CdS is produced by precipitation from a mixture of solutions of cadmium perchlorate Cd(ClO₄)₂ and sodium sulfide Na₂S

\[
\text{Cd(ClO}_4)_2 + \text{Na}_2\text{S} \rightarrow \text{CdS} + 2\text{NaClO}_4.
\]

The growth of nanoparticles of CdS is interrupted by a sudden increase of the pH of the solution.

The colloid particles of metal oxides are produced by hydrolysis of salts. For example, TiO₂ particles form easily in hydrolysis of titanium tetrachloride

\[
\text{TiCl}_4 + 2 \text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{HCl}.
\]

**A synthesis of dispersed oxides**

in melted metals is a new method of preparation of highly dispersed particles. The working medium is the gallium melt at temperatures of 323 ÷ 423 K, the lead melt at 653 ÷ 873 K or Pb-Bi alloys at 453 ÷ 873 K.

The synthesis is performed in two steps: In the first step the metal M is dissolved in the melt. The chemical affinity of this metal for oxygen is higher than of the metal creating the melt. Solubility of the metal M in the melt should not be less than 0.1 wt.%. In the second step the molten metal M is oxidized by the boiling melt with water vapors or a gas mixture (H₂O + Ar). The content of water vapors in the gas oxidation mixture is usually 15 ÷ 30 vol.%. The selective oxidation leads to formation of highly dispersed oxide.

**Influencing the reaction process**
The reaction process can be influenced by:
- the specific thermal capacity,
- the enthalpy of phase transformations,
- the thermal conductivity,
- the diffusion coefficient,
- the viscosity,
- the solution pH,
- the phase equilibrium coefficient.

The resulting reactions are conditioned by the local conditions, i.e. the factors depending on:
- the heat transfer,
- the mass transfer,
- the mixing.

In these processes the reaction process is influenced also by interactions between the very reactants as well as between reactants and products.

### 4.2 Electrodeposition

This is a simple and well-established process and can be easily adapted to produce nanocrystalline materials. Electrodeposition of multilayered (1-D) metals can be achieved using either two separate electrolytes or, much more conveniently, from one electrolyte by appropriate control of agitation and the electrical conditions (particularly voltage). Also, 3-D nanostructured crystallites can be prepared using this method by utilizing the interference of one ion with the deposition of the other. The electrodeposition yields grain sizes in the nanometer range when the electrodeposition variables (e.g. bath composition, pH, temperature, current density, etc.) are chosen such that nucleation of new grains is favored rather than growth of existing grains.

This was achieved by using high deposition rates, formation of appropriate complexes in the bath, addition of suitable surface-active elements to reduce surface diffusion of ad-atoms, etc. This technique can yield porosity-free finished products that do not require subsequent consolidation. The process requires low initial capital investment and provides high production rates with few shape and size limitations.

### 4.3 Chemical deposition and condensation from the gaseous phase (CVD, CVC)

CVD – Chemical Vapor Deposition is a method for the preparation of thin layers. This method is designated as „chemical” due to the fact that a layer on the surface of the coated substrate forms as a result of a chemical reaction of precursors, in contrast to the physical deposition, where physical principles are applied for the formation of a layer. The CVD method uses for deposition chemically reactive gases heated to a relatively high temperature ranging between 900 ÷ 1100 °C. The reaction components are fed in the gaseous phase and the layer forms on the surface by the heterogeneous reaction – nucleation. The CVD method is used mainly for VPE – Vapor Phase Epitaxy for the formation of very thin layers on silicon substrates for semiconductor technology, for the manufacture of integrated circuits with a high degree of integration.

**The CVD method working process**

In the first phase the precursors are gasified at high temperatures and individual molecules are lead to the CVD reactor, where they are adsorbed on the substrate surface. The coated substrate is during the deposition subjected to effects of one or more volatile precursors, which interact between each other on its surface or they decompose, while the demanded product is originating.

Chemical deposition from vapors consists of three basic steps:

(1) Transport of atoms, molecules or ions of the precursor to the substrate surface at high temperature.
(2) Chemical reactions on the substrate surface involving formation of the new material (chemical reactions).

(3) Removing more volatile side products from the substrate surface using a gas stream or vacuum.

The first and the third step are generally dependent on each other, because the diffusion rate of reactants affects the diffusion rate of side products. These two steps are conditioned by the stoichiometry of the chemical reactions and they influence the resulting speed. The second step is usually the most complicated and involves the following reactions: simultaneous adsorption and desorption (chemisorption and physical absorption) and nucleation processes.

In order to create perfect films the control of nucleation in the gaseous phase is the primary and necessary step during the growth process. Above all, it is necessary to prevent the particle homogenous growth in the gaseous phase (in contrast to the chemical condensation from vapors), since it affects considerably the very deposition and results in an uneven layer thickness and deposition of undesirable particles.

If the temperature is maintained on a value substantially higher than the temperature of pyrolysis of the reactants, their faster decomposition on the substrate surface is ensured, whereas the growth rate is limited by the reactant mass transport onto the substrate surface through the border layers, particularly by its kinetics and a change in the free energy.

**CVD precursors**

The chemical deposition from the gaseous phase is a very flexible and complex method of the manufacture of thin films applicable for a great number of materials from metals to semiconductors and ceramics. The input compounds – precursors – can be inorganic (e.g. hydrides, halogenides) or organic (e.g. alkoxides, organometallics), whereas the resulting layer structure can be amorphous, polycrystalline or single crystals are formed with required properties depending on the deposition conditions. A usual thickness of the deposited coating ranges from 0.1 μm up to 10 μm and its structure depends on all the deposition steps (adsorption – desorption, surface reactions, surface diffusion, nucleation, formation of a layer and ageing processes in the layer during the deposition) and the surrounding conditions.

**CVD thin layers**

CVD is used for the manufacture of thin layers, in particular for:

- Silicon and silicon oxide ((Si, SiO₂), namely by pyrolytic decomposition of silane (SiH₄) or its chlorine derivatives (SiHCl₄, SiH₂Cl₂, SiCl₄). Another possibility is deposition of SiO₂ layers by the TEOS method, using tetraethyl orthosilicate as a precursor.
- Silicon nitride (Si₃N₄) by means of the reaction between dichlorosilane (SiH₂Cl₂) and ammonia (NH₃) at temperatures 700 °C – 800 °C,
- Silicon carbide (SiC), where the source for the deposition are hydrogen reduced alkylsilanes (e.g. CH₃SiCl₃),
- Highly pure metals, mainly molybdenum, tantalum, titanium, nickel and tungsten,
- Carbon based layers, namely due to decomposition reactions of low-molecular hydrocarbons (CH₄, C₂H₂) in the presence of hydrogen at high temperatures up to 1500 °C.

**Modified CVD methods**

Chemical reactions on the substrate surface are not spontaneous. Various ways are used to activate them, e.g. the TCVD method – Thermal CVD. This method can be performed either by heating a reactor containing samples (a hot-wall reactor) or by direct heating of samples (a cold-wall processes) to the defined temperature of the deposition. Thermally activated deposition is used in particular to create hard layers, e.g. TiC, TiN and in deposition processes in the manufacture of semiconductor components (Si, SiO₂, Si₃N₄). As an example, the deposition reaction of titanium nitride from the titanium tetrachloride precursor using nitrogen as a carrier gas is shown:

\[ \text{TiCl}_4 + \frac{1}{2} \text{N}_2 \rightarrow \text{TiN} + 2 \text{Cl}_2 \qquad (T = 1100 \, \text{°C}) \]

A need to keep the substrate at a high temperature is considered the essential disadvantage of this method both from the point of view of a commercial usage and in term of a selection of the coating material. For example this method cannot be used for coating of high strength steels, because subjecting the substrate to the high temperature should result in changes in its structure and a loss of its mechanical properties.
The following methods using lower temperatures are the solution: PA/ECVD – Plasma Activated/Enhanced CVD, where the direct-current or alternating-current charge at frequencies in the order-of-magnitude of MHz up to GHz is used to initiate the plasma. The principle of the plasma coating is that the sample is put in the direct-current circuit as a cathode, the charge is initiated between the cathode and the anode and it results in coating the cathode surface, because it is bombed by positive ions accelerated by the electric field. In the case of insulators the alternating-current charge needs to be used in order to prevent the influence of charging. Plasma can influence the gaseous phase composition, mainly by formation of intermediate products, radicals, excited molecules and ions or it can also modify the gaseous phase and coating conditions. The deposition process using plasma is used to make hard coatings on steels and also to produce electronic components.

Another method of activation of chemical processes can be the use of laser (LCVD – Laser CVD), which can be thermal or photochemical.

The other methods are as follows: LPCVD – Low Pressure CVD or (MWPCVD – MicroWave Plasma CVD).

CVD systems
The CVD systems with an open input and output of gas incorporate the following basic parts:
- A system for gasification,
- A chemical reactor with a volume of cm$^3$ up to m$^3$, wherein coated objects are placed (Fig. 10),
- A waste processing system

CVD Reactors

- (a) Hot-wall reduced pressure reactor
- (b) Continuous atmosphere pressure reactor
- (c) Parallel-palte plasma-deposition reactor
- (d) Hot-wall plasma-deposition reactor

Fig.

10 Various types of reactors for CVD
(a) low pressure hot-wall reactor
(b) continuous flow atmospheric pressure reactor
(c) plasma deposition reactor
(d) high-frequency plasma reactor

Chemical condensation from the gaseous phase
Chemical Vapor Condensation (CVC) is a method for the manufacture of nanoparticles through a modified CVD process. The CVC principle is also based on nucleation in the gaseous phase, however, in contrast to CVD this is the homogenous nucleation and thin films do not form, but particularly fine powders.

**CVC Working Process**

In the first step, the carrier gas is bubbled through the precursor reservoir at room temperature, as in the case of the chemical deposition. Follow-up, this vapor stream (of a controlled speed) containing precursor molecules is fed via a needle valve through a heated tubing into the vacuum (reaction) chamber. In the heated tube the induction of chemical reactions among the gas molecules occurs, namely by means of the energy supplied in the form of laser or plasma heating. During a short moment and under specific conditions molecules begin to decompose thermally and coagulate to small clusters and particles. In this step the homogeneous nucleation in the gaseous phase is preferred to a deposition of a film on the walls, which explains a substantial difference between the CVD and CVD method – see Fig. 11. On the outlet from the heated tube the beam of clusters or particles extends and by this their growth moderates. In the final phase the particles condensate on a rotating liquid nitrogen cooled substrate, from which the final powder product is scraped off and collected – see also **Chapter 3.1**.

![Homogenous and heterogeneous nucleation during application of the CVD and CVC processes](image)

**Fig. 11** Homogenous and heterogeneous nucleation during application of the CVD and CVC processes

**CVC precursors**

The CVC method has a great flexibility for the manufacture of a wide scale of materials using a vast database of chemical precursors used for the CVD processes. The precursors can be both gases and solid substances or liquids, however, in these cases application of sublimators or bubblers is needed to create the gas phase (gasifier). As typical precursors to create metal oxides, organometallic compounds or chlorides are used as the commercially most available materials with a low pyrolytic temperature.

A typical reaction is for instance a reaction of tin tetrachloride and water vapor resulting in tin tetroxide:

$$\text{SnCl}_4(\text{g}) + 2 \text{H}_2\text{O}(\text{g}) \rightarrow \text{SnO}_2(\text{s}) + 4 \text{HCl}(\text{g})$$

**CVC possibilities**

The CVC method allows creation of doped or multicomponent nanoparticles using several precursors.

This way e.g. europium-doped nanocrystalline yttrium oxide ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$) was prepared from organometallic yttrium and europium precursors or doped silica nanoparticles containing erbium were prepared using disilane and organometallic erbium compounds. Aluminum-doped zirconia particles and nanoparticles of indium oxide, tin oxide and indium oxide doped with tin oxide were made for applications in semiconductors, catalysts and gas sensors.

Recently the preparation of a series of binary semiconductor oxide nanobelts, nanoribbons, nanorings from $\text{ZnO}$, $\text{In}_2\text{O}_3$, $\text{Ga}_2\text{O}_3$, $\text{CdO}$, $\text{PbO}_2$ and $\text{SnO}_2$ by simply evaporating from the source was successful. The
synthesized oxide nanobelts were pure, structurally uniform, and single crystalline, and most of them were free from defects and dislocations. They had a rectangle-like cross section with typical widths of 30 ÷ 300 nm, thickness about 5 ÷ 10 nm and lengths of up to a few millimeters. Such created nanobelts have a huge potential for applications in sensors, transducers and active members in micro- and nano-electromechanical systems.

Both CVD and CVC methods are based on the same principle, however, during chemical deposition the heterogeneous nucleation on the substrate surface occurs and thin layers (nanolayers) form, in contrast to chemical condensation where the homogenous nucleation is dominating and is used mainly for the manufacture of powder materials (nanopowders).

Summary of terms:
- Chemical methods for preparation of nanomaterials from the liquid phase.
- Precipitation from colloid solutions.
- Synthesis of dispersed oxides.
- Electrolytic segregation.
- Chemical deposition and condensation from the gaseous phase (CVD and CVC).
- CVD and CVC precursors.
- Working process of the CVD and CVC methods.
- Equipment for application of the CVD and CVC methods.
5. PHYSICAL METHODS OF THE MANUFACTURE OF NANOMATERIALS

Time needed to study: 480 minutes

Aim: After studying this chapter you will:

- Define the particular physical methods for the manufacture of nanomaterials.
- Define the methods of the high-temperature and low-temperature plasma deposition.
- Describe the methods: electric arc deposition, pulse laser deposition, electron beam deposition, deposition by sputtering.
- Describe the methods of the nanoparticle deposition using the high-temperature and low-temperature plasma.

Reading:

5.1 Physical Vapor Deposition

Physical Vapor Deposition (PVD) is the name of a group of procedures and technologies, which enable to deposit thin layers with thicknesses of nanometers to micrometers onto the substrate surface. Various surfaces and tools with surface areas sometimes to several m² are coated.

PVD covers several technological processes:
- Pulse Laser Deposition.
- Cathodic Arc Deposition from the cathode.
- Electron Beam Physical Vapor Deposition.
- Sputtering Deposition – the deposition consists of bombarding a material with ions.

General description of PVD

All the PVD methods need a vacuum chamber in which the deposition is performed. Very high vacuum (UHV) needs to be created in the chamber. This vacuum is needed for atoms emitted from a target (a source of the deposited material in the solid state) to propagate freely through the space. The better is the vacuum, the longer the free path of a particle and the better the deposition process. In operation, various types of vacuum pumps are used, such as molecular, turbo-molecular, diffusion, ion and others.

In some cases the chamber may be filled with a so-called “background gas”, which is a specific gas (oxygen, nitrogen, inert gases), which forms compounds with the evaporated material deposited onto the substrate. Sometimes, this gas is used just for the development of the deposited material gas component. This gas pressure, compared to the atmospheric pressure, must be low, otherwise the deposition could not occur at all or only with difficulties. The material intended to be deposited in a form of a layer is taken off the target – the layer and the target composition has to be the same.

Cathodic Arc Deposition

This procedure uses the electric arc to evaporate a material from the target, which serves as the cathode. This is used for the deposition of metallic, ceramic and composite materials. The electric arc effect leads to formation of a so-called “cathode spot”, which is a small area where the electric charge has impinged and evaporation of particles from the target has occurred. This process has a huge power (temperature c. 15000 K) and the particles reach the speed up to 10 km/s. However, the emission of particles only lasts for a short time, it fades and the next charge “impinges” another spot afterwards, but very near to the original incidence.
Using the electric field, the arc is moved across the entire area of the target to avoid burning a hole into it. A disadvantage is that when the arc impacts, aside from evaporated atoms of molecules, electrons and ions, larger particles of the material are created as well – micro-particles with dimensions up to several micrometers. These macro-particles are undesirable for the deposition of a thin layer. This problem is solved by a fast move of the arc across the target and cooling the target with water or using filters. The most widely used is the Aksenov method (see Fig. 12) of the macro-particle filtration with the aid of the magnetic field.

In the case we have a chamber filled with a proper background gas, its ionization occurs, as well as ionization of the evaporated material and thus the required compound is deposited onto the substrate.

The cathodic arc deposition is often used for coating of tools with extremely hard layers (tools for cutting, drilling etc.), thus enhancing their effectivity and extending their service life. The so-called DLC deposition (Diamond Like Carbon Films) is often used to reach very high hardness.

**Fig. 12 Aksenov’s quarter-tours macroparticle filter**

**Pulse Laser Deposition (PLD)**

The pulse laser deposition technology (Fig. 13) uses the high-energy laser pulse for evaporation of material from the target. The depth, in the material which the laser penetrates, depends on the laser wavelength and the material properties. The lasers for PVD have a wavelength within the UV radiation field (usually about 10 nm). The laser electric field in this material volume excites electrons (actually tears them away from the atomic cores), which then oscillate in the laser beam electromagnetic field. This leads to collisions of the electrons with the target material grid, resulting in heating and evaporating the material. A so-called “plasma plume” originates, which is an aggregation of atoms, molecules, clusters, ions and electrons forced out from the target by the laser beam. The target is rotating during the deposition, possibly moving along the horizontal and vertical direction, so that the laser pulses cover as large the target area as possible.

The shape and distribution of this “plasma plume” depends above all on the pressure in the chamber. For this method a very high vacuum level needs to be achieved (approximately $10^{-7}$ Pa). Sometimes, if oxides are to be deposited, PLD is performed in the oxygen atmosphere. Nucleation and growth of the layer on the substrate depends on several factors, which can be varied so that the required result is achieved. These are in particular:

- the laser properties (power, the incidence angle, the pulse frequency)
- the substrate surface temperature,
- the substrate surface structure,
- the gas pressure in the chamber.

The advantage is that during the lasting of the pulse, supersaturation on the substrate occurs (the partial pressure of the component is higher than the given matter vapor pressure), thus increasing nucleation and leading to much smoother layer surface. Formerly the pulse laser deposition was used solely for deposition of crystalline layers. Today this method allows deposition of ceramic layers and varied multilayers as well.

**Fig. 13 PLD process arrangement**
Electron Beam Physical Vapor Deposition

In this method the target (anode) is bombarded with electrons (Fig. 14). The electron source is usually a charged tungsten filament. The electrons striking the target with a high kinetic energy, heat the target in the given spot, causing the material to melt and sublimate and then it can be used for the deposition. The vacuum in the chamber must be at least $10^{-2}$ Pa to allow easy passage of electrons. Accelerating voltages of the electrons can range from 3 to 40 kV, however, the highest efficiency can be reached when the accelerating voltage is between 20 to 25 kV.

The advantage of this method is the possibility to vary the deposition rate from units of nm/min as high as to several μm/min. This technology has a great industrial potential and can be used for deposition of thermally isolation layers, tool coating for enhancement of strength and a variety of other applications in electronics and optics.

Sputtering Deposition

Sputtering (Fig. 15) is a method involving ejecting atoms from a target by other atoms or ions striking the target at a high speed. The vacuum chamber is filled with gas, serving for bombarding the target. To prevent this gas to become a part of the deposited layer, a inert gas needs to be chosen, the most frequently argon, but krypton or xenon are used, too. An important thing is that the atomic weight of the sputtering gas should be close to the atomic weight of the target material. In a case we want to deposit oxide compounds, we can use reactive gases for sputtering, for instance oxygen.

Electrons confined in an electromagnetic field are used for ionization of the gas. In this field the electrons move along a helix towards a target. Doing so, they collide with the gas atoms, ionizing them this way. These ions are then accelerated by the electric field toward a target, resulting in sputtering.

The advantage of this method is that even a low melting material can be sputtered. Layers deposited by this method usually exhibit better adhesion to the substrate. A drawback is that e.g. a “layer-by-layer” growth is hard to be performed here, in contrast to other methods, such as PLD. In this method the final composition of the deposited layer and the target composition differ slightly, as lighter elements are more influenced by the present gas and thus their flow decreases.
Sputtering is a method applied in operation relatively frequently. It is used e.g. in the semiconductor industry, for anti-reflective coatings of optical lenses and for metal deposition in the manufacture of CD and DVD discs.

PVD is a group of complex methods having a wide range of applications in coating of tools and other objects. The deposition process must be performed in a vacuum chamber, so all the PVD methods require an advanced vacuum technology. To evaporate a material, heating is usually applied, possibly bombarding with other particles, which can be achieved by various methods, as described above. Each of these methods has its advantages and disadvantages. In the sputtering method almost arbitrary material of the target can be used, because it is not heated too much, the PLD method can control and influence the layer growth much better.

5.2 Plasma methods

The plasma methods are widely used chemical procedures for preparation of nanomaterials. Highly dispersed powders of nitrides, carbides, borides and oxides, and also of pure metals, can be made. Reactions of elements or molecules in the gaseous state occur. The gaseous phase methods are environmentally more acceptable for preparation of nanoparticles.

A synthesis of powder materials on the basis of gaseous phase reactions is based on random processes of formation of particles. An essential preposition for plasma processes is evaporation of an input material through high temperatures achieved in the plasma and following re-nucleation of products in a form of nanoparticles as a result of rapid cooling. Thanks to random formation of particles the resulting powder materials prepared from the gaseous phase are highly dispersed and they are of various sizes.

Plasma is considered a state of matter consisting of positively and negatively charged particles (electrons, ions, protons or nanoparticles), so that the total charge equals zero. All components of plasma are charged electrically and they are mixed with a neutral gas of atoms or molecules, which can be in the excited state. Plasma can occur in the equilibrium or non-equilibrium state. In the former case all plasma components have the same thermal energy and this state is designated as a high-temperature plasma. In the latter case the plasma components have different thermal energy levels. In the non-equilibrium plasma, electrons have the highest thermal energy, ions lower and the neutral gas has the lowest thermal energy. This state is designated as a low-temperature plasma.

The main conditions of producing highly dispersed powders by this method is the occurrence of a reaction away from equilibrium and the higher rate of formation of nuclei of a new phase at a low growth rate of this phase. In the real conditions of plasma chemical synthesis, the formation of nanoparticles can be carried efficiently by increasing the cooling rate of the plasma flow in which condensation from the gas phase takes place; this decreases the size of particles and also suppresses the growth of particles by their coalescence during collisions.

Plasma chemical synthesis is carried out with the use of low-temperature (4000-8000 K) nitrogen, ammonia, hydrocarbon plasma, argon plasma of arc, glow, high frequency (HF), medium frequency (MF), radiofrequency (RF) or microwave discharges (MW). Starting materials are represented by elements, halides and other compounds. The characteristics of the produced powders depend on the starting materials used, synthesis technology and the type of reactor. The particles of plasma chemical powders are single crystals and their size varies from 10 to 100 ÷ 200 nm or larger. Plasma chemical synthesis ensures high rates of formation and condensation of the compound and is characterized by relatively high productivity. The main disadvantages of plasma chemical synthesis are the wide size distributions of particles and, consequently, the presence of relatively large (up to 1 ÷ 5 μm) particles, i.e. the low selectivity of the process. The other disadvantage is a high content of the impurities in the powder. Up to now, the plasma chemical technique has been used to produce highly dispersed powders of nitrides of Ti, Zr, Hf, V, Nb, Ta, B, Al and Si, carbides of Ta, Nb, Ti, W, B and Si, and oxides of Mg, Y and Al. The plasma chemical technique is used most widely for the synthesis of groups IV and V transition metal nitrides with a mean particle size smaller than 50 nm.

Large amounts of the required material can be produced (up to kg/hour).

High-temperature plasma processes

The high-temperature plasma processes work at atmospheric pressure and electric charge from a direct-current, alternating-current or high-frequency source is used to excite the plasma. The energy distribution is usually near the thermal equilibrium.
Fig. 16 shows two types of injecting of precursors for the powder materials synthesis with plasma excitation using AC or DC electrical energy. In both the cases the plasma is created between two coaxial electrodes. The generated plasma charge is blown off thanks to the auxiliary gas stream. This gas stream fulfills two functions: supplying the gas for the plasma and cooling the electrodes, thus preventing their overheating. If there are systems with high power, solid parts can also be cooled using additional water cooling. Both the systems for transport of precursors (see Fig. 16) into the plasma can be used for the transport of solid precursors supplied in a form of powders or liquid precursors, most frequently aqueous or organic solutions. In Fig. 16 on the right-hand side, where the injector of precursors is placed outside the burner, the plasma flame energy is influenced dramatically.

![Plasma arc evaporation method](image)

**Plasma arc evaporation method**

**Gas Evaporation** method serves for preparation of nanoparticles by evaporation of metal in plasma. The method must be performed in the helium or argon atmosphere under pressure of several hundreds to thousands pascals. Through the method of reactive plasma arc evaporation, the inert atmosphere of diatom gases can be used (nitrogen or hydrogen under atmospheric pressure). The application of these gases influences nanoparticle formation mechanism significantly.

The mechanism of nanoparticle formation: in the plasma arc the hydrogen molecules dissociate to atoms and these atoms are subsequently conveyed to and dissolved in a molten metal precursor. The transfer of these atoms in the molten metal oversaturated region is a result of the convective flow. The hydrogen atoms agglomerate again and are pushed to the surface. At the same time the excited metal particles evaporate from the melt surface and demanded nanoparticles are obtained from the condensing evaporated metal particles. Hydrogen can catalyze the process of nanoparticle formation. The obtained nanoparticles are caught on a filter or in a cyclone with the aid of circulation of the carrier gas (a mixture of a diatom molecular gas and an inert gas).

![Low-temperature plasma processes](image)

**Low-temperature plasma processes**

are performed in low pressure systems. The low-temperature plasma processes are performed at temperatures below 8000 K. In these systems, energy is mostly supplied using a radiofrequency (RF) or microwave electrical energy source. In spite of the fact that the results of the both of the energy sources appear the same, the physical background of both the sources is different.

Considering the effectivity of the energy transfer to electrons at the RF sources, it is necessary to work at low pressures to prevent occurrence of too high temperatures. Usually the pressure in the system ranges between 10 ÷ 100 Pa. These processes are used for a synthesis of a small amount of special materials. A typical arrangement uses capacity-bound plasma and the schematic arrangement is shown in Fig. 17 a). In this type of reactor, aside from simple oxides, complex oxides featuring high-temperature superconductivity can be also prepared, and nitrides as well.

The synthesis of metal powders is possible, providing that the product condensation on the reaction cylinder walls does not occur. Another arrangement for the preparation of nanoparticles using the RF energy source is shown in Fig. 17 b). This technology uses a pulse radiofrequency source of plasma. A pulse
length is up to 30 s. FePt intermetallic compound was prepared through this method. Platinum and iron organic compounds were used as precursors.

Fig. 17
a) General arrangement of a system with the capacity-bound plasma and RF source for a synthesis of nanoparticles under the reduced pressure,  
b) A design of a system for a synthesis of nanopowders with a pulse RF source (during the synthesis the particles are lead between the permeable electrodes).

The plasma temperature, reaching up to 10000 K, determines the presence in the plasma of ions, electrons, radicals and neutral particles which are in the excited state. The presence of these particles leads to high rates of interaction and a short time of reactions (up to $10^{-3} \div 10^{-6}$ seconds). High temperature ensures the transfer of almost all starting substances into the gaseous state followed by their interaction and condensation of the reaction products.

Plasma chemical synthesis includes several stages. The first stage is characterized by the formation of active particles in arc, high frequency and microwave plasma reactors. The highest power and coefficient of efficiency are shown by arc plasma reactors, but materials produced are contaminated with products of electrode erosion. High frequency and microwave plasma reactors do not have this shortcoming. As a result of quenching, the next stage results in the generation of reaction products. The selection of the place and the rate of quenching makes it possible to produce powders with the required composition, shape and size of the particles. The powders produced by the plasma chemical technique are characterized by regular shapes and a particle size of 10 ÷ 100 nm or larger.

**Microwave systems**

Using the low-pressure microwave plasma system the lowest temperatures can be reached. During this process the lowest amount of agglomerates in the product is formed. A typical design of this system is in Fig. 18. The design is characterized by a long reaction tube. Plasma is formed in a place of intersection of the reaction tube with a cavity.

Fig. 18 Scheme of a microwave plasma system working at low pressures

Evaporated precursors are conveyed by a carrier gas into the reaction zone. For the preparation of oxides, oxygen is added to the carrier gas, nitrogen for nitrides, or ammonia etc. In the low-pressure plasma, particles carry a positive electric charge. By adding water the positively charged plasma particles are neutralized. This results in a decreased repulsion of particles and the resulting material contains substantially larger particles than in a system without added water.
Application of the plasma methods

The above mentioned methods can be used for a synthesis of nanoparticles of pure metals, but also of oxides, carbides, borides, nitrides etc., including high-melting point substances and those that can be prepared only with difficulties. Multicomponent powder crystalline materials containing mixtures of carbides, nitrides, oxides etc. can be prepared, too. Molecule clusters, which are new structure modifications of substances, can be prepared as well.

Other possible applications of these methods cover preparations of ceramic composite nanomaterials with specific chemical, mechanical, optical, thermal, electric and magnetic properties. Possibilities for the use of these materials are shown in Fig. 19.

A large group of materials, which can be prepared by the plasma processes, are carbon nanostructures presented by clusters based on a graphite structure. These are fullerenes and carbon nanopipes, which are new allotropic modifications of carbon. Fullerenes are commonly produced using the arc plasma (the high-temperature process) in the helium atmosphere at the gas pressure about 1.3 \cdot 10^{4} \text{ Pa}. Due to the arc the carbon electrode burns off, following by formation of soot that condense subsequently. The obtained soot are caught in hot toluene or benzene and after the following evaporation of these solvents a black condensate is obtained, which contains c. 10 ÷ 15 % of C_{60} and C_{70} fullerenes mixture. Another method allowing a synthesis of carbon nanopipes and fullerenes is evaporation by an electron beam or a laser ablation.

Fig. 19 Used ceramic powders with required properties and possibilities of their applications

In the formed mixture, C_{60} molecules occur in highest quantities due to their highest symmetry and stability. In the fullerene structure (Fig. 20) the carbon atoms create pentagons and hexagons, thus allowing enclosing the whole molecule to a spherical shape, which is hollow. Each carbon atom has three bonds, which belong to two hexagons and one pentagon. A diameter of this molecule ranges between 0.72 to 0.75 nm. Fullerene molecules can also crystallize. These crystals are called fullerites and the crystal has the fcc lattice with the lattice constant of 1.417 nm. A higher stability was observed for C_{70} fullerenes, which have 70 carbon atoms in the structure and create closed ellipsoids.

Fig. 20 Structure of C_{60} and C_{70} fullerenes. All fullerenes consist of hexagonal and pentagonal formations.

Further special (non-conventional) methods for preparations and characterization of metals, oxides, intermetallic compounds or carbon nanomaterials can be found in technical literature [1-11].
5.3 Synthesis by Detonation and Electric Explosion

There is another type of mechanical treatment which creates simultaneously the conditions for both the synthesis of the final product and its dispersion. It is the shockwave. The shockwave treatment of mixtures of graphite with metals at a pressure in the shockwave of up to several tens of GPa is used to produce nanocrystalline diamond powders with a mean particle size of 4 nm. It is more efficient to produce diamond powders by explosion of organic substances with high carbon content and relatively low oxygen content.

The detonation of explosive substances, i.e. explosion energy, is used quite widely for ensuring phase transitions in substances and synthesis by detonation. Synthesis by detonation as a high-rate process makes it possible to produce ultrafine powders in dynamic conditions where the important role is played by kinetic processes.

Detonation synthesis of diamond was carried out for the first time by shockwave loading rhombohedral graphite up to 30 GPa. Grains of explosion diamond were agglomerates of individual particles. Diamond powders were produced by shockwave treatment of mixtures of graphite and metal. The duration of the shockwave was 10 ± 20 ms, and the pressure generated by the wave 20 ± 40 GPa. It was shown that the diamond powder, produced in these conditions, contains single crystals not larger than 50 nm, and also tightly bonded agglomerates with a size of up to 5 µm or larger. These agglomerates consist of individual crystals with sizes of 1 ÷ 4 and 10 ÷ 160 nm.

The process of production of diamond particles with their subsequent cooling in the gas phase (the so-called “dry” synthesis) was realized in detonation decomposition of carbon containing explosive substances with subsequent expansion of explosive products in an inert atmosphere. This process is used for industrial production of ultrafine diamond particles for various applications. The volume of explosion chambers is not smaller than 2 ÷ 3 m³. The synthesized diamond powder forms in the zone of chemical decomposition during a period not longer than 0.4 µs and consists of compact cubic particles with a mean size of approximately 4 nm. The application of more powerful explosive substances makes it possible to produce larger, up to 1 µm, diamond particles.

Pressures of 10 to 40 GPa and temperatures of up to several thousand degrees, characterizing the detonation process, correspond to the range of thermodynamic stability of the diamond phase on the $p-T$ diagram of possible states of carbon (see Fig. 21). The application of the detonation method for synthesis of diamond in the dynamic conditions is fully logical. It must be taken into account that in synthesis by detonation at a short duration of high pressures and temperatures, required for the formation of diamond, a significant role is played by the kinetics of formation and growth of nuclei of the diamond phase. This is confirmed by explosion decomposition of trinitrotoluene characterized by the generation of the maximum amount of free carbon. The parameters of the detonation wave in the Chapman-Jouguet plane ($p \approx 18$ GPa, $T = 3500$ K) when the chemical reaction has already been almost completed, correspond to the region of stability of the diamond phase (Fig. 21). However, detonation of trinitrotoluene is not characterized by a large yield of the diamond phase.

**Fig. 21** Equilibrium phase $p-T$ diagram of carbon indicating the regions of synthesis of diamond by different methods [4]

1) detonation (impact wave) synthesis using graphite,
2) static transformation using a catalyst,
3) static transformation without a catalyst,
4) detonation synthesis using a mixture of trinitrotoluene and hexogene at a ratio of ~ 1:1.
To obtain a large yield of the diamond powder it is necessary to use more powerful explosive substances. It makes possible to increase the pressure and temperature generated by the shockwave. Usually, ultrafine diamond powders are produced using mixtures of trinitrotoluene and hexogene. In this case, the pressure and temperature in the detonation wave are $p > 15$ GPa and $T > 3000$ K. The process takes place in special explosion chambers, filled with an inert gas or carbon dioxide, which prevents oxidation of the produced diamond particles and their transformation to graphite. The formation of diamond nanoparticles takes place up to reaching the Chapman-Jouget plane and is completed within $0.2 \div 0.5$ $\mu$s. In detonation synthesis at a very short time of formation of the diamond particles, the rate of growth of these particles is several orders of magnitude higher than that in the static conditions. The yield of the diamond powder is $8 \div 9$% of the initial mass of explosive substances

Russian industry has mastered a conversion method of producing diamond nanopowders by explosion of ammunition in special chambers. High pressures and temperatures, developed during explosions, lead to the synthesis of diamond from carbon-containing explosive substances. Synthesis is catalyzed by particles and vapors of the metal from the shells of ammunition.

Another detonation method of synthesis of different morphological forms of carbon and nanopowders of oxides of Al, Mg, Ti, Zr, Zn was described in the literature. A layer of starting substance (high-porosity metallic medium, chemical compound, sol or gel of a metal hydroxide) is subjected to the shockwave treatment from a contact charge of an explosive substance. The compression and heating of the high-porosity metal or dissociation of the starting compound to the oxide with subsequent stabilization of the oxide phases take place in a shockwave. After exit of the shockwave to the free surface of the starting substance, the material is dispersed into the gas atmosphere of the explosion chamber.

**Electric Explosion method**

A rapidly developed method of producing ultrafine powders is the electric explosion of a conductor during the passage of a powerful current pulse with a duration of $10^{-5} \div 10^{-7}$ s and a density of $10^4 \div 10^6$ $\text{A}\cdot\text{mm}^2$. Wires with a diameter of $0.1 \div 1.0$ mm are used for this purpose. The electric explosion of a conductor is a large change of the physical state of the metal as a result of the intensive generation of energy during the passage of a high-density current pulse. Electric explosion is accompanied by the generation of shockwaves and makes it possible to heat rapidly metals at a rate greater than $1 \cdot 10^7$ K·s$^{-1}$ to high temperatures of $T > 10^4$ K. The capability of electrically exploded conductors to rapidly change properties and efficiently transform the primary electric or magnetic energy of accumulators to other types of energy (thermal energy, the energy of radiation of the plasma, energy of the shockwaves) is used in particular for producing ultrafine powders.

In the initial stage of electric explosion, the Joule heating of a conductor is accompanied by its linear expansion at a relatively low rate of $1 \div 3$ m·s$^{-1}$. In the stage of an explosion the passage of a current pulse superheats the metal above the melting point, the expansion of the material of the exploded conductor takes place at a rate of up to $5 \cdot 10^4$ m·s$^{-1}$ and the superheated metal is dispersed in an explosion-like manner. The pressure and temperature at the front of the shockwave reach several hundreds of MPa and $\sim 10^4$ K, respectively. Particles of very small sizes form as a result of condensation in the flow of the rapidly expanding vapor. Regulating the explosion conditions, it is possible produce powders with a particle size from 100 $\mu$m to 50 nm. The mean size of the particles monotonically decreases with increasing current density and shortening of the pulse time. Electric explosion in an inert atmosphere makes it possible to produce powders of metals and alloys. Adding of additional reagents into the reactor (air, mixture of oxygen and inert gas, nitrogen, distilled water, decane C$_{10}$H$_{22}$, paraffin, commercial oil) allows produce ultrafine powders of oxides, nitrides, carbides or their mixtures.

### 5.4 Self-Propagating High-Temperature Synthesis

The self-propagating high-temperature synthesis (SHS) represents a rapid process of solid combustion of reagents (a metal and carbon for carbides or a metal in nitrogen for nitrides) at a temperature from 2500 to 3000 K. Usually carbides are synthesized in a vacuum or an inert atmosphere (argon). The mean size of grains in carbides produced by the SHS method is $10 \div 20$ mm, while the size of nitride grains usually is smaller and equals $5 \div 10$ mm. To decrease the grain size in synthesized carbides or nitrides, the starting mixture was diluted with the final product (for example, up to 20 wt. % TiC carbide is added to the Ti + C mixture). Some carbon in the mixture was replaced by polymers (polystyrene, polyvinylchloride) during synthesis of carbides.
Titanium carbide was synthesized using a Ti + C + mNaCl mixture. The synthesis was realized in a standard reactor under an argon atmosphere at a pressure of 0.5 MPa. Combustion was initiated by a current pulse (the voltage $U = 15 \div 20$ V and the pulse time of $1.0 \div 1.5$ s), which is fed to the sample via tungsten wire. The starting mixture is homogenised spontaneously during combustion thanks to melting of Ti and NaCl. The powder includes irregularly shaped particles 20 to 300 nm in size with an mean size of about 100 nm.

### Summary of terms:

- Physical vapor deposition
- Cathodic arc deposition
- Pulse laser deposition
- Electron beam physical vapor deposition
- Sputtering deposition
- High-temperature plasma processes
- Plasma arc evaporation method
- Low-temperature plasma processes
- Microwave systems
- Synthesis of nanopowders by detonation
- Electric explosion method
- Self-propagating high-temperature synthesis
6. TYPES AND PROPERTIES OF NANOSTRUCTURED MATERIALS

Time needed to study: 120 minutes

Aim: After studying this chapter you will:

- Classify various sorts of nanomaterials according to a structure type.
- Describe phase types of nanostructured materials.
- Specify and describe various methods of diagnostics of nanostructured materials.

Reading:

6.1 Classification and properties of intermetallic nanomaterials

Nanocrystalline materials can be divided into three categories according to a structure type:

- (a) layered or lamellar,
- (b) filamentary,
- (c) equiaxed.

A layered or lamellar structure is one-dimensional (1-D) nanostructure, in which the size of the length and width is much larger than the thickness, it is only several nanometers. Others arrangements can be two-dimensional (2-D) with a circular shape, the so-called filamentary structure. Here the length is substantially longer than the width and diameter, which have nanometric dimensions. The most common nanostructure is the equiaxed one, which has nanometric dimensions in all directions and is called nanostructured crystallites (3-D arrangement).

The nanostructured materials may contain crystalline, quasicrystalline or amorphous phases, which can be metals, ceramics, polymers and composites. If the grains consist of crystals, the material is called nanocrystalline. On the other hand, we may encounter nano-quasicrystals and nanoglasses (amorphous phase). Further, the nanostructured materials can be classified according to the composition, morphology and the nanocrystalline component distribution.

Physical, chemical and mechanical properties of nanocrystalline materials can be determined no sooner than after consolidation of nanostructured powders into the “consistent” compact material. In comparison with coarse-grained particles, nanocrystalline materials feature 4 ÷ 5 fold higher hardness and strength, enhanced diffusivity, lower density, lower modulus of elasticity, higher electrical resistance, higher specific heat, higher thermal expansion coefficient, lower thermal conductivity and improved properties of soft magnetic materials. The above mentioned properties depend on the consolidation of nanostructure powders into a compact material without occurrence of a high number of pores, cracks and other discontinuities in samples. Many “enhanced” properties of nanocrystalline materials cannot be applied in porous-less samples. The highest attention in the research of nanocrystalline materials is nowadays focused mainly on improving toughness and plastic deformation of nanocrystalline ceramic materials, such as TiO$_2$ and CaF$_2$, because the most of intermetallic compounds, as well as ceramics, are brittle.

To study the size, morphology, physical, chemical and usable properties of nanomaterials, special diagnostic methods need to be used with regard to dimensions of nanoparticles and clusters:

2. Transmission Electron Microscopy with (High Resolution (HRTEM).
6. Energy-Dispersive X-ray Spectroscopy (EDX) or (EDS).
7. X-ray Diffraction Analysis.

Nanostructured intermetallics have been synthesized mostly by mechanical alloying (MA), even though some have also been produced by electrodeposition and devitrification of the amorphous phases.

Only those intermetallics that are synthesized directly by MA have grain sizes in the nanometer range. Sometimes the intermetallics may not form directly after MA. In those cases MA forms only an intimate mixture of the component metals; an additional heat treatment is required to provide the necessary diffusion for the formation of the intermetallics. The intermetallic formed under these conditions may not always have nanometer-sized grains. If the heat treatment was carried out at relatively low temperatures, the intermetallic may be nanostructured.

MA has produced nanostructured intermetallics under three categories:
- Quasicrystalline phases.
- Metastable intermetallics.
- Equilibrium intermetallics.

6.2 Metastable Quasicrystalline Intermetallic Phases
Quasicrystalline phases are metallic phases that exhibit traditionally forbidden translational symmetries. MA was shown to be another technique to produce these phases under non-equilibrium conditions, but with the advantage of having nanometric dimensions. The quasicrystalline phases synthesized by MA are summarized in Table 3. It may be noted that all of these phases are of the icosahedral type (having the 5-fold symmetry). A number of the latter category (with 10-fold symmetry, etc.) were synthesized by other techniques such as rapid solidification processing (RSP) from the melt.

Table 3 Nano-quasicrystalline phases synthesized by mechanical alloying [3]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Phase</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al}<em>{65}\text{Cu}</em>{20}\text{Co}_{15} )</td>
<td>( \text{Al}<em>{70}\text{Cu}</em>{12}\text{Ru}_{18} )</td>
<td>( \text{Al}<em>{70}\text{Pd}</em>{20}\text{Mn}_{10} )</td>
</tr>
<tr>
<td>( \text{Al-Cu-Cr} )</td>
<td>( \text{Al}<em>{25}\text{Cu}</em>{15}\text{V}_{10} )</td>
<td>( \text{Mg}<em>{3}\text{Cu}</em>{7}\text{Al}_{42} )</td>
</tr>
<tr>
<td>( \text{Al}<em>{65}\text{Cu}</em>{20}\text{Fe}_{15} )</td>
<td>( \text{Al}<em>{60}\text{Mn}</em>{20}\text{Ge}_{30} )</td>
<td>( \text{Mg}<em>{12}(\text{Al,Zn})</em>{49} )</td>
</tr>
<tr>
<td>( \text{Al}<em>{60}\text{Cu}</em>{10}\text{Mn}<em>{25}\text{Ge}</em>{25} )</td>
<td>( \text{Al}<em>{60}\text{Mn}</em>{20}\text{Si}<em>{20}\text{Ge}</em>{10} )</td>
<td>( \text{Mg}<em>{5}\text{Zn}</em>{5.3}\text{Al}_{X} )</td>
</tr>
<tr>
<td>( \text{Al}<em>{65}\text{Cu}</em>{20}\text{Ru}_{15} )</td>
<td>( \text{Al}<em>{70}\text{Ni}</em>{10}\text{Fe}_{15} )</td>
<td>( \text{Ti}<em>{5}\text{Co}</em>{10}\text{Fe}<em>{10}\text{Si}</em>{16} )</td>
</tr>
</tbody>
</table>

6.3 Metastable Crystalline Intermetallic Phases
MA has also been shown to be capable of synthesizing some metastable crystalline intermetallic phases. Metastability here refers to the property obtaining when a phase stable at high temperatures or pressures is retained at room temperature and pressure. Alternatively the phase synthesized may not be present in the equilibrium diagrams at either high temperatures or high pressures, i.e. the phase is entirely new. A similar situation has also been obtained by other non-equilibrium processing techniques, most notably through RSP. As a good example being the formation of deformation-induced metastable \( \varepsilon \) (hcp) martensite in austenitic stainless steels. Table 4 lists the crystal structure data of the metastable intermetallic materials synthesized by MA.

6.4 Equilibrium Crystalline Intermetallic Phases
Both disordered and ordered intermetallics with nanometer-sized grains have been synthesized by MA. The intermetallics synthesized include aluminides (mostly based on titanium, nickel, and iron), silicides, composites, and some exotic varieties. Table 5 presents a listing of the categories of nanostructured intermetallics synthesized by MA.

Synthesized \( \gamma \)-TiAl phase by mixing titanium hydride (instead of pure titanium) and the \( \text{Al}_{3}\text{Ti} \) intermetallic (instead of pure aluminum) powders in the proper proportion, according to the reaction:

\[
\text{Al}_{3}\text{Ti} + 2\text{TiH}_2 \rightarrow 3\text{TiAl} + 2\text{H}_2.
\]
On mechanically alloying the above powder mixture for 52 hours in a SPEX mill, they were able to obtain 55 vol. % of the γ-TiAl phase (the remainder being the un-reacted reactants). The amount of the γ-TiAl was increased to 95 % on hot isostatically pressing the mechanically alloyed powder at 1023 K and 285 MPa for 5 hours. This technique has been subsequently employed to synthesize the TiAl, TiAl, Al₃Ti phases by milling the titanium hydride and aluminum powders in Ti:Al ratios of 3:1, 1:1, 1:3.

### Table 4 Metastable intermetallics synthesized by mechanical alloying [3]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Phase / Composition</th>
<th>Crystal structure</th>
<th>Alloy</th>
<th>Phase / Composition</th>
<th>Crystal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Cu</td>
<td>33 at.% Cu</td>
<td>bcc</td>
<td>Cu-Zn</td>
<td>martensite</td>
<td>-</td>
</tr>
<tr>
<td>Al-Ge</td>
<td>γ (30 at.% Ge)</td>
<td>rhombohedral</td>
<td>Fe-B</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al-Hf</td>
<td>L₁₂, Al₃Hf</td>
<td>cubic</td>
<td>Mg-Sn</td>
<td>33 at.% Sn</td>
<td>-</td>
</tr>
<tr>
<td>Al-Hf-Fe</td>
<td>L₁₂ (Al,Fe)₃Hf</td>
<td>cubic</td>
<td>Nb-Ge</td>
<td>15-18 at.% Ge</td>
<td>-</td>
</tr>
<tr>
<td>Al-Hf-Ni</td>
<td>L₁₂ (Al,Ni)₃Hf</td>
<td>cubic</td>
<td>Ni-Al</td>
<td>Ni₃Al</td>
<td>-</td>
</tr>
<tr>
<td>Al-Mn</td>
<td>18 at.% Mn</td>
<td>fcc</td>
<td>Ni-Sn</td>
<td>β⁺</td>
<td>-</td>
</tr>
<tr>
<td>Al-Ti</td>
<td>L₁₂, Al₃Ti</td>
<td>cubic</td>
<td>Ni-Sn</td>
<td>β⁰</td>
<td>-</td>
</tr>
<tr>
<td>Al-Zr</td>
<td>L₁₂, Al₃Zr</td>
<td>cubic</td>
<td>Te-Ag</td>
<td>π(CT)</td>
<td>-</td>
</tr>
<tr>
<td>Al-Zr-Fe</td>
<td>L₁₂ (Al,Fe)₃Zr</td>
<td>cubic</td>
<td>Ti-Si</td>
<td>67 at.% Si</td>
<td>-</td>
</tr>
<tr>
<td>Al-Zr-Ni</td>
<td>L₁₂ (Al,Ni)₃Zr</td>
<td>cubic</td>
<td>Ti-Si</td>
<td>C₄₉ TiS₁₂</td>
<td>-</td>
</tr>
<tr>
<td>Cu-In-Ga-Se</td>
<td>Cu₅In₃Ga₅S₁₃Se₂</td>
<td>cubic</td>
<td>Zr-Al</td>
<td>D₀₁₀ Zr₃Al</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 5 Intermetallics synthesized by mechanical alloying [3]

<table>
<thead>
<tr>
<th>Category</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminides</td>
<td>$\xi$(Ag-Al), $\mu$(Ag-Al), Al₆Fe, AlFe, Al₃Fe, Al₅Fe₂, Fe₁₇Al, Al₃Mg₂, Al₁₂Mg₁₇, Al₆Mn, Al₁₂Mn, Al₁₂Mo, Al₃Mo, Al₃Mo₃, Al₃Nb, Nb₃Al, Al₃Ni, NiAl, RuAl, Al₃Ti, AITi, Ti₃Al, AlZr, Al₃Zr₂, MnAl, Nb₂Al, Ni₃Al, Ni₃Al₆, (Fe,Ni)Al, Ni(Al,Ti), PdAl</td>
</tr>
<tr>
<td>Beryllides</td>
<td>NbBe₁₂, NbBe₁₇</td>
</tr>
<tr>
<td>Chalcogenides</td>
<td>Ag₂S, Ag₃Se, CuInS₂, CuInSe₂, Cu₂Se₂, CuSe₂, FeS, Nb₃Sₕ, Ni₁S₂, Cu(In,Ga)Se₂</td>
</tr>
<tr>
<td>Silicides</td>
<td>Cr₃Si, CrSi₂, $\alpha$-FeSi₂, $\beta$-FeSi₂, FeSi, MgSi, Mo₅Si₃, $\alpha$-MoSi₂, $\beta$-MoSi₂, Nb₅Si₁₂, $\alpha$-Nb₅Si₁₂, $\beta$-Nb₅Si₁₂, Nb₃Si₁₂, Ni₃Si₁₂, Ni₃Si, Ni₃Si₂, Ni₃Si₃, Pd₃Si, Pd₃Si, Pd₃Si, Ta₃Si, Ti₃Si₁₂, Ti₃Si₁₄, V₃Si, V₅Si₁₃, V₃Si₂, WSi₂</td>
</tr>
</tbody>
</table>

Nanostructured nickel- and iron-aluminides such as Ni₁₃Al, NiAl and Al₃Ni have been synthesized by MA in the appropriate composition ranges. An interesting observation is that the equiatomic NiAl phase is produced via a combustion synthesis (also known as the **self-propagating high-temperature synthesis reaction**) that occurs during milling. In this case, the combustion reaction took place only after “interrupted milling”, i.e. milling of the powders for a given length of time, aging the powder at room temperature after stopping the milling, and then resuming the milling operation. For example, in the Al-Ni system, an intimate mixture of Al and Ni phases was detected after milling the blended elemental Al-Ni mixture for 2 h in a SPEX mill. If the milling is stopped and the powder is stored at room temperature for 30 min, and then milling is resumed. The NiAl phase forms after just 1 minute of milling due to the occurrence of an explosive reaction.

The time required to form a particular phase depend on the initial concentration of the solute in the powder mixture. If the solute content is much less than the exact stoichiometry, the expected phase (although the proportion of the phase in the mixture of phases is less), would form only at much longer milling time. The time can be probably reduced if the temperature at which milling is conducted is increased.

Nanostructured superconducting compounds such as Nb₅Sn and YBa₂Cu₃O₇−δ have also been prepared by MA. The capabilities of MA in synthesizing a variety of intermetallic phases appear unlimited.
Mechanical milling of ordered intermetallics has been shown to result in one of the following three transformations:

1) Formation of a solid solution of one component in the other, i.e. the terminal solid solution based on the major component; this has been observed in compounds such as Nb₃Al, V₃Ga, Fe₃Ge, Ni₂V and NbAu₂.

2) formation of an amorphous phase, observed in Nb₃Sn, NiZr, NiV₂ and CoZr,

3) formation of a different phase with a complex crystal structure in Ni₃Sn and TiS₂.

Upon milling, an ordered intermetallic can transform, with or without complete loss of long-range order, either into a disordered crystalline phase (solid solution) or amorphous phase. If the product is a crystalline phase, the material has an extremely fine grain size, usually in the nanometer range. Figure 22 summarizes the types of changes that can occur on milling an intermetallic compound.

Fig. 22 Expected situation on mechanically milling an intermetallic compounds (schematic) [3]

An alloy can become disordered either at higher temperatures or on mechanical milling. It has been noted that among 700 binary intermetallic compounds only a very few compounds as CuZn and Cu₃Au are reversibly ordered compounds, i.e. they exhibit the order-disorder transformation before melting.

Summary of terms:
- Layered, lamellar, filamentary and equiaxed nanomaterials.
- Metastable quasicrystalline intermetallic phases.
- Metastable crystalline intermetallic phases.
- Equilibrium crystalline intermetallic phases.
7. APPLICATION OF NANOTECHNOLOGIES AND NANOMATERIALS

Time needed to study: 120 minutes

Aim: After studying this chapter you will:

Describe the basic scientific fields, where nanotechnology and nanomaterials are applied.
Describe the past and present state of the art and future perspectives of nanotechnology and nanomaterials.

Reading:

Nanotechnology along with information technologies and biotechnologies belong to the so-called “emerging” technologies. An important advance in understanding phenomena and processes in the nanoworld, which nanoscience has made in the last twenty years, enables to predict that their application and mastering will bring break-through changes particularly in electronics, photonics and computers, but also in other fields, such as health care and pharmacy, power industry and environment protection, agriculture, military and other industries, e.g. textile. **Fig. 23** shows the variety of spheres, which nanotechnology has something to do with more or less. The inner yellow rectangle in the **Figure 23** refers to the fields, which nowadays are closest to the realization phase or where implementation of results of the research and development has begun already. These are materials, chemistry, health care, information and communication technology, power engineering and living environment. In the coming years (the outer blue rectangle), application of nanotechnology in other fields is expected, such as biomimetics, quantum computers, nanomachines, modelling and analyses and in the so-called extreme nanotechnologies (especially in technologies of self-assembly, self-organization, self-replication, DNA-based equipment etc.). This is to be a long-lasting gradual development, estimated up to 50 years.

**Fig. 23** “Nanoworld” (as described by Prnka, T., Šperlink, K. in the *Sixth framework programme of the European research and technical development*. Ostrava: Repronis, 2004, 67 pp., ISBN 80-7329-070-7.)
7.1 Nanotechnology nowadays

At present nanomaterials in many cases have left laboratories already and have become objects of the practical usage. The first applications of nanomaterials emerged in systems, in which powders with nanometer dimensions could be used in a bulk form, without compaction and mixing. TiO$_2$ and ZrO$_2$ nanopowders are commonly used in cosmetics in face creams, in suntan face lotions. Fe$_3$O$_4$ nanopowders are used as a base material for lipsticks and make-ups. Recently they were used experimentally for detoxification and recovery of a contaminated area in the North Carolina (USA). Today, paints with reflective properties are made with addition of TiO$_2$ nanoparticles.

Nanostructured **abrasion-resistant coatings for cutting tools** and their components have been used for several years already. Tiles with a nanoparticle surface film, to which either water or dirt does not stick, have been put on the market. In the automotive industry, nanocomposites polymer – clay have been used. Addition of only 5% of nanoparticles of montmorillonite in the polymer matrix results in a significant increase in the composite strength. CeO$_2$ nanoparticles addition to the engine fuel in order to decrease its consumption has been tested, too.

Lately the much sophisticated use of nanomaterials has been realized in information technologies. In the manufacture of silicon transistors, the controlled deposition of layered structures only several atoms thin (c. 1 nm) has been used and lateral dimensions of the transistor gate critical length have commonly reached 180 nm; in 2003 some manufacturer have announced achieving the value of 90 nm. A shorter length of the gate enables the manufacture of smaller, **faster and more energy-efficient transistors** and the corresponding reduced price and improved output of every digital device. Similarly, the **read heads of standard harddisks**, thanks to the layered heterostructures of nanodimensions, take advantage of the giant magnetic resistance, significantly increasing their memory capacity, while reducing a price. Microelectronics leads towards **nanoelectronics**.

In the **biomedicine field**, structures called liposomes were synthesized, allowing improved targeted distribution of therapeutic agents. Liposomes are lipid spheres of a diameter c. 100 nm. They are used for encapsulation of anti-cancer drugs for treatment of Kaposi’s sarcoma related to AIDS. Various companies use magnetic nanoparticles for analyses of blood, urine and other body fluids to accelerate separation and improve differentiability.

Other companies have developed **fluorescent nanoparticles**, which are the basis for new detection technologies. These active nanoparticles are used in devices and systems for analyses of infectious and genetic diseases and research of medicaments. One Chinese company has put an antibacterial nanopowder on the market.

Nanoparticles have found a wide usage in the **defence industry** and in **scientific and technical instruments**. Manufacturers of optical materials and electronic substrates, such as silicon and gallium arsenide (GaAs), use nanoparticles for chemical-mechanical polishing. **Silicon carbide, diamond and boron carbide nanoparticles** are used for lapping of components in order to minimize surface waviness to 1 ± 2 nm. An opportunity to produce high quality components is important for scientific applications and will be still more important for gradual miniaturization of electronic devices and development of optoelectronic systems.

Nanotechnology has broken even to **clothing** and **sports**. For instance, crease resistant and soil and stain resistant cotton fabric with nanoparticle addition is produced, tennis rackets with frames reinforced with carbon nanotubes and tennis balls with the inner layer of polymer-clay nanocomposites extending their service life.

7.2 Near future of nanotechnologies

Within the 3–5-year horizon, many new products produced by nanotechnologies and using nanomaterials will be launched. **Fig. 24** shows only the most probable applications.

Specially prepared semiconductor crystals – **quantum dots** are tested, which are intended i.a. for **analyses of biological systems**. Upon putting on a light, these dots emit different colours of light depending on their dimensions. Quantum dots of different dimensions can be connected to various molecules in biological reactions, allowing monitoring of all molecules participating in biological processes at the same time. Quantum dots may also be used as a tool for faster **DNA and antibodies testing** than at the present time.
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Progress in **nanopowder filling** into **commercial sprays** is promising, too. In the near future this will enable to coat plastic materials with nanopowders, improving their abrasion resistance and corrosion resistance.

**Automotive industry** investigates possibilities for applications of **polymer nanocomposite materials** in parts requiring meeting conditions of low weight and high impact strength at the same time.

Some companies have already presented parts manufactured by **injection moulding**. Prototypes of these parts are subjected to demanding tests and full use of these materials is expected in the immediate years. In the **aerospace technology**, research programmes for the use of **aluminum** and **hafnium nanoparticles** for **rackets fuel** are performed. For this purpose of use, the important factors are improved burning and ignition velocity of particles.

Applications of nanomaterials in **surface finishing** in abrasion-resistant and corrosion-resistant coatings formed on various substrates and in coatings on surfaces participating in catalysis have been developed. The leading candidates for the manufacture of **filters for fluid separation** in industrial processes or **cleaning of waste liquids** are TiO$_2$ and ZrO$_2$ nanoparticles, exhibiting ability to capture heavy metals and bioorganisms. New **ceramic nanomaterials** will be applied in the manufacture of **water jets, injectors, lasers, telescope mirrors** of low weight, **jacketing of arm systems** and for **anode and cathode surface coating in power industry facilities**.

Advancements in the research of **photonic crystals**, which are elements based on phenomena exhibiting in nanodimensions, offer their applications in **optical communication networks** resulting in a significant increase in their efficiency. Small and cheap **optical switches** are a key to the development of a full potential of rapid and wideband **optical communication networks**.

In the "Modern Drug Discovery“ journal the following prediction of applications of nanomaterials has been published.
In the field of high-speed computers and “post-silicon” electronic devices:
- Continuation of the Moore’s law (Intel company plans the manufacture of nanotransistors for the manufacture of 10 GHz chips),
- High-speed modelling of a genome (Intel, Compaq and Celera companies cooperate in construction of 100 gigaflop proteomics analytical engine).

In the field of nanomaterials manufacture:
- Bulk sale of carbon nanotubes,
- New and improved textile matters (water, soil and crease resistant clothing),
- New paints and coatings (fire resistant, crack closing),
- New cosmetic preparations, biosensors, wear-resistant polymers, soil and abrasion resistant fine-grained ceramic composites.

In the field of health care and pharmacy:
- NEMS (Nanoelectromechanical systems) and nanoequipment for separation of DNA fragments and high-speed sequencing,
- Bio-silicon interface for diagnostics, sensors, pharmacogenetics and drug testing (Nanogen company prepares an automated molecular analytical system lab-on-chip).

In the field of living environment and power industry:
- Application of carbon nanotubes for hydrogen storage for fuel cells,
- Removing ultra-fine impurities from biological wastes by their encasing,
- Biodegradable chemical substances for agricultural growing purposes and for protection against insects.

7.3. Long-term perspective

In future, so far unknown phenomena acting in nanodimensions will be discovered, materials with new properties will be synthesized, new technologies of their synthesis will be elaborated and new applications found. One of the main target groups of the research and development will be information and communication technologies. Within a longer time horizon, nanoelectronics will replace the nowadays microelectronics step by step in a broad scale. Transistors made from carbon nanotubes may be smaller and faster than any possible silicon transistors.

Molecular switches show possibilities to construct very cheap memories with high density. Single-electron transistors (SET) have been already presented, which were tested as exceptionally sensitive indicators of the electrical charge for various applications, from detectors of biological molecules to quantum computer components. Quantum dots are used as markers in DNA diagnostics. They are also interesting for the use in quantum computers. New methods of synthesis of nanowires will be developed, which will enable the manufacture of new nanosensors for detection of chemical substances. Their use can be expected e.g. in sensors for management and control of industrial processes, for detection of chemical and biological dangerous substances, for the manufacture of instruments, for living environment monitoring etc.

Future applications of the so-called extreme nanotechnology are expected (Fig. 23), on the upper right hand side). This term involves atomic and molecular manipulation and self-organization and self-assembly of the matter. This is a great opportunity for future “designers” to create materials and to build structures, which occur in nature and are expected to have completely different functional properties than their basic components. The fundamental research in this field is very intensive nowadays. These processes will enable to create two- and three-dimensional highly integrated structural elements using carbon nanotubes, organic molecular electronic components, quantum dots etc. for fast building of more complex electronic systems, e.g. logic and memory devices. Such devices could have operating characteristics and data storage capacity exceeding contemporary devices many times.

Nanomaterial properties will be enhanced. More and more new, better and cheaper nanopowders, nanoparticles and nanocomposites will be available for wide-scale applications. Another important application of future nanomaterials can be expected in highly selective and effective catalysis of chemical processes and in energy transformation. Catalysis based on the usage of nanomaterials can play a great part in photovoltaic cells, fuel cells, in energy bioconversion, in biotechnological systems (in foodstuff production and in agriculture) and in waste processing and air monitoring.

Nanoscience and nanotechnologies will permanently influence various fields of biomedicine, such as therapeutics, diagnostic apparatuses and biocompatible materials for implants and prostheses. Applications of nanomaterials for drug transportation will be developed. Combining new nanosensors with nanoelectronics,
ic components will lead to further reduction of dimensions and improved functionality of diagnostic apparatuses and systems. **Implants with cell dimensions** will be possible to be made, which will act in vivo and will diagnose and monitor disease development.

It is assumed that within 15 to 20 years nanotechnology will transform science, technology and society root and branch. Just nowadays nanotechnology has enabled a noticeable progress in health care, e.g. in targeted transportation of medicaments, in regeneration of biocompatible tissue and in development of sensors. The main aim is e.g. early diagnosis of cancer and its treatment.

Application of nanotechnology in electronics appears particularly perspective. New directions, such as quantum computing, spintronics, molecular and biomolecular electronics and photonics represent a great challenge.

**LITERATURE**


