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Introduction into Nano- and Biomaterials

Translated materials from the original work of Ryzhonkov, D.I., Levina, V.V., Dzidziguri, E.L. were used in this chapter.

There is no substitute to hard work....
Thomas Edison, inventor (1847–1931)

1.1 Definition of Nano- and Biomaterials

Nano (from Greek, *nannos*), meaning dwarf, is one billionth of or 10^{-9} part of a thing, for example, $1\,nm = 10^{-9}$ m. *Nanomaterials* consist of nanostructured materials and *nanoparticles,* which can be defined as nano-sized complexes of interrelated atoms and/or molecules. *Nanotechnology* is defined as the knowledge and management of processes on a scale from 1 to 100 nm and application of object properties on a nanometer scale. Significant works in nanotechnology started in 1980. Definition for the term *nanotechnology* was given for the first time by Norio Taniguchi, a professor of Tokyo University, in 1974 in his paper *Basic concepts of Nanotechnology,* which mentioned "Nanotechnology mainly consists of the processing of separation, consolidation, and deformation of materials by one atom or one molecule."

Biomaterials can be defined as "materials intended to interface with biological systems to evaluate, treat, or replace any tissue, organ or function of the body" [1] or "any synthetic material which is used to replace part of a living system or to function in intimate contact with the living tissue [2]."

1.2 History of Nano- and Biomaterials Application

Nanomaterials and biomaterials are important because of their primal and initial applications, which date back to ancient times and the Middle Ages, when glassblowers insensibly used nanotechnology. They added gold chloride ($AuCl_3$) to melted glass to change its color to ruby. Thousands of years BC, people knew and used natural fabrics such as cotton, silk and flax, and wool [3]. The Romans had the Lycurgus Cup during the fourth century AD (Anno Domino), which comprises silver and gold nanoparticles at a ratio of roughly 7 : 3, with a diameter

Nano- and Biomaterials: Compounds, Properties, Characterization, and Applications,
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size of 70 nm, as disclosed by modern analytic methods. The cup demonstrates a unique color display because of the presence of these metal nanoparticles. It appears green when observed in reflected light, for instance, in daylight, but turns red when light is propagated through it, which is now in the British museum. Historical applications of biomaterials include the use of linen threads by ancient Egyptians to close wounds. Europeans used a fiber made from catgut to close the wounds during the Middle Ages 4000 years ago. Inca surgeons repaired cranial fractures with gold plates in neurosurgery. Mayans used sea shells to create an artificial teeth. In the nineteenth and early twentieth centuries, a number of physicians began to explore the way in which the body reacted to implanted materials. After World War II, observations began to demonstrate the tolerance of the human body to some metals *in vivo*. Physician Harold Ridley who worked with World War II aviators had noticed that pieces of shattered cockpit canopies inadvertently embedded in the eyes of pilots were well tolerated; thus, he made the 1st formal assessment of "biocompatibility." Later he created implantable intraocular lenses from polymethylmetacrylate [1].

1.3 Methods for Preparing of Nanomaterials

Recently, a huge number of methods for nanomaterial preparation were developed, which led to a variety of nanomaterial properties and expanded the ranges of nanomaterial classes with the creation of a new and unique materials. The formation of high-dispersive structures might happen during phase changes, chemical interactions, recrystallization, amorphization, high mechanical stress, and biological synthesis. Improvement of primary methods for nanomaterials syntheses defined the main requirements such as:

- Method should provide control of composition and properties for obtaining of nanomaterials.
- Method should provide permanent stability of nanomaterials, principal protection of particle surfaces against oxidation and sintering during synthesis.
- Method should be highly productive and economical.
- Method should allow acquisition of nanomaterials with definite sizes or grains.

Basically, preparation of nanomaterials can be divided into *up-bottom* and *bottom-up* processes, which are based on crushing and integration, respectively. These processes are essential for nanomaterials syntheses, especially of mechanical, physical, chemical, and biological methods. Mechanical dispersion methods are based on the interaction between pressure, curve, vibration, friction, and cavitation processes. *Physical methods* for nanomaterial syntheses are based on physical transformations: evaporation, condensation, sublimation, hardening, thermocycling, and so on. *Chemical methods* are based on chemical dispersion process, chemical reaction, electrolysis, reduction, and thermal decomposition. *Biological methods* for nanomaterials syntheses are based on the use of biochemical processes in the protein-containing body.

1.3.1 Mechanical Dispersion Methods for Nanomaterial Synthesis

Most mechanical dispersion methods involve mechanical milling, intensive plastic deformation, and mechanical interactions between various mediums.

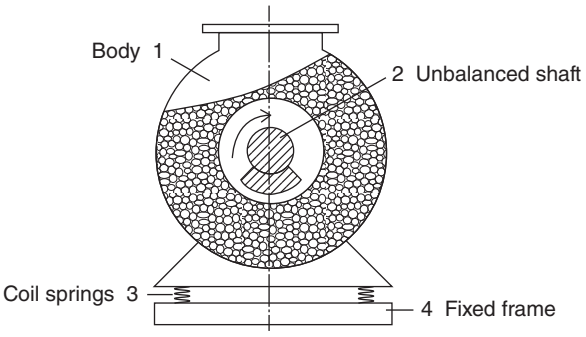


Figure 1.1 Scheme of vibration mill for nanomaterial preparation (reproduced with permission of BKL Publishers).

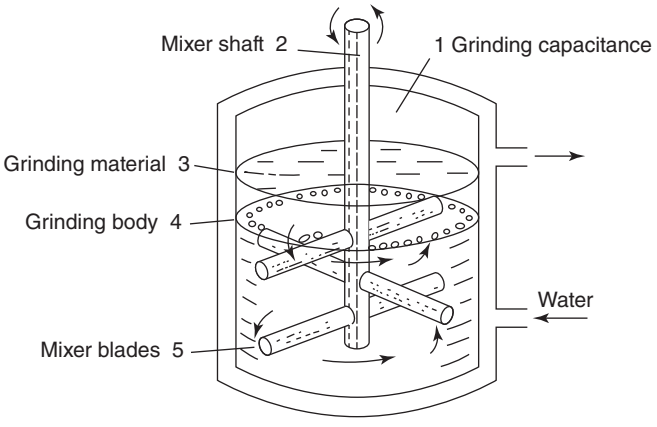


Figure 1.2 Scheme of attrition milling device for nanomaterial preparation (reproduced with permission of BKL Publishers).

Mechanical milling is determined by local mechanical interactions appearing in the strain field of the given material. Due to locality and impulsivity in the area of dispersing material, loads can be focused for a short time and cause formation of particle defects, stacking faults, deformations, and cracks. Finally, milling of materials will occur, as well as acceleration of mass transfer, mixing of components in material, and activation of chemical interactions between solid reagent compounds. Mechanical milling or grinding is conducted by using of various equipment such as vibration mills (Figure 1.1), ball mills, hygroscopic mills, attrition mills (Figure 1.2), vortex mills (Figure 1.3), and jet mills.

Grinding in vortex mills is primarily intended for ductile metal conversion into nanopowders. In these devices, collisions between the abrasive particles of grinding material will occur. Inside the working chamber of a jet, mill propellers rotate in opposite directions with a speed of 3000 rotations per minute (Figure 1.3). Depending on the nature of the grinding material, particles might be obtained in splintered, flaky, and rounded forms.

Another type of mill for nanomaterial preparation is the planetary *centrifugal mill*, which allows fast and fine crushing of hard milling materials. In hygroscopic mills, the grinding drum rotates horizontally and vertically at the same time.

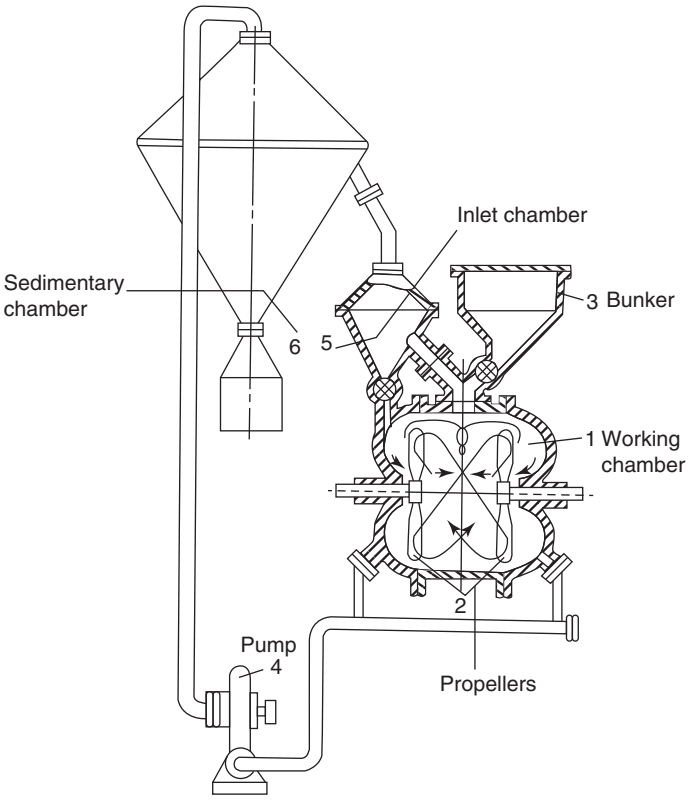


Figure 1.3 Scheme of vortex mill device for nanomaterial preparation (reproduced with permission of BKL Publishers).

Jet mills are designed for the effective production of nanopowders. They provide fine crushing of material by inserting compressed gas jet (air, nitrogen, etc.) or hot steam into working chamber from the nozzles, with sonic or ultrasonic velocity. Inside the working chamber, grinding materials undergo vortex motion and multiple collisions, resulting in their intensive abrasion. Jet mills are used for grinding of metals, ceramics, polymers, and their different combinations.

Also, the grinding of fragile and specially embrittled materials, for example, electrolytic sediments and spongy metals, can be conducted inside jet mills. An inert atmosphere can prevent the oxidation inside the working chamber of jet mills.

Moreover, for effective grinding, it is recommended that the grinding process be conducted in liquid organic mediums, such as hydrocarbons and oleic acid. Nanoparticles obtained by mechanical milling methods usually have various shapes, ranging from uniaxial to flaky or lamellar. As-obtained powder size depends on synthesis conditions and ranges from 1 to 100 nm.

Mechanochemical method is one of the means to grind materials and involves increase in the physical interaction between mixtures of various components, as well as *mechanochemical reactions* likely initiated or accelerated by mechanical

interactions due to the deformation and destruction of the grinding material. Thus, in the solid phase, chemical reactions might occur in solutions and melts at high temperatures. The flow of mechanochemical reaction depends on the dispersity of initial substances, their characteristics, and conditions of grinding. The effect of deformation on material properties can be characterized by *mechanical activation*, referred to mechanical processes, during which reaction ability of solid material will increase.

1.3.2 Intensive Plastic Deformation Methods for Nanomaterial Synthesis

In order to form nanostructures in bulk materials, special mechanical schemes for deformation are applied. They allow significant distortions in samples at relatively low temperatures. Intensive plastic deformation methods include the following:

a) Torsion under high pressure
b) Equal-channel angular pressing
c) Comprehensive forging method
d) Equal-channel angular extraction
e) Hourglass method
f) Intensive sliding friction method.

Among these, torsion under high pressure and equal-channel angular pressing are mostly applied. There are several requirements to form nanostructures in bulk materials by using of plastic deformation:

- The final result of the aforementioned methods is the formation of nanostructures with large angular borders of grains.
- These methods should form homogenous nanostructures within the whole volume of material.
- The material obtained should not have any mechanical damages and destructions.

For the implementation of deformation by *torsion under high pressure,* initial substances should have disk-like shapes. The initial material is inserted between punches and pressed under pressure of several gigapascal (Figure 1.4).

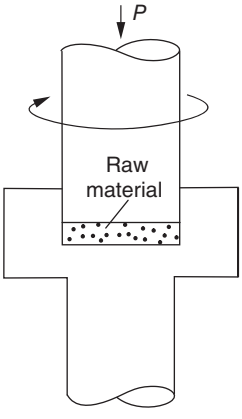


Figure 1.4 Schematic illustration of deformation by torsion method under high pressure (reproduced with permission of BKL Publishers).

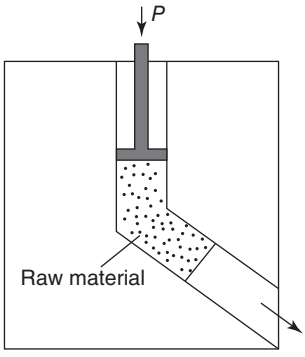


Figure 1.5 Principle of equal-channel angular pressing method for nanomaterial preparation (reproduced with permission of BKL Publishers).

Only the upper punch will be rotated, deforming the main volume of material by friction force. Hydrostatical compression and applied pressure lead to nondestruction of the sample by deformation. The process occurs at room temperature, as well as at temperatures up to $0.4T_{melt}$. The obtained samples by intensive plastic deformation have disk-like shapes, with sizes of 10–20 mm and thickness of 0.2–0.5 mm; significant grindings of sample structure can be observed right after the deformation at half turnover, but for the preparation of homogenous nanostructure, deformation at multiple turnovers is required.

Raw materials for *equal-channel angular pressing* are samples with round or square transverse section and a diameter of 20 mm; for example, the maximum diameters of raw materials treated through this method are 40 mm for Ti, 90 mm for Al, and 150 mm for Mo. The length of raw materials was 70–100 mm. To obtain the necessary level of deformation, the sample was repeatedly pressed inside a special equipment through two channels with similar transverse section, crossing at an angle of 90° (although this angle might be larger (Figure 1.5)). The quantity of passages depend on the nature of deformation material. For example, Cu tolerates sixteen passages, while the Al–Cu–Mg alloy is destroyed after three passages.

The transformation speed of the sample during pressing depends on temperature, with the average being 60 mm min^{-1}, that is, one passage being finished in 10 seconds.

There are several routes for deformation such as (Figure 1.6):

- Orientation of raw material does not change (route A).
- After each passage, the raw material turns around its cross-sectional axis to 90° direction (route B).
- After each passage, the raw material turns around its cross-sectional axis to 180° direction (route C).

The direction of shift during repeatable passages through the crossing channels for the raw material changes according to the aforementioned routes, leading to the formation of various structures in the raw material.

Comprehensive forging is another way of nanostructure formation in bulk samples and is based on the use of multiple (up to 20 times) repetitions of free forging (Figure 1.7). By starting the treatment at high temperatures $(0.3–0.6)T_{melt}$ through this technique, it is possible to obtain a nanostructured condition for

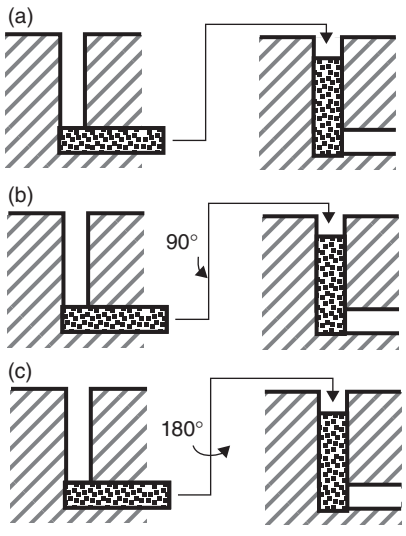


Figure 1.6 Routes for raw material orientation during equal-channel angular pressing: (a) orientation of raw material does not change during all passages; (b) the raw material turns to 90° after each passage; (c) the raw material turns to 180° after each passage (reproduced with permission of BKL Publishers).

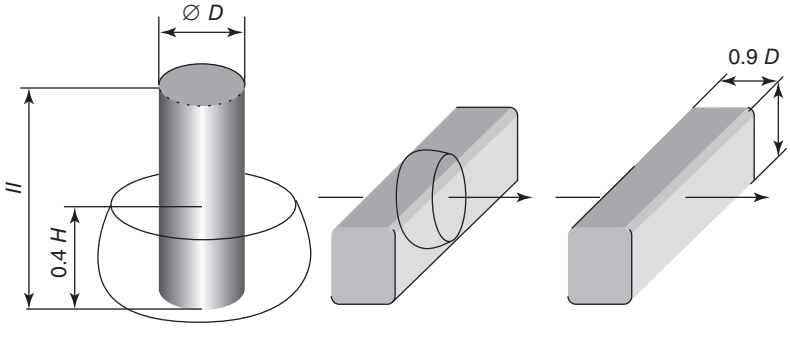


Figure 1.7 Scheme for comprehensive forging method (reproduced with permission of BKL Publishers).

fragile materials. By increasing the deformation percentage, the temperature can possibly decrease.

Intensive plastic deformation methods exhibit a number of certain advantages:

- The possibility for obtaining of bulk materials, and also nanostructures with complex profiles, at a single stage
- The possibility for the formation of continuous process based on equal-channel angular pressing.

Below are some goals, which can be achieved by the improvement of technology:

- Small size of product
- Nonhomogenous microstructure of the final product
- Complicated and expensive technical equipment.

1.3.3 Obtaining of Nanomaterials by Mechanical Interaction of Various Mediums

Recently developed methods are hydrodynamic cavitation, vibration, shock wave, grinding by ultrasound, and detonation synthesis.

Hydrodynamic cavitation aims to synthesize suspensions of nanopowders in various dispersion mediums. *Cavitation* comes from the word *cavitas,* which means hollow, and hence is defined as the formation of hollows (cavitation bubbles or caverns) in liquids filled with gas, steam, or gas–steam mixture. Cavitation results from a decrease in the local pressure of liquid, which might happen due to the increase of its velocity (hydrodynamic cavitation) or due to the passing of most intensive acoustic waves during the intensity subperiod (acoustical cavitation). During the transfer to the large flow region with high pressure or during subperiodical pressing, cavitation bubble slams, thus emitting a shock wave. The destruction caused by cavitation impact is also used in the grinding of nanomaterials by ultrasound.

Vibrational method is based on the synthesis of nanomaterials by resonance. This allows minimal energy use and high level of homogenization in multiphase mediums. The procedure is based on definite vibrational interaction of the dispersing reagent vessel. *Shock wave* in mechanical interaction can be used to obtain nanomediums. Nanodiamond powders with an average particle size of 4 nm are synthesized by shock wave treatment of graphite and metal mixture under a pressure several tenths of gigapascal and for an interaction period of 10–20 μs. Also, the shock wave treatment is used for grinding of porous structures. Investigations done on the ZrO_2–Y_2O_3 system showed that shock wave completely grinds initial dimensional compounds into fragments with size not less than 100 nm and with a particle size of 10 nm. Diamond particles are also obtained by using the *detonation synthesis* method. In this method, explosion energy is used to reach pressures up to hundreds of atmosphere and temperatures up to several thousands of degrees. These conditions are suitable in the thermodynamical stability region for diamond phase. In order to achieve a significant production of diamond powder, a mixture of trinitrotoluol and hexane (with mass ratio of 50 : 50 or 60 : 40) is used under a pressure of 15 GPa in detonation wave and a temperature of 3000 K. The detonation synthesis is carried out inside a special chamber, with a capacity of 10 g to several kilograms of initial reaction mixture. To prevent the reduction of diamond powder and its transformation into graphite, reaction chambers are filled with inert carbon dioxide gas. Synthesis lasts for 0.2–0.5 μs. In order to remove the carbon soot and other contaminants after synthesis, condensed product is treated with hot acids and then dried after multiple washings. The productivity of diamond powder is 8–9% of the total initial reaction mixture mass. The amount of main synthesizing product has a particle size of 4–5 nm. Explosive compounds containing carbon have an important role during the synthesis procedure. Carbon exists in the form of several complex morphologies: nanotubes, funnels, hollow spherical particles, and plates. Also, synthesis products plaques by carbon layer with a thickness of 10–20 nm. Mechanical interaction methods have the following advantages:

- High productivity
- Possibility for waste utilization
- Possibility for formation of protective layers during dispersion.

However, the following disadvantages are present:

- Contamination of product by material of reaction medium
- Necessity of a special complex equipment.

1.3.4 Physical Dispersion Methods for Nanomaterials Preparation

This group of methods includes spraying, evaporation–condensation processes, vacuum-sublimation technology, and solid state transformation methods.

Solid spraying method is one of the common methods for spraying of melt flow by liquid or gas (Figure 1.8). In this complex physical process, aerodynamical forces play a main role, determined by the relative speed of transferring dispersive material and its density. The mechanism of liquid stream dispersion is determined by a step-by-step splitting of more disperse particles into primary drops and then into secondary drops.

In contrast to gas dispersion, *liquid spraying* method is characterized by a high-density medium, which influences the kinetic energy of the liquid stream. The high density of the separating liquid provides high-speed preservation at significantly large distances from the nozzle section, which allows relative position of stream and makes construction of streaming equipment easier. One of the possible schemes for the dispersion of metal alloy melt is presented in Figure 1.9.

Taking out of the working liquid happens through holes in the circular disk, which rotates at a high speed. For example, to obtain nanomaterials with a particle size less than 100 nm, the jet undergoes cold gas spraying to cool the sedimentation surface. The particle size can be influenced by the working pressure of the separating jet: the larger the pressure, the smaller the particle size of the dispersing material. Also, particle size distribution and powder particle morphology can be affected by melt temperature during spraying and the square jet cross section. It is possible to obtain powder with a particle size of 50–100 nm. The shape of

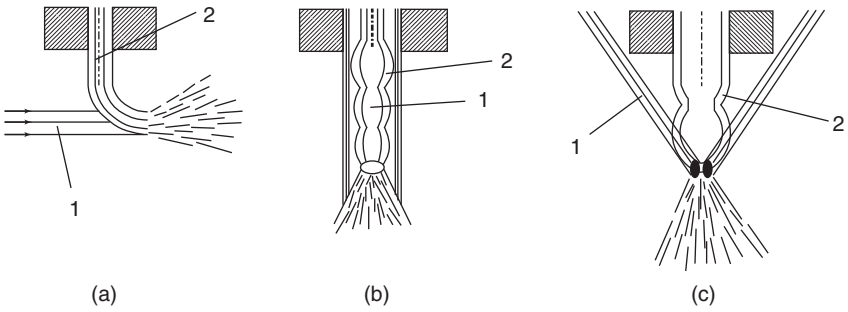


Figure 1.8 Scheme of jet melt spraying method: (a) gas flow, directed perpendicular to the melt jet; (b) spraying by subaxial gas flow; (c) gas flow, directed under the angle to melt jet. 1 – breaking gas flow; 2 – dispersing melt flow (reproduced with permission of BKL Publishers).

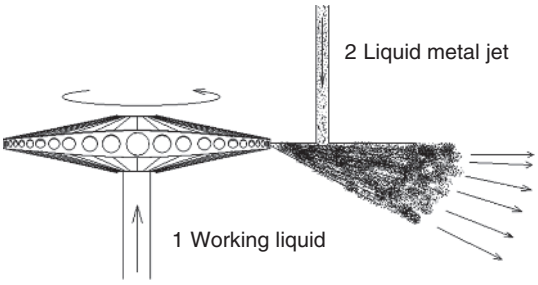


Figure 1.9 Spraying method of metal melt by liquid jet.

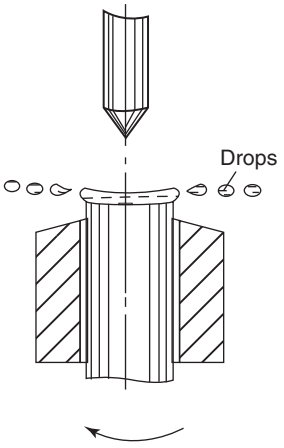


Figure 1.10 Scheme of centrifugal spraying method under centrifugal force or rotating method (reproduced with permission of BKL Publishers).

spraying material is usually drop-like or spherical. However, during high-speed cooling, the formation of particles with an inappropriate shape is possible.

During *centrifugal spraying* method, nanopowder is obtained through melt material spraying in nonoxidative atmosphere by centrifugal force. During melting in the electric arc furnace or in the low-temperature plasma, the electrode (Figure 1.10) rotates at high speed.

From the surface of being melted and fast rotating electrode end, liquid drops are separated and converted into dispersive powder during solidification. The main advantage of this process under centrifugal force is the possibility for dispersion in inert gas or vacuum. By regulating the atmosphere inside the furnace, it is possible to disperse refractory metals and metals with affinity to oxygen. The particle size obtained by using this method is about 100 nm.

Spinning is a method for nanomaterial formation by hardening the liquid phase. This method is based on obtaining thin tapes at fast cooling stage, with a speed not less than 10^6 K s^{-1}, and cooling the melt on the surface of a rotating cylinder.

1.3.5 Preparation of Nanomaterials by Evaporation–Condensation Method

All *evaporation–condensation* methods are based on the synthesis of nanomaterials by fast change in aggregate condition and by phase transformations: steam–solid matter or steam–liquid–solid substance. The final material evaporates by intensive heating and then is sharply cooled. Evaporation–condensation methods are classified according to the heating type of evaporating material,

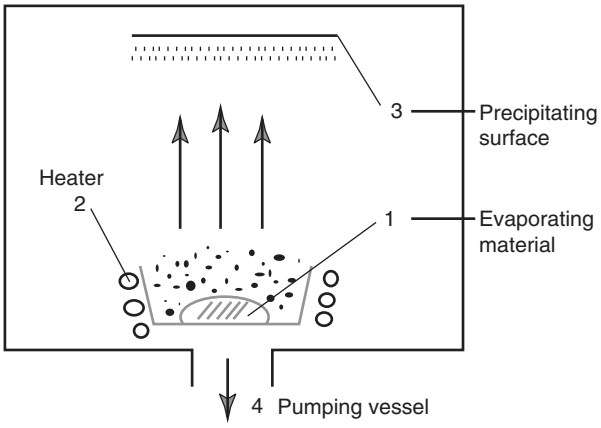


Figure 1.11 Scheme of equipment for obtaining nanopowder by evaporation–condensation method (reproduced with permission of BKL Publishers).

such as resistive, laser, plasma, electric arc, induction, ionic, and so on. In addition, evaporation–condensation process can be conducted in vacuum or neutral gas medium and can also be applied in various cooling ways. The evaporating material is usually inserted inside the crucible or vessel made from refractory, chemically inert materials, such as wolfram, tantalum, graphite, and glass carbon (Figure 1.11).

Plasma technology is widely used for metal nanoparticle preparation. Plasma can be defined in terms of partially or fully ionized gas, forming as a result of thermal ionization of atoms and molecules at high temperature. There are several types of plasma: weakly ionized or low-temperature plasma, moderately or fully ionized plasma, and high-temperature plasma. In technological processes, low-temperature plasma is usually used, obtained at a temperature of 2000–20 000 K and pressure at diapason of 10^{-5}–10^{3} MPa. For the generation of plasma, electric arc, high-frequency, and super-high-frequency high-power plasma torches, which are able to heat gas up to high temperatures, are applied. Stable and low-pressure plasma can be achieved by using an inert gas and hydrogen. Figure 1.12 shows the scheme of equipment for obtaining of nanopowders by plasma jet. Heating and evaporation of dispersing material is achieved by low-temperature plasma jet energy, followed by discharging from the plasma torch. The evaporating material is inserted into the plasma zone in the form of powder or consumable electrode (or anode). The cooling speed of the formed strongly heated gas bears importance for the dispersity, powder structure, and production process. Condensation of the dispersing material in the plasma processes is achieved using the cooling gas stream and cooling surfaces, which permits the temperature gradient to be more than 10^{5} °C min^{-1}, which is suitable for refractory metal powders with a particle size of 5–100 nm. At a cooling speed of 10^{5}–10^{8} °C s^{-1}, it is possible to obtain Al powder with a particle size of 0.5–50 nm.

Combined plasma allows an effective evaporation of the dispersing material. In this method, two kinds of plasma are used: plasma by constant electricity to heat

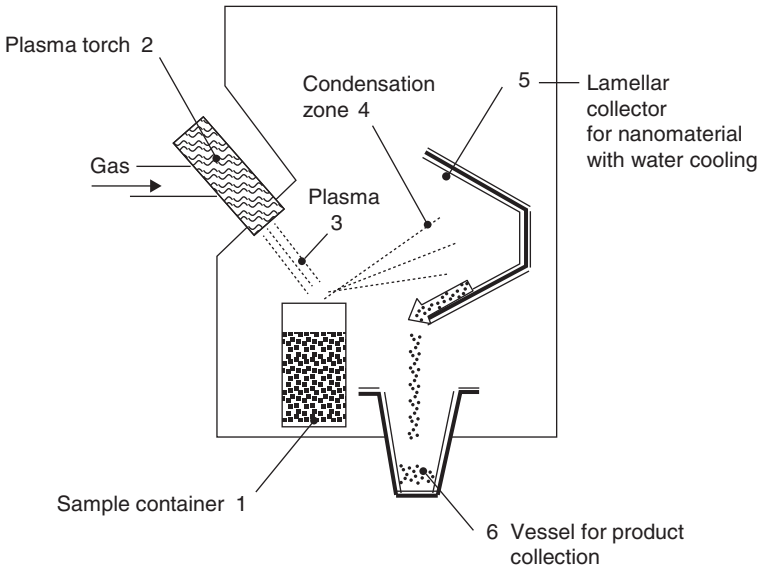


Figure 1.12 Scheme of equipment for the synthesis of nanopowders by plasma jet (reproduced with permission of BKL Publishers).

the material and high-frequency plasma, which permits melting and evaporation of final large-size powder or flakes. This method enables the acquisition of powders of most metals and metallic compounds with spherical shape and size of more than 50 nm.

Laser heating is used to avoid disadvantages associated with plasma method by keeping the working temperatures stable. Using this evaporating technology, nanopowders of Ti, Ni, Mo, Fe, and Al with an average particle size of several nanometers can be obtained. *Laser,* determined as an optical quantum generator, is a source of optical coherent radiation, characterized by high focus and large energy thickness. Laser types include gas, liquid, and solid.

Electric arc melting is one of the effective ways for metal nanopowder synthesis. Figure 1.13 shows the scheme of reactor with electric arc plasma torch and direct current.

Electric detonation of semiconductors is considered as an evaporation–condensation method wherein thin metal wires with diameters of 0.1–1 mm are inserted into the camera, where high electricity is applied (Figure 1.14).

As mentioned previously, evaporation–condensation methods depend on the working medium and cooling.

Conducting the synthesis process in vacuum is effective for obtaining powders with special properties and a large number of heavy and refractory materials. Through this method, Ni, Al, Zn, Pb, Mn, Fe, and Co with a particle size of 50–100 nm can be obtained.

Condensation of steam in the inert gas is usually maintained at 10–10^2 Pa. Inert gases such as He, Ar, Xe, or N_2 are used. The size of as-obtained particles is 10–100 nm.

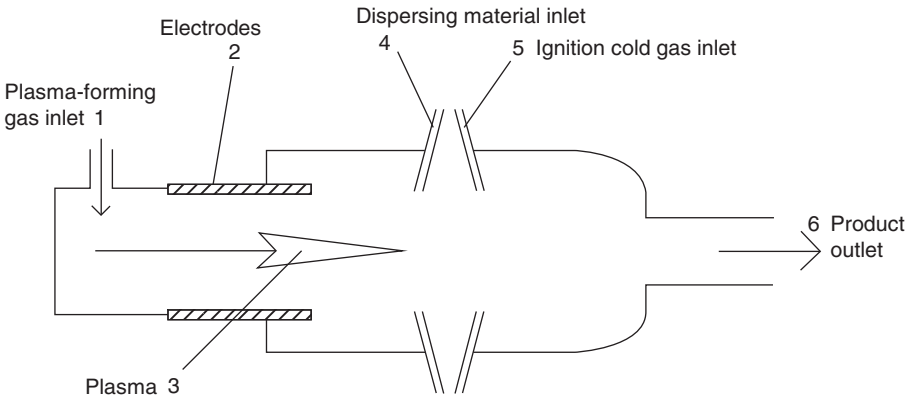
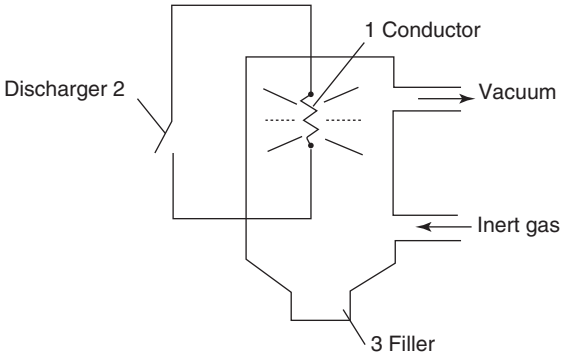


Figure 1.13 Scheme of reactor with direct current electric arc plasma torch (reproduced with permission of BKL Publishers).

Figure 1.14 Principal scheme of equipment for obtaining nanopowder by semiconductor detonation method (reproduced with permission of BKL Publishers).



1.3.6 Obtaining of Nanomaterials by Vacuum-Sublimation Technology

The change in the aggregate state of material sublimation underlies the physical methods for obtaining of nanomaterials.

Vacuum-sublimation technology is a process of obtaining nanomaterials that involve three basic stages. In the first stage, an initial mixture of processed materials is prepared. The second stage is called solution freezing, aims to fix the uniform dimensional distribution of components in the liquid to achieve crystallite sizes as small as possible in the solid phase. During the third stage, crystallites are removed from the freeze solution by sublimation. After completion of these three stages, a porous material is obtained, which consists of crystallites of solvent particles. *Evaporative freezing* (or self-freezing) of solution is realized by intensive evaporation of solvent in vacuum. Figure 1.15 shows the principal scheme for obtaining of nanomaterials using this method. The working pressure is 0.05 mmHg and the temperature is not higher than 40 °C. In this case, liquid jet disperses into drops, which undergoes freezing during flight. The formed cryogranules fill the volume of the entire heater, in which sublimation from solvent will take place. As a result, a spherical mass-like product consisting of dissolved substances will form.

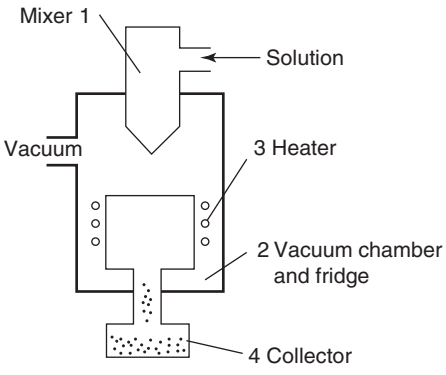


Figure 1.15 Scheme of equipment for obtaining nanopowders by vacuum-sublimation technology (reproduced with permission of BKL Publishers).

Using the vacuum-sublimation technology, a wide range of nanomaterials can be produced, including ferrites, oxides, nitrides, carbides, and high-temperature and high-superconductivity compounds. Advantages of vacuum-sublimation technology are:

- Granularity of product, which allows its transportation with minimal dusting and ability to be kept for a long time without significant property changes
- Low dusting, which increases safe synthesis of nanomaterials
- Good background for organization of continuous production.

However, the following disadvantages still exist:

- Limitation on solubility, which narrows the number of obtained products
- Necessity of special equipment for conducting the sublimation process.

1.3.7 Obtaining of Nanomaterials by Using Solid Phase Transformations

There are a number of methods for nanomaterial acquisition, in which the dispersing process is carried out in the solid material without a change in its aggregate state. *Controlled crystallization from amorphous state* is one of the ways for obtaining the bulk material. The method is based on obtaining amorphous material, with hardening from liquid state and then crystallization in controlled heating conditions. Through this method, it is possible to obtain the following nanomaterials (various transition metal and nonmetal alloys) prone to amorphization: Fe–B, Fe–Si, Fe–Si–B, Fe–Cr–B, Fe–Mo–Si–B, Fe–Mo–Si–B, Ti–Ni–Si, Ni–P, Fe–Cu–Nb–B, Se–Fe–Zr, and Al–Cr–Ce–Co. The sizes of the obtained crystallites depend on the nature of materials and the type of thermal treatment. In thermal annealing, the grain size of Se crystallites with hexagonal modification varies from 13 to 70 nm, and the size of Fe–Mo–Si–B alloy is from 15 to 200 nm.

1.3.8 Chemical Dispersion Methods for Nanomaterial Preparation

Methods for the synthesis of nanomediums by chemical reactions are very diverse but can be grouped into three: the first group includes methods in which dispersing occurs during the chemical reaction. The second group includes methods based on the different variants of electrochemical reactions. The third group includes methods that combine chemical and physical transformations.

1.3.9 Obtaining of Nanomaterials by Using Chemical Reactions

Precipitation method is widely used and is based on the sedimentation of metals from their salt solutions using precipitators. Base solutions such as NH_4OH, NaOH, KOH, and so on are used. In general, the process is as follows:

$$Me_x(A)_y + K(OH) \rightarrow Me_x(OH)_y + KA$$

where A denotes anions: NO^{3-}, Cl^-, $SO_4{}^{2-}$; *K* is for cations: and Na^+, $NH_4{}^+$, K^+; *x,* and *y* are coefficients.

By regulating the pH and temperature of the solution, it is possible to produce optimal sedimentation conditions to obtain nanomaterials. Under these conditions, high-speed crystallization and highly dispersive hydroxide can be achieved. The produced precipitate goes through washing, drying, annealing, and, when needed, reduction. Metal nanoparticles obtained through this method have a particle size range from 10 to 150 nm. By varying the process parameters, it is possible to alter the shapes of particles, including spherical, needle-like, lamellar, and other shapes.

Coprecipitating is used for the synthesis of complex metal hydroxide compounds. In this case, in a reaction vessel, precipitant–metal–salt mixture is supplied. Under constant mixing and heating conditions, the following reaction occurs:

$$Me'_a(A)_b + Me''_c(A)_d + K(OH) \rightarrow (Me', Me'')_x(OH)_y + KA$$

where A are anions; Me′ and Me″ are various metal cations and bases, respectively; and *a, b, c,* and *d* are coefficients. Then, analogous to the precipitation method, the obtained powder is thoroughly washed to separate dissolved anions, is dried, and then undergoes thermal decomposition or reduction. The given method allows to obtain complex oxygen-containing compounds with specified ratio of cations, which leads to an increased solubility of metals in each other. Emulsion precipitation is an example of this method, occurring in non-mixing solvents. Through this way, it is possible to obtain nanoparticles covered with shell or layer of organic molecules. For example, for the synthesis of α-Fe_2O_3 with shell, a water solution of $FeCl_2$ at a concentration of 0.01 mol l^{-1} and sodium dodecylbenzol sulfonate and benzene are used. Emulsion is obtained after intensive mixing of liquids. For the precipitation of Fe compounds in organic mediums, NaOH is added. The average particle size of α-Fe_2O_3 covered with shell from organic molecules is 2.1 nm, as observed using transmission electron microscope (TEM). Through precipitation and coprecipitation, oxide, metal, and metalloxide powders and composites and ferrites and salts (e.g., $BaTiO_3$) with various particle shapes, chemical and physical compositions, dispersities, and size distributions in nanostate can be obtained. Additionally, materials synthesized using this method are characterized by chemical homogeneity and reaction ability.

Obtaining of nanomaterials through *heterophase interaction method* is based on the replacement of solid phase cations or anions by ions of the surrounding medium. This method is used to obtain composite particles, in particular, nanoparticles comprising one material and covered by a layer of another material. For example, CdS nanoparticles covered by PbS layer can be obtained by replacing the Cd ions with Pb ions. For this purpose, CdS nanoparticles stabilized by

polyvinylpyrrolidone are placed in a solution containing Pb^{2+} cations. Depending on the concentration of Pb^{2+} and the length of time of interaction, it is possible to replace one part or all Cd with Pb. For CdS nanoparticles with a size of 6 nm, the time of full transformation to PbS can be over 2 h. This method also allows to obtain a variety of metallic powders with a particle size of 10–100 nm when solid salt interacts with base solution. For example, the particle size of as-obtained Ni nanopowder is 20 nm. The shape of final metal nanoparticles is determined by crystal morphology of initial solid salts.

Initially, *sol–gel method* was developed for obtaining of Fe powder. The method is based on the precipitation of metallic compounds from water solutions in the form of gel and their further reduction. As practically shown, chemical purification of product will occur in the process. For example, the composition of Fe in the final powder is 98.5–99.5%. As initial substances, Fe salts are used, as well as metallurgical industry waste: metal scrap or waste pickle liquor. The use of secondary raw materials provides the opportunity for pure and relatively cheap Fe nanopowder. Other materials in nanostate, such as oxide ceramics, alloys, and metal salts, can be obtained also. In the sol–gel method, sol is obtained first, followed by gel after drying, which can be used in obtaining of films and monolithic materials.

Solvent evaporation is important in the precipitation process, which is complicated by long-term stages. *Cryogenic technology* is one of the ways for solvent evaporation, in which a solvent with necessary composition is prepared and sprayed inside a camera under cryogenic conditions and fast freezing, for example, liquid nitrogen. On the next stage, the pressure of gaseous medium will decrease below the triple point value of dispersion system equilibrium, and the temperature will increase for solvent sublimation. As a result, product consisting of thin porous granules will be obtained. By annealing of granules in the air, it is possible to obtain oxides; by reduction, it is possible to achieve metal powders, for example, Cu, W, and their salts; by selective reduction, oxide mixtures and metals, such as $Cu–ThO_2$.

Sublimated drying is based on spraying a metal saltwater solution in organic liquid at low temperature. In this process, immediate freezing will occur and then water from the precipitate under low-temperature and low-pressure conditions will evaporate. The final product will be obtained after thermal decomposition. For example, Li-doped Ni nanooxide used in the fuel cells can be obtained through this method.

In *evaporative thermal decomposition* method, a metal solution is sprayed into the surrounding atmosphere heated at high temperature. Evaporation of solution and thermal decomposition of metal salts occur as a result. Using heat generated during burning, alcohols are used as solvents. This method allows one-stage acquisition of ferrite nanopowders, which is further used for the production of high-quality ceramics.

In *reduction methods,* nanomaterials, particularly, metals, are obtained by reducing them from initial oxygen-containing compounds. The reduction

process can also be the final step in obtaining metal nanopowders by other methods.

Reduction of metal oxides and other solid compounds is a cheap and popular method for obtaining of nanomaterials by using of hydrogen, carbon monoxide, natural gas, solid reductants – carbon, (coke, soot), metals (sodium, potassium), and metal hydroxides. The final products include oxides, hydroxides, other chemical metal compounds, mine, and concentrates after preparation (enrichment, removal of impurities), waste and impurity materials after metallurgy manufacturing. The size and shape of synthesizing powder depends on the composition and properties of the initial and reductant materials, as well as on the reaction temperature and reaction time.

Upon the *interaction between metal oxides and gases* (H_2, CO) and carbon, the following metals can be obtained: Fe, W, Ni, Re, Mo, Cu, and Co. This process is expressed by the following chemical equations:

$$MeO + H_2 \rightarrow Me + H_2O$$
$$MeO + CO \rightarrow Me + CO_2$$
$$MeO + C \rightarrow Me + CO$$

By using of hydrides as reductants, it is possible to obtain Zr, Ta, Hf, Cr, Nb, and B nanopowders. In this case, chemical reaction will flow as follows:

$$MeO + CaH_2 = Me + CaO + H_2$$

where MeO is a metal oxide. To obtain high-purity nanomaterials, the use of reagents containing fewer impurities is a necessity, since the purity of the final products depend on the purity of the initial substance and the reductant.

Metallothermic method is used for Pt, Ag, Cu, Zn, Co, Ni, Fe, Mo, and Cr nanopowders. Reduction process is conducted in the presence of naphthalene in anhydrous medium:

$$Me'_a(A)_b + Me'' = Me''_c(A)_d + Me'$$

The average particle size of as-obtained particles in Au, Ag, and Pt is 10 nm, and for other metals, it is about 30 nm. Particle size distribution is narrow. Obtained powders are pyrophoric and thus require specific conditions to keep them. Metal ions are reduced in water solutions and salts by reductants such as H_2, CO, hydrazine, hypophosphate, and formaldehyde. In the case of gaseous hydrogen or carbon monoxide used as reductants, the process is conducted at high temperatures (about 200 °C) and high pressures (more than 5 MPa) in autoclaves. In this case, the initial raw materials are sulfuric acid and ammonia solutions of metal salts. Using this method, Cu, Ni, Co, Ag, and their composites were obtained. Synthesis of metal nanopowders from their salt solutions is possible using strong reductants such as hydrazine, hypophosphite, formaldehyde, and so on. In this method, nanopowders of Fe, Ni, Co, Cu, and their composites with spherical particles and size not less than 5 nm were obtained.

Obtaining of nanoparticles on carriers is one of the important ways aimed for decreasing the reaction ability of material. As for carriers, activated carbon is fed into metal salt solutions. Advantages of reduction method for the synthesis of nanomaterials depend on the following:

- Obtaining of alloy powders with component composition from 0% to 100%,
- Obtaining of homogeneous product (solid solution and chemical compound) as well as heterogonous system,
- Using cheap raw material for economy purpose.

However, disadvantages of this method are existing, such as:

- Limitations based on metal activity against various reductants,
- Pollution of nanomaterials by reductants.

Gas phase chemical reaction method is based on the synthesis of nanomaterials during chemical interaction, taking place in the atmospheric steam of volatile compounds. It is possible to divide all gas phase chemical reactions into decomposition reaction, occurring by participation of one of the initial chemical compounds (A = B + C), and the reaction between two or more chemical compounds (A + B = C + D). A mandatory condition for the use of the first type of gas phase chemical reaction is the existence of suitable chemical compound containing all the elements of final product, which is a rare case. The second type of gas phase chemical reaction is a common case. For conducting the gas phase reaction, initial substances should be volatile. As initial compounds, halogenides are used, especially metal chlorides, MO_nCl_m, metal steams, and so on. Equipment used for conducting the gas phase reaction is shown in Figure 1.16.

Pipes I and II are used for inserting of gas into the reaction vessel. Furnace 1 allows the heating of the reaction zone. An additional furnace 2 is used for heating of an substance 3; when needed, the evaporation occurs directly inside the reaction vessel (Figure 1.16). Reaction products in gas phase will enter vessel 4, where they undergo cooling and condensation. As a rule, reaction vessel is made of quartz, ceramic material, or clay. The main problem with this method is the

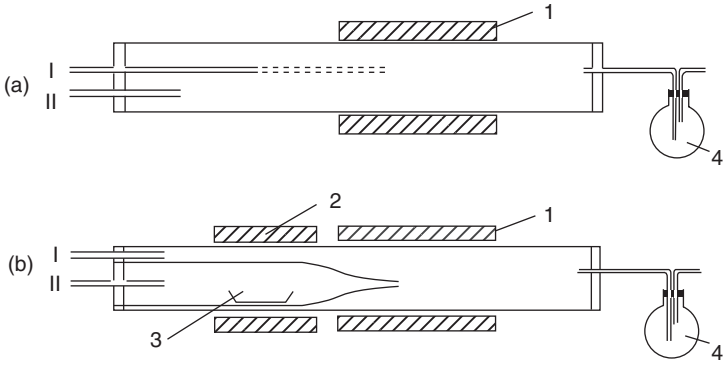


Figure 1.16 Scheme for obtaining nanopowders by outer heating of reaction zone: (a) inlet of initial gaseous substances; (b) use of initial solid substances. Number labels are explained in the text (reproduced with permission of BKL Publishers).

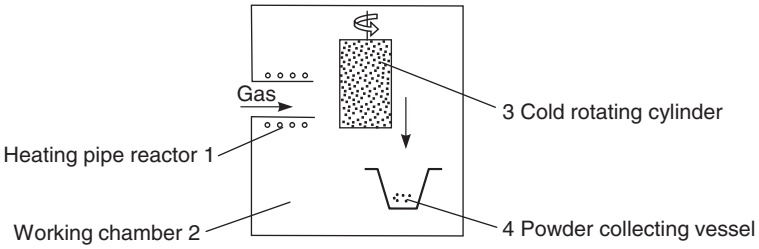


Figure 1.17 Scheme for obtaining nanopowders by gas phase chemical reactions (reproduced with permission of BKL Publishers).

separation of nanoparticles from the gas phase. For particles with nanosize and low gas flow concentration, the gas temperature is significantly high.

For trapping of nanoparticles, special filters, such as ceramic filters and electrofilters, as well as cyclones with liquid films, special gas centrifuges, and cold rotating barrel for gravitational precipitation, are used (Figure 1.17).

Advantages of gas phase reactions are:

- Possibility for synthesis of unique compounds
- Narrow size distribution of particles
- High purity of product

This method requires a special equipment, which is a disadvantage.

Thermal dissociation or pyrolysis is used for preparation of nanopowders of various compounds, as well as individual materials. As for initial substances, salts of low-molecular-weight organic acids, including metal formates, metal oxalates, metal acetates, metal carbonates, and carbonyls, are used. Dissociation is carried out at temperature intervals of 200–400 °C. Decomposition can be initiated by several methods. Heat energy is often used, as well as high-quality radiation, laser radiation, ionizing radiation, plasma flow, electron flow, and heat generation during friction.

Formiate pyrolysis can be expressed by the following equations:

$$(HCOO)_2Me \rightarrow MeO + H_2 + CO + CO_2 + H_2O + Me$$

Metal oxide reduction by CO and H_2 gases, generated during pyrolysis, is considered as secondary reduction reaction in this case. According to the above equation, decomposition of Cu and Zn formiates will occur. In the case of Mn, Fe, Co, Ni, Zn, and Ca preparations, in the first stage, decomposition of formiates will occur as:

$$(HCOO)_2Me \rightarrow Me + H_2 + 2CO_2$$

Decomposition of Mn, Fe, and Cu metal oxalates is expressed as:

$$MeC_2O_4 \rightarrow MeO + CO + CO_2$$

Co, Ni, Cu, and Zn oxalates are dissociated, as in the following equation:

$$MeC_2O_4 \rightarrow MeO + 2CO_2$$

Through pyrolysis of metal formates, oxalates, and other metal salts, powders with a particle size of 100 nm can be obtained. Thermal decomposition of carbonyls occurs as follows:

$$Me_x(CO)_y \xrightarrow{t} xMe + yCO$$

There is a possibility for obtaining Ni, Mo, Fe, Cr, and W nanopowders by this reaction. Also, carbonyl dissociation method is used to obtain polymetallic films with nanostructures. Reaction is conducted at a temperature of 500 °C; crystallite size in films is 20 nm.

Methods for obtaining of nanomaterials based on the oxidation of initial substances have been developed recently. To obtain the carbon soot–amorphous carbon, low-temperature burning method of hydrocarbons was developed. The process is carried out inside the double section reactor. Inside the first section, where the temperature is 423–773 K, preliminary heating occurs. In the second section, at a temperature of 1073–1173 K, flaming and controlled heating occurs, with the formation of soot, which has a particle size of 100 nm.

Precipitation from the metal alloy is based on the oxidation of metals or alloys by gases. For example, during the passage of an air after the completion of the precipitation process, material with metal and metal oxide particles.

Metal salt hydrolysis is used to obtain colloidal particles, in particular, nanooxides of Ti, Zr, Ir, and Al, by hydrolysis of appropriate chlorides, hypochlorites, and sulfates. In order to avoid nanoparticle coagulation, for stabilization of colloidal solutions, polyphosphates, amines, and hydroxyl ions are used. For example, Si alcooxide hydrolysis gives an opportunity for SiO_2 synthesis, which has less number of soluble salts and does not contain cations of alkali metals. Also, alcooxides are well dissolved in alcohols (ethanol); they are easily obtained by mixing of metals with alcohols.

1.3.10 Preparation of Nanomaterials by Electrochemical Methods

The use of electricity allows conducting processes that are not possible under usual conditions.

Electric precipitation method is based on the passage of direct current electricity through saltwater solutions during the precipitation process. Procedure of electric precipitation can be expressed as follows: cathode and anode as a rule have a film shape and are submerged into specially chosen electrolyte solution. To provide a product with purity, as anode, the same metal as precipitating metal should be used. But this condition is not always possible. For this reason, during the production of Cu powder, alumina anode is used, and for the production of Fe powder, Mo or Cr–Ni alloy anode is used. By this method, it is possible to obtain about 30 metals. Refining occurs in this process, which allows achieving materials with high purity. Metals precipitating on cathode, depending on the process conditions, can be obtained in the form of easily crushable powders, pores, or dendrites.

Electroflotation is a method for obtaining disperse powder based on crystallization of metals in double-layer bath with the presence of surfactants in the

organic medium. Obtained dispersive powder has needle- and rod-like shapes (Fe, Co) and is applied in the production of magnets and magnetic varnishes.

Salt melt electrolysis is a process carried out at high temperatures. As for electrolytes, metal salts are used. By this method, it is possible to obtain metal powders of Fe, Ni, Cr, Ag, Th, Nb, Ti, Zr, and Be.

Obtaining nanopowders is also possible by using the *liquid metal cathode*. In this case, liquid metal such as mercury is used as a cathode, in which metal powder is precipitating. The process is carried out in inorganic acid solution. By this method, Fe, Co, Zr, or Fe–Co alloys can be obtained. Particle shape is usually dendritic (10–20 nm). Obtained powders are mainly used for magnets.

Electrochemical synthesis method is based on obtaining chemical compounds inside liquid baths by passage of electric current. Reaction occurs at high temperatures, which allows the synthesis of high-temperature phase materials. By changing the electric parameters in this process, it is possible to control the sizes of obtained materials.

1.3.11 Preparation of Nanomaterials by Combinations of Physical and Chemical Transformations

Dispersion in this method on one hand is directly related to physical interactions and chemical reactions. In particular, physical interactions are caused by the decomposition of metal steams by various radiations during chemical reactions.

If the *laser* is used for the reaction, the reactor should have transparent windows for the passage of beams. In the simplest way, one of the laser beams that are directed to each other will pass through the first and second reactor windows. Reaction mixture flow will cross the laser beam perpendicularly. Particle size depends on the pressure inside the reaction chamber (reactor) and on the intensity of laser beam radiation. By this method, silicon nitride is obtained, with a particle size of 10–20 nm, from the SiH_4 and NH_3 mixtures.

γ-Radiation was used for obtaining Cu and Ag powders by decomposition of heavy metal azides (MeN_n). The main advantage of this method is the acquisition of non-defect metal particles.

In the *arc-discharge method*, the anode is made of Ni, Fe, or W metal or metal compounds. Arc discharge is produced in the atmosphere of reaction gas. As an example, high-density magnetic recording carriers are synthesized by metal halogenides with hydrogen at an atmospheric pressure of 50–600. Size of obtained particles is 17–39 nm.

Chemical flame in gas mixtures is used for nanomaterial synthesis. As initial substances, fluorides, chlorides, and metal oxides are used, and the chemical flame is produced by hydrogen and fluorine, hydrocarbon, and oxygen gas mixtures. By this method, Mo, Cu, and Ni alloys and oxides are obtained. Spherical nanopowders have particle sizes of less than 100 nm.

In the *plasma method* the metal source undergoes evaporation and the steam interacts with the reaction gas that contains metal compounds, and directed to the plasma burn. Figure 1.18 presents the scheme of equipment for obtaining nanopowders in impulse plasma with condenser-type discharge.

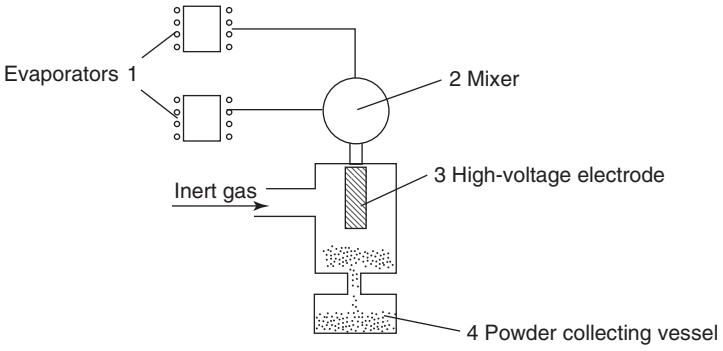


Figure 1.18 Scheme of equipment for obtaining nanopowders in impulse plasma with condenser-type discharge (reproduced with permission of BKL Publishers).

Obtaining nanopowders is also possible by *shock wave loading* of porous metals. In this method, a layer of initial powder undergoes physical loading by contact charge of detonating material. As a result, nanooxides with a particle size of 50–100 nm were produced [4].

1.4 Main Achievements in Nanotechnology

Table 1.1 shows the significant achievements in nanotechnology and Nobel Prize awards in the field of chemistry and physics.

Table 1.1 Significant achievements in the nanotechnology.

Nobel Prize in chemistry	Nobel Prize in physics
1996 Discovery of fullerenes	1986 Creation of HRTEM and TEM
1998 Development of quantum chemistry	1998 Discovery of quantum Hall effect
2000 Discovery of conductive polymers	2000 Creation of semiconductor
2008 Development of fluorescent protein	2010 Graphene research

Case Study 1: Synthesis of Nanoparticles and Environmental Safety Considerations

- Several methods exist for nanomaterial synthesis, such as physical, chemical, and biological methods. Nanomaterial synthesis requires a number of chemicals, conditions, and techniques. Each synthesis method is characterized by definite equipment, necessary laboratory glassware, and utensils for the synthesis process.
- Also, nanomaterial synthesis process is followed by structural, phase composition, and morphological characterizations and analyses of obtained nanomaterials. The person conducting X-ray diffraction analysis of synthesized nanomaterials should obey safety rules in order to not suffer from radiation.

- Synthesis and characterization analyses require knowledge and technical skills. Being informed about chemical hazards and laboratory safety rules is mandatory. Also, the conducting person should know and follow environmental safety rules without polluting or harming nature. Laboratory waste subproducts and end products should be collected and kept in preferred and appropriate places and their disposal should also be arranged.
- Working in the laboratory requires responsibility, good communication, and comprehensive skills. Working in agreement with other members of the research team is preferred, which helps eliminates undesirable conditions. Every person conducting synthesis must be responsible to keep the working space clean and well organized.
- The above problem is related to that in the article of Groso *et al.* [5] in which management of nanomaterials safety in research environment was described.

Case Study 2: Property Control of Nanomaterials by Setting Experimental Conditions during Synthesis

- A set of experimental conditions such as equipment settings (temperature, pressure, reaction time, etc.), initial chemical types, concentration, and pH allows the synthesis of nanomaterials with definite properties (shape, size distribution, phase composition, etc.).
- Subnanometer control of mean core size during mesofluidic synthesis of small ($D_{core} < 10$ nm), water-soluble, ligand-stabilized gold nanoparticles was reported by Elliott *et al.* [6] in *Langmuir*. A key advantage of this synthesis is that simply adjusting the pH of the gold salt solution led to control over the Au NP core size. The synthesis involved the reduction of an Au(III) species with sodium borohydride in the presence of a functionalized alkyl thiosulfate (Bunte salt) to yield thiolate-protected Au NPs. The average core size increased as the pH was raised for each ligand studied.
- Another study focused on the controlled synthesis and electric conduction properties of anatase TiO_2 nanoparticles via the polyol method [7]. In this work, the preparation state and particle size were controlled by varying the synthesis parameters such as the precursor concentration, hydrolysis rate, and synthesis time.

Control Questions:

1) Define the term of nano- and biomaterials.
2) List the main achievements in nanomaterial and biomaterial application history.
3) Describe the basic methods and requirements for nanomaterial preparation.
4) Discuss the mechanical dispersion method and its features in nanomaterial preparation process.

5) Define and describe the intensive plastic deformation method for nanomaterial synthesis.
6) Describe the process of obtaining nanomaterials by mechanical interaction of various mediums.
7) Which kinds of methods are included in physical dispersion methods for nanomaterial preparation?
8) Discuss evaporation–condensation method and its difference to other preparation methods of nanomaterials.
9) Describe vacuum-sublimation technology and its features for the synthesis of nanomaterials.
10) What kind of methods are available for obtaining of nanomaterials by using the chemical reactions?
11) Describe the preparation of nanomaterials by electrochemical methods and its specific difference to other methods.
12) Define electric precipitation method for the synthesis of nanomaterials and its main requirements.
13) List chemical reaction synthesis methods suitable for the preparation of metal nanomaterials.
14) Describe laser-based method for the preparation of nanomaterials.

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