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High temperature methods for the synthesis and industrial production of nanomaterials

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Introduction

The conversion of a natural or recycled raw material to a product with desirable properties proceeds via "*production process*". Each production process is being performed through established technological regime, predetermined by the corresponding technology.

The term "technology" comprises the entire combination of all stages and related processes, composing given technological process. In this sense, each production stage consists on one or more processes, occurring in the work space of an appropriated apparatus, which construction enables the conditions, required for the performance of the respective processes at desired parameters. The direct indication for the proceeding of whatever physical or chemical conversion process is the change of the work parameters of the respective reaction system. The unique exclusion from this rule belongs to the systems with established dynamic equilibrium, inherent for the reversible reactions. Such reversible reaction systems are not an object of any interest for the industrial practice. Thus, in the industrial production systems, the changes occurring in properties of the reaction systems, such as colour, viscosity, density, pressure, etc should be submitted to continuous precise observation and control. Indeed, the technological regime provides the proper conditions that predetermine the proceeding of these desirable changes that result at last to the complete conversion of the raw materials and precursors into desirable industrial product (**Fig.4.1**).



FIGURE 4.1

Correlation among the components composing the industrial production process

All parameters and conditions for proceeding of each one of the conversion stages, in their subsequence composing the entire production process are predetermined by a special technological regime. Every deviation from predetermined parameters of the technological regime for given industrial production process results in products with unsatisfactory quality, or/and damage of the used equipment. Both these consequences always lead to loss of time, energetic and material resources.

Thus, for the industrial sector, it is important to follow and maintain predetermined production parameters and conditions, which predetermine the properties and the resulting performance of the materials and assembled units produced, at the conditions of their exploitation by the customer. These parameters and conditions, on the other hand should correspond to national standards, international standards, or at least to industrial specification certificates of the respective producer. The correlation among the composition, structure, form and the properties of given material, as consequence of the method and condition of its synthesis, resulting in the entire performance at working conditions is described for the sol-gel derived materials **[1]**, and spray pyrolysis products **[2]**. A modified schematic view, including the economical aspects, related to the production and subsequent application of whatever industrial product is represented in Fig. 4.2.



FIGURE 4.2

Correlations among the components composing of product creation and utilization

Besides the conventional standards and producer's specifications, new, alternative materials, methods for their synthesis, as well as advanced equipment for their production are objects of continuous elaboration and further improvement.

On the other hand, both the scientific and technological progress and the permanent increase of the customer requirements impose the permanent need for elaboration of new generations and entire classes of advanced materials which possess peculiar combinations of properties enabling creation of completely new generations of engineering products (facilities, equipment, engines and devices). Simultaneously, the constant increase of the human population imposes the size diminishing of the industrial hi-tech products, leading to lowering of the energy and material resources expenses for each unit of product. By this manner, a higher accessibility to the hi-tech products is achievable, allowing the improvement of life quality of the human population in general terms.

Various classifications could be done on the basis of large variety of distinguishable features and inherent characteristics. According to their composition, the solid materials can be divided into simple elements, (graphite, diamond, pure metals, etc.), mechanical mixtures solid solutions, and solids composed by chemical compounds. Karl-Heinz Haas & Klaus Rose **[3]** have composed a versatile classification, dividing the solid materials into four basic groups:

- 1- Inorganic materials (glasses, ceramics as well as metals and alloys),
- 2- Organically modified inorganic materials,
- 3- hybrid materials and, at last:

1-4- completely organic substances.



FIGURE 4.3

Classification of the basic groups of materials, according to Haas and Rose [3]

The hybrid materials combine the advantages of both the organic and inorganic moieties, in their composition. This peculiar advantage of the hybrid materials is remarked by Zheludkevich, et al. [4], as shown figure 4.4:



FIGURE 4.4

Combination of the advantages of both the organic and inorganic part, possessed by a hybrid material

It is worth mentioning, that there is a significant difference between the terms: "*hybrid*" and "*composite*" material. In the former case, the organic and inorganic moieties are bonded by covalent bonds, whereas in the latter case, the composites could be composed by two or more phases without of chemical bonding among them. Thus, the reinforcing phase is retained by the

basic matrix by intermolecular attraction forces, causing modification of the mechanical properties of the resulting material. An example could be found in the literature, related to the formation of hybrid, nano-composite coating, by in-situ polymerization of a hybrid matrix, with preliminary introduced SiO_2 sol [5]. At these systems, another problem arises, related to the agglomeration of the reinforcing phase particles, followed by their irregular distribution inside the resulting material.



FIGURE 4.5

Schematic view of involved nano-particles during the hydrolysis-polymerization processes of the basic matrix **[5]**

For excessive agglomeration prevention, the polymerizing systems should be submitted to ultrasound agitation or treatment by surfactant addition. This process of in-situ preparation of hybrid nano-composite materials is known as Self-assembling of NAno-Particles (SNAP) [6 - 8]. Regardless the fact that this group of materials could possess a form of massive bodies, they also belong to the group of the nano-materials. In general, the term "material" comprises each substance in condensed state, since the condensed matter always possesses own structure, with higher or lower level of ordering. Consequently, it can be assumed that all materials, which have at least one phase with a submicron size, in at least one dimension can be classified as "nanomaterials". Hence, besides the nano-composites which have reinforcing phase composed by submicron particles, the thin films, membranes, and multilayered coatings also could be recognized as nano-materials. Thus, the nanomaterials can have a submicron size in one dimension (such as thin films and layers), two dimensions (hollow or dense fibers and filaments), or in all the three dimensions of the space (such as fine dispersed powders, or stable colloidal systems with fine dispersed phase). Obviously, when the question is related to the nano-materials, these substances are almost always contain a solid phase, with the unique exclusion of the fine dispersed water/oil type suspensions. It is worth to mention that in general terms, the matter could be in different states of aggregation, and to transform its state from one to another according to the surrounding environmental conditions, as is illustrated below:



FIGURE 4.6

Aggregated states and phase transitions of the matter

Classification of the high temperature methods according to the heat source

The methods for synthesis and/or preparation of nanomaterials can be grouped according to different factors, such as for example, the inherence of the conversion processes, (occurrence or absence of chemical conversion reactions, application of mechanical impacts, and presence of phase transitions, etc.). A summarized classification of the most widely used methods is given below:

According to the occurrence of phase transition phenomena – Examples for such phenomena are fusion, evaporation, dissolution, crystallization, etc.

According the presence or absence of chemical conversion reactions – Not always the methods for material synthesis or preparation proceed by chemical conversion reactions.

According to the energy source – As is already mentioned, all operations imparting given technological process proceed by energy consumption. Thus, the processes that proceed at room temperature and atmospheric pressure require energy for mixing of the respective reactants, material transport, etc. There are even technologies that require an introduction of energy for decrease of the thermal content of the precursors by freezing agents, such as liquid nitrogen in thermally insulated installations, etc.

According the type of the energy source, the high temperature processes can be divided into the following groups:

Spontaneous – These processes proceed spending the energy of a chemical reaction with intensive exothermal effect (often accompanied by controlled explosions).

Gas flame methods - based on the combustion processes.

Electrical resistance heat induced processes – These processes occur in electrical resistance supported furnaces.

Electrical charge based processes – These processes proceed in conditions of high voltage electric arc between two usually graphite electrodes. In this case, the heat is rather consequence of the strong electric current, than a result of the high voltage.

Electrical inductance supported processes – These processes need intensive electromagnetic fields, induced by the current flowing through coils with mi8ld steel cores.

Electric capacitance related processes – this kind of processes requires electrostatic fields, between electrically charged metallic plates, connected to high frequency alternating current generators.

Laser beam induced processes – These processes require a laser beam for their proceeding.

Electron beam processes – These processes proceed as a result of an accelerated thermoelectron emissions in deep vacuum chambers. In the focal areas of contact between the emission and the treated material, various secondary resultant emissions appear, including heat. Alternative classifications of the high temperature methods for synthesis and treatment of the materials could be also found in the literature **[9]**, as the illustrated one in the next figure:



FIGURE 4.7

Distribution of the basic high temperature methods for superficial treatment according the radiation intensity and treated surface area [9]

This classification is based on the possible constrains of the energy intensity and the lowest possible treated surface area. Among all the methods mentioned above, the electrical charge, the electrical inductance, and capacitance based as well as the laser induced ones enable the transition of the initial precursors to a plasma state. As was shown in Fig. 4.6, the plasma state is a separate aggregation state of the matter. In the nature, it is relatively rare observed, basically in form of thunderbolts. Thus, the plasma state can be considered as a gas, which is ionized, by the impact of external energy source. This source splits the chemical bonds, composing the molecules of given gas and the resulting free atoms release electrons from the external valence orbitals, resulting in the formation of cloud of positively charged ions surrounded by chaotically moving electrons. Distinguishable features of the plasma are the coincidence of strong light radiating effect (in both the visible and ultraviolet ranges), electrical conductivity, etc. When the plasma igniting energy source activity is interrupted, the plasma cloud immediately undergoes recombination, converting into the initial gaseous state. By point of view of energy expense diminishing, the noble gases (i.e. the VIII group of the periodical table) are the most beneficial for plasma ignition, since these gases do not require energy for chemical bond splitting because these gases are monoatomic in standard conditions.

Explosion ignited methods for nanomaterial production

Introduction

This group of methods, following its name, obviously is based on material synthesis through explosion. The term *"explosion"* comprises each process that proceeds by sharp rise of the reaction system volume, accompanied by intensive energy release for extraordinary short time in the range of parts of one second). Exactly, because of the remarkably high rate of the processes in the exploding systems, these processes are considered as adiabatic, because the too short time for their proceeding does not allow any notable heat exchange between the exploding system and the surrounding environment. The energy, released after the explosion propagates in several different forms:

- Under the form of light emission (sometimes in the UV spectrum).
- Mechanical as shock wave.
- As sound propagation wave.
- As thermal wave.

The power released by given explosion is the entire energy generated under all the above mentioned forms. The specific power generation capability of an explosive substance could be quantified by TNT – equivalent for unit of quantity of the characterized explosive compound.

The efficiency of whatever explosive material can be estimated by the energy distribution among the corresponding waves (e.g. shock wave, light emission, thermal wave, etc.), where the high efficient explosive substances are distinguishable through the predominance of the energy released by the mechanical shock wave. It is accepted that the explosions with super sound speed of mechanical shock wave propagation are named "*detonations*", whereas slower ones are known as "*deflagrations*".

The explosions are not always directly related to chemical reactions (since the explosions can be ignited in high pressure containers, compressors, water boilers, steam generators, heat exchangers, etc), but al chemical reactions that cause explosions are exothermal oxidation/reduction reactions (i.e. combustion).

Generally, the detonation could proceed after ignition of the reaction system. Various manners of explosive ignition exist:

- By pressure elevation until reaching of a critical threshold value.
- By increase of the temperature until achieving of a critical flash point value.
- By electrical spark.
- By mechanical impact.

Alternatively, explosion could be spontaneously ignited, after mixing of reducer and an oxidant. That is why, the simultaneous storing of strong oxidants, as bichromates, perchlorates, nitrates, peroxides, permanganates, etc together with organic substances is incompatible to the good chemical practice, and should absolutely ever be avoided.

Explosion ignited methods for carbon based nanostructures

It could be assumed that the carbon is one of the most widely spread elements in the Nature. The majority of the carbon content on the Earth composes all the organic compounds, including the ingredients the living Nature (i.e.: practically all known living species).

As simple substance, the carbon occurs in thee form of graphite or diamonds. In artificial conditions, other carbon materials can be obtained, such as the recently discovered graphemes, fullerenes, and carbon nano-tubes, shown in **Fig. 4.8**.



FIGURE 4.8

Various configurations of single walled carbon nanotubes [10]

Unlike the jewelry diamonds, nano-diamonds have wide application in the practice, due to their exceptional hardness, and the possibility – to be obtained in artificial conditions. The graphite and diamond are well known allotropic forms of the carbon. The main difference between these two

forms of existing of the carbon as a simple substance is the manner of ordering of its atoms (i.e. structure, or in other words – the ordering of the corresponding atomic crystalline lattices).



FIGURE 4.9 Diamond (a) and Graphite (b) structures

The structure of a solid material has a major impact on its properties. The similarity between these carbon solids is that both these materials are composed by atomic crystalline lattices, maintained by non-polar covalent chemical bonds among the composing carbon atoms. The difference between the respective lattices, as is demonstrated in **Figure 4.9**, is originated from the manner of particle ordering, since the graphite is composed by layered hexagonal lattice, whereas the diamonds possess cubic, face-centered structure **[11]**. Namely these structural differences predetermine the properties and the related behavior of the respective materials: such as hardness, transparency, conductivity, etc. The conversion of the graphite to diamond is relatively complicated process, because it requires coincident presence of high temperature and pressure, in inert medium (without of oxidant agents), as is depicted in the next figure:



FIGURE 4.10 Phase diagram of the transitions between graphite and diamond [12]

Diamond conversion from graphite was done by Hannay, at 1880, followed by Moissan, at 1894. The first serious scientific research activities, including synthesis and subsequent characterization of the obtained diamonds are performed by Bundy et al. in the General Electric Company Research Laboratory NY – USA at 1955, followed by Svenska Elektriska Aktiebolaget, at the same year. Since 1960s, the nano-diamond production becomes a routine industrial practice **[11]**.

Among the most widely spread methods for nanosized diamond synthesis are the so called "*explosion ignited methods*", known also as "*shock wave methods*", or even as "*high temperature self-propagation synthesis methods*". These methods stay on the basis of the synthesis of the so called "Detonation nanodiamond (DND) **[13, 14]**. This process proceeds by explosion of mixture of trinitrotoluene and hexogene (cyclotrimethylenetrinitramine) in limited oxygen containing medium for a time of about several milliseconds, resulting in formation of nano-diamonds with size dimensions in the order of 5 nm on the front of the shock wave.



FIGURE 4.11 Structural formulas of TNT and hexogene [13]

This synthesis process requires thick wall devices, which usually are shaft-type, so that a part of these devices are underground. By this manner, if the explosion is strong enough to destroy the equipment, the resulting shock wave should be re-directed in vertical direction, leaving the surrounding area around the exploded apparatus, relatively intact. In addition, these devices should be mounted on mechanical buffers (dampers), since the explosions cause to mechanical impacts (impulse vibrations), which can result in concrete crumbling of the floors of the respective industrial building constructions. When the explosion is ignited by sharp increase of the pressure, this process can be performed in devices composed by cylinder and piston. By this manner, the change of the pressure could be additionally regulated during the shock wave propagation.

In the practice, it is preferable to use a large number of relatively small sized cartridges with thick walls, mounted inside steel blocks, on vibration dampers. Thus, the consequences of the excessive waves, provoked by uncontrollable explosions able to destroy the respective devices can be efficiently diminished. Other advantages of the use of cartridges with small size is the possibility to decrease the thermal effects by efficient cooling, as well as the relatively more uniform distribution of the resulting heat in the limited work spaces. The main problem related to this method of nanosized diamond synthesis is that a part of the already obtained diamonds could convert into graphite, and also a part of the total carbon (so the diamonds, so the residual smut) could enter in an undesirable combustion process with the excessive oxygen in the chamber, resulting in formation of CO_2 or even the toxic CO. Hence, a considerable part of the nano-diamonds already formed on the shock wave front, subsequently convert to a graphite (because it is the more stable crystalline modification), or even undergo combustion in the excessive oxygen. Exactly, this is the reason for the use of limited oxygen content in the reaction systems.

Applications of the nanodiamonds

The nano-sized diamonds are mainly used for production of working tips of steel cutting and drilling mashines, including stomatological equipment. These tools encounter also applications for stone polishing mashines in the jewellery, the fine sculpture (especially- drilling and polishing of glass and stones). Also similar instruments are also used in some laboratory applications, related to archeology and paleontology (namely, mechanical separation of fossile bones from surrounding solids).

Other applications of the explosion ignited synthesis methods

Undoubtedly, different variations of the explosion involving syntheis methods and technologies enable production of other matrials, predominantly in powder form. Thus, in the literature a large number can be found of examples for production of metallic oxides, as intermediated products of the hi-tech ceramic industry, especially for elaboratrion of ceramics with elevated density and for powder metallurgy, as well. The most classical methods are related to the use of *thermite* – a mixture of pyrophoric metal with metallic oxide of nitrate. The pyrophoricity is an aptidude for combustion of some metals when these are exposed to air being in for of fine dispersed powders. Such combustible mixtures are often used for welding of details with particularky big size dimentions. The classical thermite mixture is composed by powderlike metallic aluminium and iron oxide [14]. This mixture is patented by the german chemist Hans Goldschmidt, at 1895 y. [15].

$$Fe_2O_3 + 2AI \rightarrow 2 Fe + Al_2O_3 \tag{1}$$

Similar mixtures could be prepared by other metals, and particularly the most active are the alkaline and alkaline-Earth ones. Nevertheless, these metals are rarely used in the practice, because these elements are exceptionally reactive, resulting in considerable difficulties, related to their storage, mainly originated from the potential dangers from unexpected spontaneous explosions. Piercey and Klapötke **[16]** mention that besides Fe_2O_3 , other metallic oxides such as MnO_2 , CuO, WO_3 , MoO_3 , and Bi_2O could be employed in presence of metallic aluminium.

Zheng and co. **[17]** have published an article related to the synthesis of eutectic ceramic mixture of corundum and zirconia. For this purpose, the authors have used initial thermite mixture, composed by metallic aluminium and zirconium nitrate, thus the reaction can be described as follows:

$4AI + 2Zr(NO_3)_4 \rightarrow 2AI_2O_3 + 2ZrO_2 + 2NO + 6NO_2$	(2)
Where:	
$4Al^{0} - 12e^{-} \rightarrow 4Al^{3+}$ reducer	(3)

(The reducer donates electrons, increasing its own oxidation state, whereas the oxidant accepts these electrons). In this particular case, the stoichiometric equation reveals that two nitric oxides are produced, where the nitrogen possesses two stated of oxidation:

$2N^{5+} + 6e^{-} \rightarrow 2N^{2+}$ oxidant 1	(4)
$6N^{5+} + 6e^{-} \rightarrow 6N^{4+}$ oxidant 2	(5)

The reaction described abobe comprises all the intermediated stages, in their subsequence, which proceeds so fast that it becomes impossible to insulate and analyse the intermediated products. It

is worth to mention that the authors propose another concept for the chemical inherence of the explosion process, which sugests reduced simple nitrogen as a product:

$$Al+Zr(NO_3)_4 \rightarrow Al_2O_3 + ZrO_2 + N_2Al + Zr(NO_3)_4 \rightarrow Al_2O_3 + ZrO_2 + N_2$$
(6)

At the front line of the shock wave, probably there are only gaseous atoms and even ionised particles (i.e. plasma). Immediately after the crossing of the chock wafe, a recombination of the already ionised particles becomes, followed by formation of molecular compounds, as final product. Thus, the reaction described above summarizes all the processes during the explosion and the subsequent cooling of the reaction system. It should be noted that all these processes proceed literally for eye blinking period. Also, in the closed spaces, the initial shock wave is always followed by resonance waves in the opposide direction (i.e. from the cartridge walls to the ingition location, and vice-versa with gradual decrease of their power).

Besides thermite mixtures, various organic explosive compounds mixed with mineral precurtsors are also often used for ceramic nano-material synthesis. Tsvigunov and coauthors **[18]** have performed investigations on the possibility to obtain corrundum (α -Al2O₃) from mixture of gibbsite ((Al(OH)₃) and hexogene. Thus, according to them, the following subsequence of processes occur during the explosion:

$$AI(OH)_{3} \rightarrow \gamma - AIOOH \rightarrow \gamma - AI_{2}O_{3} \rightarrow \Theta - AI_{2}O_{3} \rightarrow \alpha - AI_{2}O_{3}$$
(7)

Consequently, the gibbsite dehydration to boehmite, and γ -Al₂O₃, together with the subsequent polymorphical transitions proceed immediately on the shock wave front. Other variations of this method for synthesis of nano-sized corrundum by use of ammonium and nitrate salts are proposed, as well **[19]**.

Finally, it is worth to mention that in a review paper of Patil, **[20]** other explosive materials are described, which can be used for nano-material synthesis, such as simple gun-powder ($KNO_3 + S + C$), ammonium perchorate NH_4CIO_4 , hydrazine ($H-N\equiv N-H$), and its derivatives, urea $CO(NH_2)_2$, etc. Regardless their high productivity, these methods possess a number of disadvantages. All the typical advantages and disadvantages owed by this group of methods are listed briefly below:

Typical features of the explosion ignited synthesis methods:

Advantages:

- Low energy demands - exterior energy source is only necessary for initial ignition.

- Relatively high productivity

<u>Disadvantages</u>:

- Low purity grades of the obtained products (especially in the case of nano-diamonds synthesis, the resulting product is in form of grey powders with high smut content).

- Inability for direct control on the production process (i.e. the shock wave power, temperature variation rate, etc.).

- Inability for use of continuous production equipment and lines.
- Diffuculties related to the obtaining of low temperature allotropic crystalline modifications.
- Unexpected explosion dangers, during the transportation and storage of the explosive materials.

- Formation of poisionous gases, as a product of the explosion processes, occurence of shock and vibration waves, so that this group of methods is related generally to environmental contaminantion effects.

Plasma induced methods for nanomaterials production

Introduction

The main distinguishable feature of this group of methods is the preliminary conversion of the initial precurtsors to a plasma state, prior to the product synthesis. The most appropriated classification of the plasma induced methods can be done on the basis of the plasma induction energy source nature. These can be divided according the energy source used:

- Electric arc (electric charge) plasma

– Electric induction plasma – obtained between coils, charged by high frequency, or radio frequency AC electric curremnt generators.

– Electric capacitive plasma between metallic plates, charged by high frequency AC electric currents, often with frequencies of the microwave interval.

- Laser induced plasma - by concentrated intensive laser radiation.

According the work temperature, the plasma methods can be divided into high or low temperature plasma methods, predetermined by the energy radiation in the thermal (i.e. Infrared) spectrum (it will be explayned below). According to their application, the plasma induced methods can be classified as methods for material synthesis, or methods for posterior material surface-treatment. The devices for plasma induction are named "*plasma generators*" or just simply – "*plasmotrons*". As will be mentioned at the end of the present section, the basic advantage of these methods is the possibility to be used in continuous production regime.

The basic components of a typical plasmotron are schematrically illustrated in the next figure:



FIGURE 4.12

Scheme of a typical plasma generator **[21]:** 1- resulting plasma torch, 2- cooling agent, 3- gas arc charge, 4- accelerating spiral channel, 5- cathode, 6- gas flux, 7 – upper fitting, 8- gas charge chamber, 9 – plasma formation coil, 10 – cooling chamber

High temperarture plasma synthesis

Plasma torch ignition

In the case of this group of methods, the work space where the plasma occurs is named "*plasma torch*". Exactly in the plasma torch bulk proceed all of the processes, related to the ionisation of the carrier gas, which provides the work temperature necessary for the precursor decomposition and the coinciding conversion processes.

The plasma torch can be induced by trespassing of the carrier gas (usually H_2 , N_2 , or Ar) through a nozzle, followed by its activation by a powerful energy source, which serves for gas ionisation. The precursor materials can be supplied either through the same nozzle, together with the carrier gas, or by additional tubes, mounted after the nozzle, as is shown in the next figure:



FIGURE 4.13

Precursor feeds of the plasma torch [22]

In both cases, the nozzles are charged directly by electric current. It is possible to use so direct, so alternating currents. In the former case, besides the high potential (i.e. voltage), necessary for overcoming the dielectric properties of the carrier gas and its efficient ionization, a strong current is also required. The voltage should be enough high, in order to achieve the threshold value, known as *"breakdown voltage"*, which enables a partial ionization of the trespassing carrier gas, in order to provide an electrical charge pathway, necessary for electrical circuit completion between the electrodes. At these conditions, low temperature non-equilibrium plasma appears. In its interior, the individual particles possess different temperature. Thus, the particles with the lowest weight (the electrons) have the highest temperature, whereas the heavier ones (the ions) have lower energy content, and the free atoms possess the lowest temperature **[22].** This phenomenon can be explained taking in account that the heavier particles possess superior inertial capability, so that they need more energy, in order to reach higher specific energy content. It influences directly the kinetic energy, and respectively the mobility of the respective plasma composing particles.

The high current in this case, is required in order to reach a high enough temperature, able to ionize the entire carrier gas flux. Thus, in this situation, all the particles achieve relatively equal thermal energy content. The electrical current thermal effect can be calculated on the basis of the

Joule – Lenz Law. It is formulated independently by the British researcher, James Prescott Joule and the Russian physicist, Emil Lenz at 1860 [23].

According to this Law, the thermal effect of the electrical current through an electrical conductor is proportional to its square value, multiplied by the conductor Ohmic resistance, and increases within the time.

$$Q = I^2 x R x t$$
(8)

Where:

Q = The thermal energy irradiated by the electrical conductor.

I = Electrical current intensity

R = Electrical Ohmic resistance

t = Time for the electrical current fluxing.

By physical point of view, the strong currents, limited in a relatively small cross-section predetermine a high intensity of the electron fluxes, which at high acceleration realize elastic collisions with the particles composing the conducting material, making them to perform vibration movements, releasing residual thermal energy.

When high frequency electrical impulses are generated between metallic plates, the resulting electrostatic fields permanently alter their polarity. Thus, the charged particles (i.e. the gas ions) sharply change their movement direction, achieving by this manner vibration movement between the charged metallic plates.

Similar phenomena could be observed at presence of magnetic fields, induced by electrical coils, surrounded by electrically charged particles. The mathematical relation between the frequency of the electrical signal charging the coils, and the resultant thermal effect is formulated by Wilhelm Wien (Wilhelm Carl Werner Otto Fritz Franz Wien) at 1893 **[24].**

In this case, the mathematical expression of this relation is:

$$v_{\rm max} = \frac{\alpha}{h} kT \approx (5.879 x 10^{10} \, Hz \,/\, K).T$$
 (9)

υ_{max} – Maximal acceptable frequency; α – a constant, equal to: α ≈ 2.821439, κ – Boltzmann constant - 1.3806488(13)×10⁻²³ J/K; T – Temperature in Kevin scale.

Schematically, a plasma torch with inductive plasma is shown in the Figure below:



FIGURE 4.14 Inductive plasma torch [22]

It is worth to mention, that other energy sources are also applicable for plasma ignition, such as for instance laser beams:



FIGURE 4.15

Plasma torch with laser assisted plasma ignition [22]

In order to decrease the energy demands, additional combustible organic compounds could be added to the primary precursor mixture, with coupling with enrichment of the carrier gas with oxidants as air or pure oxygen. By this manner, supplemental combustion process could occur inside the plasma torch, rendering additional thermal effect due to its exothermal effect.

Processes consisting the high temperature plasma induced methods of synthesis

It should be mentioned that in the zone occupied by the plasma torch, any synthesis process cannot be observed because of the rather high temperatures. In this area, only decomposition processes could proceed, and the subsequent product synthesis occurs in the following cooling zone. Hence, the high temperature plasma synthesis can be considered as a method, composed by two main subsequent stages, occurring in the corresponding work spaces:

- Processes occurring in the plasma torch bulk These processes are particularly decomposition processes, such as:
- 1 fusion of precursors' powders,
- 2 Evaporation of the resulting fusions,
- 3 Chemical decomposition of the precursor compounds, by chemical bond disruption;
- 4 Ionization of the free atoms originated from the already decomposed compounds.
- Processes accompanying the subsequent cooling These processes stay on the basis of the end product synthesis, such as:
- 1- Ionized particle recombination,
- 2 Proceeding of the product formation chemical synthesis reactions,
- 3 Formation of initial crystalline nuclei,
- 4- crystalline growth of the obtained nuclei (by heterogeneous layer heaping of the components of the surrounding gaseous medium).

- 5 – Agglomeration of the obtained product crystals.

The cooling rate of the resulting plasma cloud has extreme importance, since it almost entirely predetermines the particle size dimensions of the resulting fine dispersed powder product. As sharper is the cooling, as finer dispersed product will be obtained. Thus, the products synthesized by this manner are in form of fine dispersed aerosols, composed by solid powder phase of the desired product, equally distributed in the gaseous medium. Consequently, additional processes of mechanical separation of the desired solid state product from the exhaust gaseous medium and its collection together with particle size fraction separation are the next technological stages after the product synthesis completion.

Figure 4.14 schematizes the procedure subsequence of the industrial production methods via high temperature plasma related processes, according to Dieter Vollath [22].



FIGURE 4.16

Block scheme of the procedures and the corresponding stages composing the high temperature plasma related industrial production process (according to [22])

Low temperature plasma induced methods of synthesis

Basic concepts

As was remarked in the introduction part of the present Chapter, the plasma is a high energy state of the matter. This fact predetermines the capability of the matter in this state to release energy in form of various radiations. Hence, if the majority of the released energy is irradiated in the visual or the ultraviolet spectrum, instead of the infrared one, then low temperature plasma is formed, because the heat exchange processes with the surrounding environment are sufficient to compensate the thermal effect of the plasma cloud. Thus, between the ionized gas, and the surrounding medium efficient thermal convective streams are presented, efficiently cooling the plasma cloud. In addition, if the pressure of the gas submitted to ionization is low enough, then its particles should pass larger distances before to collide each other, spending higher kinetic energy amounts. Thus, the preliminary decrease of the gas pressure, prior to their ionization, guarantees the low temperature plasma formation.

Dieter Vollath **[22]** points that the term *"low temperature plasma"*, should be considered as ionized gas with temperature below 1000 K (~727 °C). According to this author, the low temperature plasma can be obtained by oscillating electrical fields (electrostatic between metallic plates, or

electromagnetic between coils, respectively). Electrical generators can generate these fields with AC currents in the ultra-short wave radio frequency range, or even with microwave frequencies. The next figure illustrates possible configurations of devices for continuous production regime with electrostatic field induced low temperature plasma (Fig. 4.17):



FIGURE 4.17

Devices for continuous production regime working at low temperature plasma [22]

The frequencies appropriated for low temperature plasma ignition, are too high to cause heavy particle vibrations (e.g. vibrations of ions), promoting emission in the infrared spectrum (i.e. heat release). Consequently, the low temperature plasma is non-equilibrium plasma, since the lighter particles (i.e. the electrons) possess higher specific energy content, than the heavier ones (i.e. the ions). Thus, due to its higher kinetic energy content, the electronic cloud moves much more intensively, than the ionic one, making thus more frequent collisions, resulting in intensive photonic emissions (in the visual and UV-spectrum).

The electrical generators output power should be concordant with the energy that these devices should generate. Vollath **[22]** gives a simple mathematical correlation between the weight of the gas particles, the oscillation frequency of the electrical field, and the respective energy emission intensity:

$$U = f\left(\frac{Q}{mf^2}\right)$$
(10)

where the energy content of a given particle U, stays in a functional dependence of its electrical charge - Q, its weight – m, and the oscillation frequency of the electrical field, applied - f.

Thus, it can be inferred from this equation that there is significant difference between the radiofrequency and the microwave plasma, because in the former case, the generators used work in the range of MHz, whereas the latter achieve GHz, ranges. As a result, the latter generators work with much lower efficiency, but this fact is compensated by the possibility to work even at room temperature. The application of the low temperature plasma is limited basically to superficial treatment of metallic details, in order to improve their surface mechanical strength against friction. Examples for such details are gear wheels, pistons, bearing components, axels for electric motor rotors, mechanical connectors for turbines, etc. Among the most widely spread methods for superficial treatment of steel details in plasma are known as "plasma ion implantation methods", and the most famous representative of this group of methods is the plasma ion nitration [25 – 31].

Low temperature plasma nitration

The characteristics and properties of each industrially produced material are directly related to its structure, which is predetermined during its production (including both its synthesis and posterior treatments), whereas its chemical composition depends on the corresponding precursors, the correlations among their quantities, as well as the respective synthesis reactions among them.

One of the most widely spread approaches for industrial application of the low temperature electric gas charge plasma is the subsurface nitration of high performance steel machine details. This method enables multiple prolonging of the exploitation life of various details, such as bearings, valves, crankshafts, gears, etc.

In simple terms, the low temperature plasma nitration is enhancement of the surface mechanical strength of engine details by subsurface nitrogen enrichment via exposition to electrically charged nitrogen containing gases at relatively high temperatures. This process proceeds in special thick wall chambers, which supply controlled low-pressure gas medium and high voltage electrical charge. Figure 4.18 shows schematic view and photographs of two-column industrial installation of EFTTOM laboratory (Sofia) [32].



FIGURE 4.18

Schematic presentation (a) and photographs of the upper (b) and the lower (c) part of chambers used for nitration of 5m long petroleum extraction tubes **[32]**

The next figure shows photographs of low temperature plasma nitration of small machine details from austenitic steel in "HABONIM Industrial valves and actuators", Kfar HaNassi (Israel) [32].



FIGURE 4.19

Small machine components during (a) and after (b) plasma nitration [32]

Nowadays, the optimization of the gaseous mixture composition, plasma temperature and electrical charge parameters, as well as the process duration is object of intensive scientific research activities. Li and coauthors **[25]** have executed a systematic investigation on the strength of metallic details treated by plasma ion implantation. For this purpose the authors have analyzed the impact of the work temperature values between 350 and 480 °C. In order to determine exactly the plasma temperature influence, the authors maintained identical values of the rest process parameters, such as the initial gaseous mixture composition: N2:H2 = 20:80%, the pressure – 600 Pa (i.e. deep vacuum), and the treatment duration – 4 hour each cycle, as well. The investigated specimens were composed by 17-4PH standard steel. As a main result, the authors report that the plasma involved post treatment leads to elevation of the strength of the respective steel details, as consequence of structural phase transitions, coupled with compositional modifications, beneath the sample surface. Thus, the authors have established transition from austenitic phase to nitrogen enriched martensitic phase. Even appearance of new CrN compound, have been registered at the plasma treatments, performed at higher temperatures.

During investigations, performed on low temperature plasma ionic nitration, at similar conditions on 340L staineless steel, Wang et al. **[31]** have confirmed the inference, that the strength increase is a result of chromium nitride formation. The compositional modification, caused by this treatment approach is combined by coincident morphological and structural changes. The relatively high temperature, coincided by ionized nitrogen lead to solid state reactions in the undersurface layers, followed by pre-crystallisation, resulting in modification of the granulometric composition near the surface. As a direct evidence for this fact, the authors have shown SEM images of two specimens, treated by plasma ionic nitration, at 400 and 480 °C, respectively (**Fig. 4.20**).

Investigations, by implantation at low temperature plasma conditions in presence of direct current on the plasma have been performed by other authors, as well. Xi and co. **[27]** have published their investigations on two stage plasma implantation, performed on AISI420 stainless steel. The firs stage has been performed in a gaseous medium, composed by 80% Ar + 20% H₂, for one hour at 250 °C and direct current ionizing charge of 400 V, followed by second step, in 25% N₂ + 75% H₂ for 15 hours, either at 350 or at 550 °C at the same potential. As conclusion, the authors have established that these treatment procedures result in the remarkable improvement of both the mechanical strength and corrosion durability of the treated samples. In another their work, the same authors **[30]** have, used impulse signals with duration of 50 µs and pauses of 300 µs. The use of impulse signals enables controlled cooling of the material between each two impulses, allowing heat dissipation of from the treated material towards its surrounds. This is the manner for maintenance of constant temperature by intermediate cyclic cooling after every charge cycle. After similar investigations, Wang and co. **[31]** have once again confirmed the results, described above. After ion nitration in plasma ignited in N₂ : H₂ = 1 : 5 gaseous medium, with electrical charge 520 V, at 600 Pa, for the temperature interval between 350 and 480 °C, at the highest temperature a complete transition from austenitic phase to chromium nitride is observed. Namely this transition stays on the basis of the exceptional improvement of the material strength.



FIGURE 4.20

Superficial morphology of 17-4 PH stainless steel samples, nitrated at: (a) - 400°C (b) - 480°C [25]

There are a number of variations of the plasma ion nitration, described in the literature. El-Hossary and coworkers **[33]** have published an original method of plasma nitration/carbonitration on AlSI 304 stainless steel by charged gas plasma, induced by radio frequency AC generation at frequency, equal to - 13.56 MHz. In order to obtain simultaneous enrichment with nitrogen and carbon, the authors have used a gaseous mixture, composed by nitrogen and acetylene in the temperature range from 520 to 590 °C and 800 Pa. The researchers have established that the ratio between the gases used possesses a great impact on the dept of the obtained carbonitride layer, as is demonstrated in figure 4.21:



FIGURE 4.21

SEM – cross-sectional images of AISI 304 specimens treated in gaseous mixture with (a) – 0%; (b) – 10% (c) – $30\% \ \mu$ (d) – 60% acetylene content [32]

Magnetron sputtering plasma ion implantation methods

An interesting variant of the low temperature plasma methods is the so called "magnetron sputtering". This method is based on the combination between electric arc plasma and constant magnetic fields. Thus, the ionized gaseous particles suffer additional acceleration by the magnetic field towards the one of the electrodes (namely the cathode), and due to the exceptional kinetic energy, these particles repulse particles composing the other electrode (the anode), and afterwards the resulting particle fluxes penetrate through the surface of the anode. The respective devices, named "plasma sputtering magnetrons", are in fact vacuum chambers with controlled gaseous atmosphere and electrodes, charged by powerful electrostatic and electromagnetic fields facilitates the repulsion of particles from one of the electrodes, and posterior inclusion in the superficial composition of the other one. Schematic illustration of such device is shown in **Figure 4.22**. The cathode serves as component provider, whereas the anode is the treated material, subjected to implantation.



FIGURE 4.22

Schematic image of a sputtering magnetron (a) and simplified process illustration (b) 1 – magnetron body, anode (deposition substrate), 3 – cooling serpentine, 4 – cathode (target), serving as solid precursor source, 5 – electromagnetic inducers (coils)

Nitration, coupled by titanium implantation in a sputtering magnetron is described in another paper by the same author's work-team **[34].** There, the authors describe plasma ion implantation with coincident nitration in nitrogen - argon atmosphere, in condition of radio-frequency plasma, on AISI 304 stainless steel, by use of titanium plate as counter electrode; resulting in titanium nitride enriched protective film formation.

Cerium oxide coatings have been successfully deposited as corrosion protective primer layers by Ershov et al. **[35]** on AA2024 aircraft alloy using reactive plasma sputtering. The CeO_x films have been simultaneously deposited on sets of 4 pieces of clad 2024 substrates with 4cm^2 each one, preliminary cleaned by acetone/methanol mixture. The method used by them is known as reactive plasma sputtering, since the processes, described above proceed simultaneously with chemical conversion reaction. The depositions have been executed by using of balanced DC reactive magnetron. Ce target (99.9% purity, 76 mm in diameter and 3 mm in thickness), positioned at 50

mm from the target has been used as cerium source. Evacuating the air from the chamber by a combination of scroll and turbomolecular pumps allowed obtaining the base pressure the order of 10^{-7} torr. The amounts of sputtering (Ar) and reactive (O₂) gases in the mixture have been controlled independently by separate mass flow controllers. The electric charging has been maintained by a 1A- direct current generator. During the experiment, both the deposition rate, and the voltage varied in accordance to the O₂ content in the gas mixture. The former changed between 35 and 265 nm/min, whereas the latter was between 180 and 300 V. As a result, the authors report obtaining of uniform cerium oxide layers with average thickness of 100 nm.

Plasma assisted vapor deposition methods with chemical conversion

This combined type of layer deposition is also known as Plasma Enhanced Chemical Vapour Deposition – PECVD. This method is related to synthesis of surface layers by simultaneous chemical conversion process resulting in altering of the superficial chemical composition of the respective substrate. It is successfully applied for growth of crystalline films with application for optical and communication equipment production **[36 - 38]**. The crystalline layer growth is a consequence of coincident deposition of precursor vapors and chemical reaction between them. This method possesses the following advantages:

- Possibility for efficient control of the chemical conversion reactions during the film growth that enables a gradual modification of both the composition, and the structure as well as the density of the resulting superficial layer.
- Remarkable film growth rates in the order of 1-10 nm/s.
- Possibility for deposition of layers with remarkable optical properties, such as high diffraction rate, etc.
- The obtained surface layers have significant adhesion to the substrates, since the mechanism of their growth includes the substrate material as a precursor. The film growth rate can be additionally controlled by the plasma ignition energy source.

Usually, for this method the plasma is obtained by ionization of at least one of the precursors by high frequency AC generators (f > 1 MHz). The experience has shown that the microwave ignited plasma is more appropriated than the radio frequency ignited. The methods based on plasma involved vapor deposition, combined with chemical conversion enable deposition of SiO₂ superficial layers at temperatures between 100 and 300°C. **[39]**, allowing significant energy expence reduction. When the precursor is SiH₄, the resulting SiO₂ film contains some amount of SiH_xOH_(4-x), fraction, where (x = 1-3) **[40]**.

Furthermore, the method can be applied with other silicon based precursors, which can be divided into four main groups:

Group 1 – Si-derivatives of saturated hydrocarbons, such as: Si(CH₃)₄.

Group 2 – oxygen containing silicon – organic compounds, such as: $(CH_3)_3Si-O-Si(CH_3)_3$, $(CH_3)_2HSi-O-Si(CH_3)_2$, etc.

Group 3 – Methyl oxysilanes, such as: Si(OCH₃)₄, H₃Si-O-CH₃, (CH₃)₃Si-O-CH₃

Group 4 – ethyl-oxysilanes, such as: Si(OC₂H₅)₄, C₂H₅Si(OC₂H₅)₃, (CH₃)₂Si(OC₂H₅)₂, and (CH₃)₃SiOC₂H₅.

Besides, a large variety of metal-organic hybgrid precursors can be used for synthesis of mixed oxide surface layers.

This method also enables application of low temperature plasma at atmospheric pressure. Besides, according the gaseous medium composition other compounds can be obtained such as sulfides,

fluorides, etc. The method can be performed either by simultaneous chemical conversion reactions, or by subsequent chemical conversion of already ionized precursors. **Figure 4.23** represents an example of film deposition by subsequent chemical conversion **[40, 41]**.



FIGURE 4.23

Schematic presentation of reactor for plasma assisted vapor deposition coincided by chemical conversion synthesis reaction. 1- high frequency inductive coil; 2- Chamber body; 3- Deposition substrate; 4- electric resistance heater; 5- thermocouple; 6-gas precursor inlet tube

Low temperature electrolytic plasma treatment in liquid media - Usually, the systems composed by metallic or graphite electrodes, immersed in an electrolyte are object of the electrochemistry. The reason is that each system, composed by at least two electrodes serving as electron conductors, and electrolyte between them, acting as an ionic conductor can be considered as an electrochemical cell. The electrochemical cells can be divided into two general groups: galvanic elements – which produce an electric current, due to the electrochemical processes on the electrode surfaces, and electrolytic cells – where the electrochemical reactions proceed, spending the electrical energy, produced by exterior source of electricity. The electrochemical reactions can be described as oxidation/reduction reactions that proceed by the participation of electrons, provided or consumed by the respective electrode. The electrodes in the electrolysis cells are

respectively: cathode – where the cations from the electrolyte receive additional electrons (i.e. suffer oxidation), and anode – where the anions render their excessive electrons, undergoing reduction (i.e. they suffer reduction). Consequently, the electrochemical red/oxy couples are separated in the space, so that the respective oxidation and reduction processes proceed on the surfaces of the corresponding electrodes, connected by an external electric circuit. However, as a rule of thumb, the electrochemical science is limited to the range of 1 - 2 V.

When a high potential (above 50 V) is applied on such a cell, the processes which occure completely alter their nature, and stop to be an object of the classical electrochemical science. Furthermore, when an electrical current with high voltage is applied, re-directs the electrical charged particles (i.e. the ions) of the electrolyte to the respective electrodes, loading them much higher kinetic impulse. Thus, these particles realize collisions among themselves, and the resulting vibration movements in the liquid medium, emitting significant heat quantity. Undoubtedly, the high currents thermal effect described in the previous section also contributes for the system heating. The produced heat causes a partial evaporation of the electrolyte by boiling. When the applied potential is high enough, the transition of the electrolyte from liquid to gaseous state (i.e. vapors), an additional ionization can be detected inside the vapor bubbles. These processes are more intensive on the electrode surfaces, because the electrodes, being usually metals posses lower specific thermal capacity (i.e. these materials need lower quantity of energy to increase their temperature). This is the way for the obtaining of plasma state, by ionization of the electrolyte vapors, localized inside the vapor bubbles.

This method is proposed by Krastev and co. for enhancement of the wear hardness of metal cutting tools, such as drills **[42, 43]**. The authors have performed systematical research on the possibility for surface wear hardness elevation high-speed steel HS 6-5-2, and cold-work tool steel 90CrSi5, by electrical discharge treatment in electrolyte, based on B_4C water suspension with addition of glycerol and Na₂CO₃. As main achievement, the authors claim that the treatment of HS 6-5-2, for 3 minutes in the above mentioned electrolyte by application of 200 V results in formation of 0.05 – 0.06 mm thick layer, with extreme corrosion durability and micro hardness shown in **Figure 4.24a**. Besides, they assert that at similar treatment conditions, (with 180 V applied voltage) the 90CrSi5 steel forms martensitic subsurface phase **(Fig. 4.24b)**.



FIGURE 4.24 Cross-sectional optical micrographs of steel details

Furthermore, the authors assume that the processes described above coincide with partial

localized spot fusion of the steel, in the locations of the sparks, and subsequent re-crystallization, after the spark quenching. Thus, regardless the fact that the temperature of the overall system is not high, in the zones of the sparks, it can reach temperatures of the order of 8000 - 20,000 °C. Furthermore, the subsequent re-crystallization rate, predetermined by the rate of heat exchange between the fusion and the surrounding material predetermines the grain size of the resulting metallic crystallites. Similar treatment procedures are described in the classical literature, as well **[44]**. There, the impact of the additives is particularized, mentioning that NaCl, NH₄Cl, HCl, and also H₂B₄O₇ salts are particularly suitable, whereas others: CaCl₂, BaCl₂ and H₃BO₃ do not result in surface modification. This difference is explained by the individual mechanism of action, provided by the respective additives. For instance, the chlorides react with the boron carbide, converting it to boron chloride, and afterwards, its subsequent dissolution in the aqueous medium, results in free boron atoms:

$$B_4C + MeCl \rightarrow BCl_3 + Me + C \rightarrow B + Cl_2 + MeC$$
where "Me" means metallic ions
(11)

Alternatively, tetraborates liberate boron atoms via other reaction:

$$Na_2B_4O_7 + B_4C \rightarrow B + CO + Na_2O$$
(12)

Nevertheless, according to another literature source **[45]**, borax can be prepared by reaction between boric acid and soda ash:

$$4H_{3}BO_{3} + Na_{2}CO_{3} \rightarrow Na_{2}B_{4}O_{7} + 6H_{2}O + CO_{2}$$
(13)

The last equation leads to the inference that the electrolytic plasma treatment can be performed by mixture of $4H_3BO_3$ and Na_2CO_3 .

It is worth to remark the significant simplicity of the equipment required (Fig. 4.25).



FIGURE 4.25

Electrical discharge treatment in aqueous electrolyte

1. - Electric motor, 2. - bearings, 3. -SiC counterelectrode, 4. - electrolyte container, 5. - treated detail (drill),

6 – graphite contact element, 7. – controlled power supply

Shen et al. **[46]** published their investigations devoted on carbonitration process, in a liquid medium, composed by ethanolamine $C_2H_5ONH_2$, dissolved in distilled water. When an electrical current with 150 V potential, and 50 Hz frequency is applied through the conductive bath body, and the treated metallic detail, an electrical charge medium forms, composed by the electrolyte ions: H_3O^+ , OH^- , $C_2H_5ONH_3^+$, $C_2H_5ONH^-$, $C_2H_5O^-$, accompanied by gaseous emissions, of ammonia, ethanol vapors, hydrogen, oxygen, etc, and a part of them undergoes ionization, forming low temperature plasma. In this particular case, the authors have investigated three different duration times of carbonitration of Q235 stainless steel, respectively: 30, 75 or 120 seconds, at controlled temperature in the range of 50 - 60 °C. In conclusion, the authors have established that the optimal residence time of the treated detail in the bath is 75 seconds, and also the further residence extensions favor reticulation processes, (i.e. carbon fiber net-formation) which deteriorate the superficial strength of the treated details. **Figure 4.26** clearly shows the densification of the surface layer of the treated steel until the 75th second. It is consequence of the simultaneous appearance of carbide and nitride phases, which afterwards convert to carbonic filament formations.



FIGURE 4.26

SEM – cross sectional images of specimens, treated after 30, 75, and 120 seconds at 150 V

Besides as surface post-treatment, of high performance steel details, the low temperature plasma ignition methods in liquids could be employed for synthesis of highly dispersed self ordered nano-materials.

Guo and coauthors, **[47, 48]** have synthesized highly ordered nano-dispersed structures, composed by boron nitride. They have applied a high voltage electric signal of about – 4 kV, across a liquid represented by equimolar mixture of boric acid H_3BO_3 and dimethylformamide. The respective electrodes used for electric charge arc were tungsten needle and titanium plate with 1 cm², superficial area, in one linear cm distance, between them. By this configuration, the authors have succeeded to obtain boron nitride nano-particles, shown in **Fig. 4.27**.

In another their paper **[48]**, the authors report successful fiber shaped nano-structures with stoichiometric composition - $B_{50}N_2$, at identical conditions, but different relation between the precursors content: HCON(CH₃)₂ : H₃BO₃ = 1 : 5.2.



FIGURE 4.27

SEM image of BN-nanoparticles [47]

Typical features of the plasma induced methods

Advantages

- Large variety of the possible materials, which can be synthesized.
- Possibility for application of these methods so for synthesis, so for post rtreatment of various materials.
- Possibility (in some cases) to be applied continuous methods of synthesis.
- Possibility of ease control of the technological process.

Disadvantages

 High energetic demands, related with the maintenance of the plasma state of the precursors.

Spray pyrolysis methods for production of nano-sized powder materials and thin layered coatings and films

Basic classification

In order to characterize whatever material, its properties should be dertemined (i.e. to be measured) and evaluated. Exactly the conjunction of all properties possessed by a material predetermines its performance in the application conditions of the resulting industrial product (i.e. the working conditions). As was mentioned in the introductional part of the present Chapter, the metarial behaviour is a result of its specific composition, structure and form. These features, on the other hand, entirely depend so on the composition of the repective precursor mixtures (comprising so the basic precursiors, so the additive substances, sugh pH buffers, etc.), so on the presence or absence of chemical interactions among them, phase transition, etc. Finally, all the

conversions suffered by the precursors, until the synthesis of the end product and its post treatment depend on the conditions of exectution of each procedure, composing the entire production process, together with the corresponding methods.

The spray pyroplysis methods are based on the submission of fine dispersed drops of a precursor solution or suspension to a high temperature conduitions. Commonly, these methods are used for synthesis of metallic oxide powders, but in some cases, at reductant gases, pure metals or alloys can be synthesized. According to the obtained product form, the spray pyrolysis methods can be divided into two basic groups:

- Methods designed for production of powder formed products, named: **Spray Pyrolysis Synthesis – (SPS) methods**. According to the conditions of their execution, these methods enable production of cave, porous, or dense oval or coarse particles, which also could possess a multilayerd structures.

- Methods developed for making of thin layers and films, known also as: **Spray Pyrolysis Deposition – (SPD) methods**. The obtained by these methods films could have various thickness, being monolayered, multilayered, porous or dense.

The composition of the resulting films depends on the composition of the initial precursor solution (or suspension), as ell as the subsequent chemical or physical-chamical conversion processes during the synthesis process. The structures and the respective forms of the obtained products are entirely predetermined by the thermal regime, comprising so the temperatures in the corresponding work spaces, so the rates of temperature changes during the synthesis and even the residence duration of the droplets in the high temperature spaces **[2]**. These features can be supplementally modified by posterior thermal treatments (annealing, tempering, etc.). The maximal temperature value predetermines the structural modification of the product crystalline lattice, by the respective polymorphical conversions. However, the temperature change rate defines the intensity of solvent evaporation and the respective porosity (during the spray heating), and also the crystal size and amorphous fraction presence, (during the subsequent cooling). Thus, the speeds of the temperature alterations predetermine the particle size, morphology and the residence time of the spray droplets, and the resulting solid paricles, as well as the temperature changes accompaining the crossing of different operation units (e.g. work chambers).

Processes related to the crossing of the spray droplets across the high temperature work space

Initially, each drop suffers heating, and evaporation of the solvent (**Fig. 4.28**, position 1), until it achieves the stage (A). It could be described as a liquid particle, represented by saturated solution, surrounded by vapors of the solvent. Afterwards, due to the evaporation, an additive solid shell forms (**Fig. 4.28**, position 2), leading to intermediate three phase system (B). This process coincides with initiation of chemical conversion reactions, among the initial precursors. These reactions could include also interactions between the already formed solid phase and the surrounding gaseous medium, and even the solvent vapors. This approach is already used by Haneda **[49]** for the synthesis of a photocatalyst by partial fluorination of TiO_2 , with enhanced photocatalytic capabilities, achieved by addition of fluorine containing modifying compounds to the initial precursor solution. As modifier for their experiments, the authors have used water solution in the droplet, and it converts to a solid particle. The solvent evaporation intensity enables formation of channel pores, since the vapors form channels from the formed particle core to its surface. The vapor pressure inside the particle is able to cause a particle splitting, as well.



FIGURE 4.28

Conversion stages and processes in a spray drop exposed to high temperature [2]

After the completion of the solvent evaporation process, due to the expense of the entire its quantity, a solid particle appears (Fig. 4.20, position C). The process can be interrupted at this moment, and the respective approach is known as "one drop – one particle". That is why, some authors prefer to use nozzles with internal needles, vibrating with ultrasonic frequencies (in the order of 20 kHz) [50 – 53], in order to obtain smaller drops, predetermining the size of the resulting product particles. This approach is widely used for production of powder materials with spherical particle shapes. An alternative basic approach for production of nano-sized powder materials is based on the further sharp heating of the already obtained solid particles (E). The additional sharp heating causes mechanical tensions in the already formed solid particle, since the sharp heating does not allow efficient heat exchange between its shell and core. At these conditions, a thermal expansion gradient arises (Fig. 4.28, position 4), resulting in a particle cracking and even splitting (D and E). Another possible particle cracking reason due to mechanical tensions can originate from polymorphic transitions near the particle surface above a critical temperature value.

When the desirable product form is a solid film, instead of powder material, it is accepted to spray a cold solution on a hot substrate surface. In this case, the processes, described above happen on the substrate surface.

Equipment for spray pyrolysis synthesis and industrial production

Remarkable variety of engineering and constructive decisions for designing and creation of spray pyrolysis equipment exists. In general, all the possible modifications of the spray pyrolysis installations are consisted on several basic operation units, which function is assisted by additional devices. The main equipment components for synthesis via spray pyrolysis method are: 1 – spraying nozzle, 2 – High temperature work space (i.e. furnace), 3 – product collector for the fine dispersed powderlike products, or film deposition substrate. In order to insure the regular function of these basic operation units, additional units are necessary, such as: initial precursor solution containers, nozzle feeding pumps, carrier gas compressors, thermal energy sources, powder fraction separators, etc.

Figure 4.29 summarizes the basic types of spray pyrolysis installations, with: (a) – vertical tubular chamber, (b) – horizontal tubular chamber, and (c) – film deposition chambers.



FIGURE 4.29

Basic configurations of spray pyrolysis installations [54]

Nozzles Atomizers and nebulizers: As can be seen from the figure, besides common nozzles, feeded only by the precursor solution, mixing nozzles, with additional carrier gas loading are also possible. The latter type configuration can be performed without solution pumps, since the compressed gas enables liquid sucking, via the Venturi effect. In order to reach higher dispersion rates, additional needle could be mounted inside the nozzle. This kind of sprayers is known as *"atomizers"*. The drop size is simultaneously driven by the narrowness of the exhaust aperture, the pressure difference before and after the nozzle, the surface tension between the liquid solution and the surrounding gaseous environment, its viscosity and density. If the needle performs a vibration movement, by charging with external electrical impulse generator, then even finer drops can be produced. In this case, *nebulizers* are used instead of nozzles.

Empirical mathematical dependence between the needle vibration frequency and the resulting drop size is described in the literature **[55, 56].** It is shown by equation 14:

$$D = 0.34 \sqrt[3]{\left(\frac{8\pi\gamma}{\rho \cdot f^2}\right)},\tag{14}$$

Where: D is the diameter of the obtained precursor solution drops (μ m); γ - superficial tension on the drop surface (N m⁻¹), ρ - precursor solution density (kg m⁻³); f – needle vibration frequency (MHz).

If a combustible compound, such as organic solvent is added together with the precursors, and an oxidant is represented in the compressed carrier gas, then the spray pyrolysis can be executed in a direct flame. In this case, the nozzle plays additional role of burner. Alternatively, the flame assisted spray pyrolysis can be executed by supplemental burners, mounted radially around the nozzle, so that the precursor drops from the nozzle cross the flames, as is proposed by Tani and co. **[57]**.

These authors have succeeded to synthesize nano-sized ZnO powder, with particles size between 10 and 20 nm, by spray pyrolysis of zirconium acrylate, dissolved in a mixture of methanol and acetic acid. In their installation 18 burners were assembled, situated at 6 mm distance from the nozzle. The flame has been maintained by burning of methane in pure oxygen.

When the combustible feeding is combined with high voltage electrical charging, the nozzle becomes be a plasma generator. An installation for plasma assisted spray pyrolysis, performed by similar method is represented by Gitzhofer **[58]**. Other examples, for plasma assisted spray pyrolysis installations, working with radio-frequency or induction plasma can be found in the literature **[59 - 61]**, as well.

Working chambers - These operation units provide the work space where all the processes of conversion of the initial precursors to the end product proceed. As was already mentioned above, they could be in forms of vertical, horizontal tubes, or deposition chambers. Hirunlabh **[62]** remarks that the basic advantage of the horizontal tubes, compared to the vertical ones is that the processes, described in the previous section are coincided by particle fraction separation, since the heavier particles fall on the chamber bottom closer to the nozzle, then the lighter ones. This phenomenon enables fraction separation inside the chamber itself, enabling industrial production of one fraction powder products, by simultaneous synthesis and product separation. In addition, for better control of the particles size, structure and morphology, the installations can be performed by several subsequent chambers with different working temperatures and length. The latter supplies different residence durations in the corresponding thermal zone.

Sources of heat - As was mentioned above, other sources of thermal energy could be applied besides the electric resistance heaters, or burners. Thus, the high temperature can be maintained by electrical inductive or capacitive high temperature plasma torches. In this situation, even cooling systems are necessary, for quenching of the excessive heat, in order to maintain the proper working temperature, as is illustrated in **Fig. 4.30**.



FIGURE 4.30

Schematic presentation of plasma assisted spray pyrolysis installation (a) and precursor / carrier gas feeding nozzle (b) 54]

1, 4 – Gas bottles, 2 – initial solution container, 3 – nozzle, 5 – top fitting, 6 – chamber ceramic body, 7 – Inductor charged by high frequency AC generator, 8 – External cooler, 9 – substrate holder, 10 – substrate, 11 – internal cooler for sample temperature control, 12 – vacuum pump

Final product collection systems – At SPD variant of the spray pyrolysis metods, the product is in form of coatings, deposited on substrate. On the other hand, the SPS installations demand additional fraction separators and collectors of the obtained powder products. These systems could be performed by simple mechanical filters or cyclones for collection of micron – sized powders, but the nano-sized products require different technical decisions, enabling more efficient product collection. For instance, the obtained nano-sized products can be cached by blowing through a liquid, resulting in colloidal system formation. This approach is used by Suh and Suslik **[63].** They collected the obtained by them magnetically active double layered nano-particles, by triple blowing through hydrolyzing solutions. After subsequent centrifugation and drying, the authors have succeeded to insulate nano-dispersed powder like magnetic material, composed by hollow, porous CoO_2 particles.

Fields of applications of the spray pyrolysis products

The spray pyrolysis appears to be a versatile technique for material production with various applications. The spray pyrolysis synthesized products encounter available applicaton practically everywhere when inorganic thin films or fine dispersed powderlike materials are necessary. The versatility of the spray pyrolysis products is clearly demonstarted in **Fig. 4.31**.



FIGURE 4.31

Fields of application of the products synthesized by the spray pyrolysis methods

Production of sensor elements - It is well known that the TiO₂ owes photoactive semiconductive properties, in the UV spectrum. Okuya et al. **[64]** have proposed titania thin layers deposition with possible application for sensor elements. Their technology is based on multiple depositions with subsequent variations of the initial precursor composition. Initially, the authors have deposited two transparent layers, composed by SnO₂:F, and pure SnO. For this purpose, they have pyrolysed 0.1 M di-n-buthyl tin diacetate (i.e: $(C4H_9)_2Sn(CH_3COO)_2$), dissolved in ethanol. The difference between these layers is that the former one was doped by NH₄F. Afterwards, they have deposited a photoactive TiO₂ layer by spray pyrolysis of 0.05 M ethanol solution of titanium acetylacetonate doped by aluminum acetylacetonate. The obtained layered conjunction has been sealed by finishing CuO layer, deposited by spray pyrolysis of 0.04 M copper acetate (CH₃COO₂Cu). Finally, a golden electrical contact layer has been deposited by spray pyrolysis in reduction medium.

Sensors for gas-analysis have been elaborated by Starbov et all. **[65]** by spray pyrolysis deposition method. These authors have successfully developed a sensor element, based on a ZnO film, deposited by 0.1 M solutions either of $Zn(CH_3COO)_2.2H_2O$ or $Zn(NO_3)_2.6H_2O$, on glass substrates, preliminary heated up to 350 °C. Finally, the authors have conduced a comparative evaluation on the annealing post treatment effect on the characteristics of the obtained by them sensors. By this manner, high performance gas detecting sensors for NH₃ and diethylene amine NH(CH₃)₂ have been developed.

A great number of research works can be found in the literature, dedicated on creation of sensor elements, based on doped titania, synthesized via spray pyrolysis.

Indeed, remarkable improvement of the characteristics possessed by TiO_2 based sensors after its chemical modification by addition of: Ni [66, 67], glassy carbon [68], noble metals [69 – 72], Rare Earth elements, [73, 74], etc.

Poroduction of photocatalysts - The most widely investigated field of titania application is the photocatalysis. The main limitation related to the TiO_2 application as a photocalayst is that its photocatalytic effect reveals only at UV illumination. So, that Di Li and co. **[75]** have elaborated fine dispersed powder of partially fluorine substuituted $TiO_{2-x}F_x$, with particle size of 0,45 μ m, by spray pyrolysis of H₂TiF₆. As a result, the authors report that the fluorine doped titania catalyst is active even at illumination in the visible spectrum.

Another example for elaboration of ZnS:Ni catalyst via spray pyrolysis synthesis is reported by Bang, & co **[76]**. The authors have performed a spray pyrolysis of 3% SiO₂ suspension in aqueous solution of 0.2 M ZnNO₃, doped by 1M thiourea and 2 x 10^{-4} M NiNO₃. This colloidal initial system was ultrasonically nebulized, in inert Ar medium in a furnace with electrical resistance heaters. Thus, at 700 °C, the authors have obtained a powder material of double layered particles with SiO2 cores and active porous shells composed by ZnS:Ni²⁺. After subsequent post treatments, by dissolving of the silica cores in HF, the authors succeeded to obtain hollow particles composed by the residual active ZnS:Ni²⁺. After supplemental tempering at 1000 °C, the hollow porous particles were efficiently spitted into nanosized coarse crumbles with 550 nm average size.

Production of advanced ceramic materials - In the classical ceramic technologies it is accepted as a common practice to submit preliminary molded units to a high temperature treatment. The unit molding is usually preformed from initial colloidal systems (slips), where the dispersed phases are commonly composed by metallic oxides. The particle size of these phases strongly affects the porosity of the obtained stoneware. In this aspect, the spray pyrolysis appears to be really perspective method for production of slip powders for ceramic products with enhanced density. Powders, composed by ZrO_2 , stabilized with Y_2O_3 (known also as yttria stabilized zirconia YSZ) with

controlled particle are obtained by Y. L. Song & co **[77]**. The main achievement of their work is the increase of the productivity, and the better particle size control, achieved by carrier gas feeded ultrasonic nebulizer. In addition, the authors remark the opportunity for coincident fraction separation in a horizontal tubular chamber. Thus, the authors have used quartz tubes with 2.5 or 7.5 cm of diameter, and 1.7 m, long, separated in three thermal zones. The product obtained by them possessed a form of spherical particles with 73-nm, of diameter by spraying of 5– 8- micron drops of 0.01 wt% precursor content.

Production of advanced constructive materials - The intensive scientific efforts for creation of entire new generations of composite materials have led to creation of composites reinforced by nanosized carbon tubes. The elaboration of these materials was committed by the need for usage of weight lightened materials with improved correlation of mechanical properties per unit of weight. Such materials are of great importance for designing of transport vehicles with enhanced security, but with reduced fuel demands. These factors are remarkably important for development of reliable transport with optimized fuel spend capability for sustainable economical development with reduced ecological impact. These factors have recently stimulated the research activities on the elaboration of carbon nano-composite panels **[78]**, and even entire carbon fiber composite automobile bodies **[79]**. Another direction of transport machine design improvement is the elaboration of advanced corrosion protective coating systems.

In this sense, corrosion protective coatings with silica **[5]**, alumina **[80 - 82]**, and also carbon nanoparticles **[83]** are synthesized and characterized. Hence, the spray pyrolysis of organic compound solutions appears a promising approach for elaboration of fine dispersed fillers for carbon fiber nano-composites. Maria Fortunato and co. **[84]** have proposed spray pyrolysis of alkaline carbonates 0.1M Na₂CO₃ or 0.1M NaHCO₃ in saccharose solution. They have performed this process in a quartz tube at 400 °C, by ultrasound mobilizing, supported by argon as a carrier gas. The obtained powderlike product was composed by mixture of elemental carbon and Na₂O. After its collection through blowing in water the sodium oxide has converted to NaOH, which was removed by vigorous cleaning. Thus, the authors succeeded to obtain nano-tubes with size dimensions between 30 and 100 nm. They propose the obtained by them carbon nano-sized materials for designing of water and air filters.

Other authors **[85]** have created an installation for production of multilayered carbon nano-tubes by spray pyrolysis of liquid alkanes, such as: n-pentane, n-hexane, n – heptane, or n-octane, as carbon sources. The pyrolysis process has been conduced by addition of ferrocene as a catalyst in a reactor at 875 °C. The product obtained by these authors possessed the form of nano-tubes with 10 nm to 80 nm of diameter.

Another important SP-application direction is the production of powder metallurgy precursors.

Production of materials for alternative energetic sources: The permanent increment of human population is accompanied by increase of energy demand and more restrictive environmental regulations. In that instance, the Solid Oxide Fuel Cells (SOFC) technology has emerged as an efficient substitution of the presently existing energy devices **[86]**. Nowadays, due to the combination between the increased energy demands and the enhanced ecological restrictions, both related to the sustainable development of the modern communities, the fuel cells have emerged as a new alternative energetic source. Their performance is predetermined by the structures, compositions, and properties of the materials employed for their construction. On the other hand, the industrial employment of SOFC material depends on the method, and the conditions applied for its synthesis. Thus, recently the advanced ceramic materials have
encountered new important application field as constituents of Solid Oxide Fuel Cells (SOFCs) **[87]**. These elements find applications so as alternative energy sources, so as electrocatalysis devices and even as sensors for combustible gas detection **[88, 89]**. All these facts predetermine the continuous increase of the scientific interest and efforts for optimization of the SOFC production technologies, in order to provide low cost production of efficient and reliable fuel cells **[89, 90]**.

It should be mentioned, that ZrO_2 , stabilized by Y_2O_3 is a commonly used ceramic material for solid SOFC electrolytes. Example for spray pyrolysis synthesis is already mentioned in the present Chapter. Also, the electrodes of these cells are composed by non-stoichiometric polymetallic oxides, usually with perovskite structures [91]. Examples for preparation of electrodes, composed by: Lanthanum strontium manganite, lanthanum strontium cobaltite, lanthanum strontium ferrite, lanthanum niobate, lanthanum cobaltate, and also non-stoichiometric doped ceramic materials as: gadolinia-doped ceria and cobalt doped lanthanum strontium ferrite etc can be found in the literature [92 – 97].

Todorovsky et al. have synthesized a large variety of metallic oxides, representatives of this group **[98]**. The authors turn a serious attention on the modification of the already obtained materials by their laser beam annealing by Nd:YAG solid state laser.

Among the investigated oxides, TiO_2 and its derivatives are also assessed as potential SOFC ingredients [99 - 101].

As was mentioned in the previous section, special one chamber installation has been constructed, which enables subsequent deposition of all fuel cell composing ceramic layers. Namely, the possibility for complete layer-by-layer SOFC assembling by SPD method, demonstrated by Gitzhofer **[58]** imposes the spray pyrolysis method as indispensable technological approach for continuous low cost SOFC production, as is demonstrated in the next figure:



FIGURE 4.32

Available technological approaches for SOFC production [87]

Another spray pyrolysis application direction is the elaboration of materials for solar energy conversion based energetic sources. Afifi & co **[102]** have already developed entire technology for production of multilayered solar cells, based only on spray pyrolysis. In their paper, the authors remark the undoubted advantages of the spray pyrolysis, comparing them with alternative methods, such as laser assisted, vapor deposition, and plasma ignited ones, since the former require rather simple equipment, and enable continuous production regime. They have used this method for deposition of photosensible ZnO layers either on preliminary oxidized silicon substrates, or glass plates. In order to synthesize photosensible films, the authors pyrolysed initial precursor solution, composed by 0,2 M Zn(CH₃COO)₂, dissolved in water-methanol H₂O/CH₃OH – 8 : 2 liquid medium. For prevention of the undesirable synthesis of Zn(OH)₂, the authors added acetic acid. After the supplemental addition of InCl₃ to the initial precursor solution an electrical

conductivity further enhancement has been achieved. Afterwards, for production uniformly distributed crystalline structure, the authors have submitted the already obtained films to subsequent annealing at 350 °C for 40 min, in inert N₂ medium.

Finally, it is important to mention that due to their peculiar light dependent electrical properties, the TiO_2 based materials have enabled elaboration of entire new class of photovoltaic cells, named: "*Dye Sensitized Solar Cells*" [103], invented by Brian O'Regan & Michael Grätzel at 1991 [104]. However, this field comprises enormous number of publications, and entire books are dedicated on this topic [105 – 107], so that it will not be discussed in the present Chapter.

Another important group of alternative energy sources is directly related to the so called "hydrogen energy", based on hydrogen production by water decomposition. This method is well known even since the end of XIX century, as "water electrolysis". During decades this method was undervaluated, due to the significant electrical energy demand. Nevertheless, recently this disadvantage was overcome by photocatalytic electrolysis, supplying a part of the necessary energy on the basis of the solar light. Thus, the spray pyrolysis synthesis was established as a valuable method for elaboration of photoactive electrodes for water splitting devices. Remarkable photocatalytic effect on the water splitting efficiency, possessed by NaTaO₃ is noticed by Kang and etc [108]. They have synthesized this oxide material by ultrasonic nebulization of aqueous solution of Ta(OC₂H₅)₅ and NaNO₃, in presence of HNO₃. This solution was dispersed in a vertical quartz tube with 3 cm of diameter 84 cm. of length. This tube was divided into two thermal zones, providing 700 and 1000 °C, respectively. The obtained powder product has undergone posterior annealing for 3 h. at 250 °C.

Other authors [109] have preferred to perform a direct photocatalytic conductive Fe_2O_3 film deposition, at 400 °C on FTO TEC-15 glasses.

Production of materials for microelectronics and automation - Magnetic hollow particles have been synthesized by Suh and Shushlik **[63]** by spray pyrolysis of cobalt compound in organic solvents and dispersion phase of "LUDOX SH 40[®]" silica particles, and subsequent removal of the product particle cores.

The photoelectrical properties possessed by TiO_2 and ZnO, as well as the specific conjunction between electrical conductivity and transparency, owed by ZnO and SnO, predetermine their capability to be applied in various electronic components. Brankovic and co [110] have proposed a technological approach for memory devices, named "Dynamic Random Access Memories -(DRAM)", on the basis of SrTiO₃, synthesized via spray pyrolysis method. The authors have successfully combined the spray pyrolysis method with the sol-gel technology for creation of SrTiO₃ thin layers. Initially, they added strontium acetate Sr(CH₃COO)₂ to titanium (IV) isopropoxide, solution in mixture of citric acid and ethylene glycol in molar ratio (1:4:16). The obtained mixture was afterwards sprayed on preliminary treated Si-substrates in presence of oxygen as carrier gas. As achievement of their investigation, the authors have succeeded to determine the optimal deposition conditions, as the gas flux speed, the substrate temperature, and the correlation between the residence time and the resulting film thickness. It is worth to note that the SrTiO₃, and BaTiO₃ are the most widely used materials for piezocrystal resonators. An important factor for reaching of desired structure and density of the obtained thin layer products mentioned by Shindov [111], is posterior annealing regime. He has deposited CdO coatings by spraying of 0.1M Cd(CH₃COO)₂ solution, on heated glass plates. As main result, the author claims that the posterior high temperature tempering results in formation of larger crystals with more uniformly distributed structure.

Examples for synthesis of $CuGaSe_2$ semi-conductive materials, based on spray pyrolysis deposition can be found in the literature **[112]**.

Production of optical materials - Nascu & Popescu **[113]** have developed a large number of of CdS light filters by spraying of CdCl₂.2H₂O solution, doped by thiocarbamide on hot glass substrates. This approach has enabled the authors to vary the optical properties, by variation of both the initial solution concentration and substrate temperature. Other authors have proposed a spray pyrolysis application for elaboration of SnO thermal refractors, deposited on glass substrates **[114]**.

A great variety of metallic compounds, basically oxides, are being investigated in order to create advanced hi-tech. devices and equipment. Nevertheless, besides the material properties of the components required for assembling of efficient, reliable and durable devices, new requirements have recently been arisen, related to environmental compatibility of the industrial products, and diminishing of the pollution impact coinciding their production. Indeed, the recent administrative restrictions, **[115 - 117]**, have restricted the industrial application of compounds of some elements, such as: Pb, Cd, Cr, Co, As, Se, Hg, etc, as well as of some toxic volatile organic compounds (often used as initial precursor solution media in some high temperature synthesis technologies) [118]. These restrictions impose new challenges for the World wide industrial sectors, related to the substitution, or at least decreasing of the employment of hazardous substances. These challenges have stimulated the research efforts for synthesis, characterization and subsequent application of Ce, Ti, Si, and Zr oxides. Indeed, recently, the interest on the lanthanides, and especially on cerium was increased, because it was found that these elements are economically competitive [119], and especially cerium is as plentiful as copper [120]. Furthermore, it is established that these elements possess a low toxicity and their ingestion or inhalation has not been considered harmful to health [121, 122].

Besides all the application fields, mentioned above, the materials based on TiO_2 and its derivatives encounter various applications due to their peculiar combination between the photoelectrical properties and the biocompatibility possessed by these materials. Besides the already mentioned fields, as photocatalysis [72, 123 - 126], sensor elements, [61, 127 - 129], electronic components [110, 130, 131], and alternative energy sources [99 – 101, 132], the titania based materials find many other applications for: photocatalytic decomposition of environmental pollutants [133 – 136], water purification and photodisinfection [137 - 140], photoelectrochromic devices [141], medical implants [142 – 147] or medicine carriers and for gradual release of active substances [148, 150], and even for corrosion protection [151]. The versatility of the TiO_2 based materials is demonstrated in Fig. 4.33, [152] where the variety of their application fields is schematically illustrated.



FIGURE 4.33 Fields of application of titanium dioxide solids [152]

Typical features of the spray pyrolysis methods

Advantages:

The basic advantage possessed by this group of methods is its exceptional versatility. Almost all inorganic materials can be obtained via spray pyrolysis either in form of powders or thin films. Other great advantage, typical for these methods is the simplicity of the necessary for spray pyrolysis production. In his work, Godbole et al. **[153]** have reported successful elaboration of nano-sized materials by "home made" equipment.

- Possibility for creation of entire assembled multilayered devices in the same installation.
- Potential capability for high productive installations.
- Possibility for continuous production regime.
- Ease quality control of the respective products.
- Relatively low energy demand, when direct flame is employed.

Disadvantage:

- Complications, related to obtaining of low temperature crystal allotropic forms.

Laser assisted high temperature methods

Theoretical backgrounds

This group comprises all methods for material synthesis, or posterior treatment including laser as energy source. The lasers can be described as sources of focused monochromatic light emission with negligible dissipation. The radiation of light emission without of notable deviation is known as *"collimation"*. The light by itself can be considered as an electromagnetic emission with dualistic wave-corpuscular inherent nature. Hence, the light propagates simultaneously as a flux of particles, known as *"photons"*, and waves with defined frequency and length. When the emission belongs to the infrared range, the energy carrier particles are known as *"phonons"*. The infrared radiations are inherent for all thermal processes, which theoretical description is not an object of the present Chapter. Hystorically, the discovery of the lasers delayed the theoretical concepts of their function by entire decades. The first theoretical ideas, related to this kind of light emitters are developed by Max Plank, and Albert Einstein at the beginning of XX century. The predecessors of the lasers, named "masers" discovered at 1951 almost simultaneously by Charles H Townes, from Colombia University; Alexander Prokhorov, and Nikolai G Basov from "Lebedev" laboratories in Moscow; and also by Joseph Weber in Maryland University (USA).

The first real laser has been elaborated by T.H. Maiman in Hughes Research Laboratories at 1960. His laser worked by illumination of rubi crystal by powerful tube lamps. Afterwards, numerous variants of lasers, such as follows **[154]**: The first helium neon laser has been developed by A.Javan, W.R. Bennet, μ D.R. Herriot, at 1961 in Bell Laboratories (USA).

The first semiconductor laser with GaAs as active emitting substance has been elaborated by R. Hall, at 1962 in General Electric Labs.

The first Nd:YAG laser is developed by J.E.Geusic, H.M.Markos, L.G. Van Uiteit at 1964, in "Alexander Bell" laboratories.

The first CO_2 gas laser emitting in the Infrared spectrum is developed by C.K.N. Patel, at 1964 in "Alexander Bell" laboratories.

The firs argon laser is elaborated by W. Bridges, at 1964 in Hughes Labs.

The creation of entire new generation of lasers with different emission media are object of development until nowadays. The term "laser" is just abbreviation of "Light Amplification by Stimulated Emission of Radiation". Unlike the usual light sources, the lasers are based on a derivative light emission from an active substance promoted by illumination by primer light sources. The primary light source irradiates a photon flux with considerable kinetic energy. When these photons collide with the particles of the active emitting substance, they render their kinetic energy, elevating the energy content of the valence electron configurations of the particles composing the active substance. After a defined time, the excited electrons fall back to the basic energy level, emitting secondary photonic emissions. The processes are shown in the next Figure:



FIGURE 4.34

Schematical illustration of the transitions between the basic and the excitised states of the active substance under illumination by primer light source ields of application [154, 155]

The transition between the ground and excited level happens by crossing of so called "forbidden zones", of energy levels, which remain inaccessible, because of the quantum nature of these energetic transitions. The theoretical bases explaining these energetic transitions, are related to the theoretical concepts, developed by Louis de Broglie, Max Plank, and Albert Einstein and do not relay to the purposes of the present Chapter. Nevertheless, it is worth to mention that the elemental units of energy are known as "*quants*", and they predetermine the allowed energy levels available for the energy transitions:

$$E_2 - E_1 = \Delta E = h V \tag{15}$$

Where: E_2 – is the energy content of the excited energy level, E_1 – is the energy content of the gound energy level; h – Plank constant, V – the frequency of the initial light emission.

The most important characteristic of the light emitted by the lasers, compared to this of the classical light sources is that it is in form of coherent beams that enter in interference among them. The coherent emissions coincide among, because of the possession of equal frequency and

phase. When two waves coincide between them a resultant wave appears, with double amplitude at the same frequency. This phenomenon is called "*interferention*" in the optics, or some times it is named "*resonance*", as is shown schematically in the next figure.



FIGURE 4.35

Schematic illustration of the interferation phenomens [154, 155]

Exactly, the ecxitation of the electrons by the kynetic energy of the photons, originated from the initial light emission is indication for the corpuscular nature of the light. It can be quantitatively determined by masures as *"light intensity"* and *"light power"*. Furthermore, the concepts for the cropuscular nature can be efficiently used for explication of phenomena, such as transition of the light across transparent bodies and its refraction from the non-transparent ones. On the other hand, the wave related inherence of the light appears by its frequencey and wavelenght, which stay in opposite proportional dependence between them. Exactly these two parameters determine the colour of given light emission.



FIGURE 4.36

Light spectrum and characteristic wave length (colors) of radiation and the basic types of lasers chematic

When a light beam toughes a surface of a solid body, it can absorb, reflect or transmit it. If the light emission is generated by a powerful laser, and the respective material is not transparent for the respective wavelenght then the material is submitted to intensive collisions by high quantity of photons which render their kynetic energy to the illuminated surface. Thus, the collisions happen accompained by energy transfer from the photons and the solid material composing particles. A part of the elevated energy content of the illuminated area converts to thermal energy, causing vibration of the structiral particles of the solid material in the zone of the illumination. Thus, temperature increase of the illuminated solid material can be registered. If the power of the laser light source is high enough to overcome the specific thermal capacity of the illuminated metarial, and also superior to the heat excange capability of the solid material, then a partial fusion and even an evaporation of the illuminated area can be observed.

Application of the lasers for high temperature synthesis and posterior treatment

From the previous section, became clear that the illumination by enough powerful lasers, for enough large time leads to elevation of the thermal content of the illuminated object surface, followed by partial fusion and subsequent evaporation. These effects can be used for thermal treatment of various materials. Among the methods applied for laser treatment, can be remarked some of the most widely used ones:

Laser drilling of apertures – This technique is widely used for engraving of information (on compact discs).

Laser cutting. This process can be described as a multiple subsequent drilling of adjacent holes.

Laser engravement – Various images can be obtained by making of pits in defined subsequence, either on the solid surface, or even in its bulk.

Laser welding – It is achievable by the simultaneous fusion of the contact surfaces of two or more details prior to their assembling, or staying in a mechanical contact during the illumination.

Laser machining - These operations are possible when a laser beam is used instead of steel cutting tools. In this case, the desired shape of the treated materieal is reached by controlled material removal through a partial evaporation, caused by the laser beam.

Laser assisted chemical synthesis – When the treated material surface is heated in defined points, or areas in defined gaseous or liquid medium, desired endothermal heterogeneous chemical reactions can be promoted between the material and its medium spatially limited only in the treated zones.

Superficial engraving - Every engine can be described as a conjunction of details with suitable shapes, enabling the possibility for transmission of various mechanical movements with direction, speed, acceleration, etc. predetermined by the constructive engineer. Besides the geometrical compatibility, among the corresponding details, these should be manufactured by sufficiently durable and resistible materials, in order to guarantee reliable long period exploitation of the resulting engineering construction. In this sense, each mechanical detail undergoes examination of its mechanical properties, such as resistance to chock, extending, shrinking, folding, twisting, etc. During the last decades, a serious attention was turned on the superficial properties of the respective details exactly in the zones of mechanical contacts among them.

It was established that the roughness is a key factor for the friction durability possessed by the corresponding details, in the zones of mechanical contact. Thus, during the 1980th decade of XX, century, besides by the average roughness value R_a and the peak density, a serious attention was turned on the superficial and cross-sectional morphology description of the contact zones. During

this decade, it has been established that more advanced techniques are necessary for obtaining of regular and uniform surfaces, then the simple sandblast grinding. Namely, the laser technologies have been appeared as the most appropriated for surface smoothing. Besides for esthetical purposes, these technologies have revealed as particularly efficient for reaching of exactly defined surface shape of pressing molds and rollers for posterior treatment of metallic panels for car bodies.

During 1982, high definition surface treatment have been elaborated for post treatment of metallurgical rolls through the "Lasertex"- technology **[156]**, which as its name shows, is based on direct exposition of the roll surface to impulse laser beam, interrupted by mechanically rotating mask, for achieving of a blinking effect.



FIGURE 4.37

Principal scheme of the installation of Lasertex treatments of rolls [156]

This technological approach has enabled high order superficial modification resulting in multiple pits at defined distances among them, and flat remaining surface with enhanced friction durability. These pits served as lubricant collectors during the steel tape rolling. Although this technique has revealed excellent results for lubricant retaining during detail extrusion, the traces of these pits on the treated by these rollers metallic surfaces revealed a detrimental effect on the shine reflection of the resulting details after their painting. This detrimental effect has been overcome by extending the distances among the holes, by decrement of the impulse frequency **[156]**.

Interior engraving - If a laser beam crosses a transparent for its wavelength body for relatively short period, any thermal effect should be not detected. This fact allows the use of glass lenses for focusing of the laser beams without of subsequent damages on the lenses.

Nevertheless, if in the bulk of such transparent body intersect two or more coherent beams then interference appears among them, resulting in multiplication of the resultant wavelength at the same frequency. Thus, the resulting amplified power in the intersection point is able to initiate a thermal effect capable to cause a partial fusion localized in this point. After the stopping of the laser beam impact, as a result of heat radiation from the affected intersection point to its

surroundings, the localized fusion become to re-crystallize again. Hence, by intersection of two laser beams a localized defect can be induces in the bulk of a transparent body. This method enables interior engraving inside a transparent body.



FIGURE 4.38

Schematization of the interior engraving of a transparent object O – Transparent object, M – point of materials fusion and posterior crystallization, ID – Induced defects

It is worth to note that it is preferred in the practice to use only one laser, with additional beam distribution optical system, able to divide the initial beam into several derivative beams. This practice enables ease maintenance of the coherence among the resulting beams and decreases the economical spends, related to the simultaneous use of several lasers. Besides, usually the optical laser beam fixing systems (able to divide the initial laser beams by semitransparent refractors) are composed by rotating refractors, in order to avoid thermal damaging due to of laser irradiation on one point of the refractor for a large time.

Laser assisted thermal treatment with shape modifications

Laser assisted optical glass fiber extusion - This technological operation is designed for extrusion of optical fibers from hollow or dense glass tubes. The predecessor of this technology was based on withdrawing of steel hooks preliminary immersed in the corresponding glass melt fused in a graphite furnace. However, the glass filaments produced by this manner, were usually contaminated by carbon particles from the furnace, leading to considerable optical losses. This deficiency, originated from the optical fiber contamination can be avoided, when the proposed in **[157, 158]**, laser assisted fiber extrusion is applied. This optimized method is schematically illustrated in **Fig. 4.39**.

The successful application of this method however demands additional optical systems for homogeneous laser emitted light distribution, in order to maintain a regular distribution of the resulting heat **[158]**. The uniform temperature distribution can be provided so by the heating of the entire workspace (by laser light refractors), so by synchronization between the velocities of the input of the glass tube (or stick) to the workspace (V) and the resulting fiber withdrawing speed (V1).



FIGURE 4.39

Laser assisted optical fiber extrusion from glass tubes (a) – laser beam heating zone, (b) – scheme of the glass fiber laser extruder

Production of glass pearls with micron and submicron scale - Another interesting application of the laser technologies is the production of spherical glass bodies, by laser fusion, with possibility for laser induced heterogeneous chemical surface modification. This method allows coincident glass spheres shaping with superficial composition modification by laser induced chemical reactions between the gaseous stream and the glass surface. Briefly, the method can be described as follows: a CO_2 infrared laser fuses the tip of spinning glass capillary or dense filament during its high speed (e.g. 9000 – 30.000 min⁻¹.) rotation combined with gradual replacement. Simultaneously, the laser beam treated area is submitted to a gas flux. As a result, the glass suffers fusion and the obtained fused drops are being repulsed by the gas stream, converting to hollow or dense balls due to the subsequent cooling. Furthermore, the gas flux enables additional separation of the obtained spherical bodies, as is well illustrated in **Fig. 4.40**.



FIGURE 4.40

Schematization of laser assisted glass pearls production

Deposition and modification of thin surface layers

The laser methods can be used for surface layer deposition and/or modification, at presence of gaseous or liquid medium with defined composition, as is shown in the next figure. Such processes can be performed even in presence of plasma (i.e. ionized gas), as is proposed in the literature. **[159, 160]**.



The next figure shows a thin film deposition in gaseous or liquid medium.

FIGURE 4.41

Scheme of scanning superficial treatment by laser irradiation in a gaseous or plasma medium (A), and in a liquid medium with coincident electrochemical reaction (B)

1.- laser beam, 2. – cantilever for simultaneous focusing of the laser beam and gas feeding, 3. – fixing lens, 4. – gas feeding tube, 5. – treated surface, 6 – substrate holder, 7. – liquid electrolyte, 8. – sample driving rods

Typical features of the laser assisted methods

Advantages

- Possibility for treatment of various kinds of materials

- Possibility for synthesis and posterior treatment of the materials so in their surface, so in their interior.

- Possibility for continuous production process.
- Possibility for ease control of the process temperature by impulse laser radiation [156, 161].

Disadvantages

- Requires a specialized equipment (i.e. powerful lasers).

Vapor and gas phase methods for synthesis and deposition

Theoretical backgrounds

Usually, it is incorrectly accepted that the water boils only at 100 B C, irrespectively that the pressure on whatever liquid is capable to change completely its boiling point. Hence, the pure water boils 100 B C, only at atmospheric pressure, while its boiling point decreases with the pressure applied on its surface. Similar pressure dependences of boiling points from the pressure are observable for various liquids (fusions or solutions.).

These vapor deposition methods are based on thin layer deposition by evaporation and subsequent condensation of metal fusions in conditions of deep vacuum.

It is worth to note that the term "vacuum" actually means a presence of gaseous medium with lower than the atmospheric pressure.

Basic groups of vapor deposition methods

A large variety of applications of this group of methods exists, and also it is permanently extending, through new patents in both directions of elaboration of new equipment and deposition of new compositions with advanced characteristics. The vapor deposition methods can be divided into two basic groups, distinguishable between them by the presence of absence of chemical conversion reactions during the deposition process.

Physical Vapor Deposition (PVD) methods – The film deposition in their cases proceeds at lack of chemical conversion reactions between the evaporated components and the diluted gaseous medium. Thus, the chemical composition of the deposited film is identical to this of the initial precursor vapors.

Chemical Vapor deposition (CVD) methods – These methods include chemical conversion reactions as an intermediated stage, so that the chemical composition differs from this of the evaporated initial precursors. This group of methods allows the obtaining of compound layers, such as metallic nitrates, chlorides, nitrides, oxides, etc.

These methods can be realized by use of various heat sources, necessary for the precursor evaporation. Thus, according to the heat source, these methods can be classified as follows:

- Electrical resistance supported vapor deposition In this case, the initial precursors are being fused in crucibles, mounted in holders, assembled with electric resistances. Thus, the heat necessary for precursor evaporation originated from the electrical current, according to the Joule - Lenz Law.
- Laser assisted vapor deposition Here, the precursor fusion and evaporation is a result of direct laser beam illumination.
- Plasma ignited vapor deposition Here, the gaseous medium is submitted to ionization, and the resulting high temperature plasma interacts with the precursors, causing their fusion and evaporation, combined by additional ionization. These methods can be additionally subdivided, taking in account the variety of plasma ignition approaches, already described in the previous sections.

Classical physical vapor deposition of thin refractive

Principally, the deposition process can be divided into several basic stages:

- 1. Precursor fusion,
- 2. fused material evaporation,
- 3. diffusion of the obtained vapors in the low pressure gaseous medium,
- 4. vapor ionization (only for plasma ignited variants),
- 5. chemical conversion reactions (these can occur also after the initial film deposition, and they are typical only for CVD),
- 6. deposition on the substrates. Technologically, the classical bell-chamber vacuum evaporator, illustrated in **Fig 4.42** works with cyclic regime.



FIGURE 4.42

Schematic illustration of classical bell vacuum assisted deposition installation 1 – bell, 2 – substrates, 3 – deposited coatings, 4 – crucible, 5 – precursor melt, 6 – electrical heater, 7 – sealing ring, 8 – valve for pressure restoration after the deposition, 9 – thermocouple, 10 – manometer for under pressure

Thus, each cycle consists of four subsequent procedures:

1. Loading – it needs four operations: removal of the bell, loading the substrates and the initial precursors and switching on the vacuum pump.

2. Work stage – it becomes with initiation of the precursor heating after the reaching of necessary underpressure;

3. Empting – this procedure becomes when the required film thickness is already achieved, or after the evaporation of the entire precursor quantity. It begins with subsequent switching of the heat source, and the vacuum pump followed by slow opening of the atmosphere equilibration valve. The bell removal is possible only after the reaching of room temperature and atmospheric pressure.

4. Preparation for the next cycle - it includes the removal of the precursor crucibles and the treated substrates followed by cleaning of the apparatus interior. It is very important to note, that the procedures 1 and 3 are related to high probability for implosions, if the vacuum is quickly reached, or explosions, when the valve is sharply opened.

Internal Vapor Phase Oxidation

Another alternative of the vapor deposition methods, developed for internal layer deposition inside hollow tubular bodies, named "*Internal Vapor Phase Oxidation* (IVPO)" is elaborated in Bell Telegraph and Telephone Company at 1974 **[162]**. It is schematically represented in the figure below:



FIGURE 4.43

Schematic Illustration of the Internal Vapor Phase Oxidation – (IVPO), for internal optically active layers in tubular substrates 1 – deposited layer, 2 – quartz tube, 3 – precursor injection nozzle, 4 – White smut particles, 5 – burner, A – precursor inlet flow, B – exhaust gases salida, C- Oxidant (oxygen) inlet flow

This method enables internal layer deposition in the internal space of a quartz tube, combined with simultaneous chemical conversion of the gaseous precursors into a solid state internal layer. The internal layers deposited by this manner possess equally distributed composition, structure and thickness, combined with remarkable adhesion to the tube walls. These characteristics are consequence of the high control level provided by this method. The high parameter control level is possible because the high temperature, necessary for the synthesis/deposition process is localized in a defined location, during the entire process. During the deposition process, the quartz tube performs rotation with a constant angular speed, combined with slow movement away towards the precursor spreading nozzle (3). The speed of the tube rotation depends on the desired film thickness, the precursor flow rate, and the tube diameter. During the deposition, the tube can be ventilated by gas flows through the tube. The regulation of the work temperature values and location (i.e. the surface area occupied by the optimal process temperature) can be additionally controlled by the gas ventilation of the tube during the deposition process. Besides, the ventilating gases serve as oxidation agents, but these can be used as chemical composition modifiers, regulators of the subsequent film cooling (predetermining the film crystallinity rate), its morphology, etc. The gas flow rates are in the order of 1.5 dm^3 /min.

The work temperature is provided by an external burner, which can stay fixed regarding the gas nozzle, or to perform forward/backward movements in parallel to the tube axel direction, providing additional annealing of the already deposited layer. It is supplied by hydrogen and oxygen. The labour temperature can be controlled by the burner combustible supply, the distance between the burner and the tube, and also by the system ventilation. The film thickness can be further increased by multiple repetition of the deposition process, enabling even gradual variation of its composition and structure (by gradual change of the deposition parameters, among the cycles) until complete filling of the internal cavity of the tube, if it is necessary. This method, also known as "white smut deposition" is used for deposition of ultra-thin porous layers of metallic oxides halogenides and chalcogenides. The multiple repetitions combined by appropriated annealing enables formation of dense layers with desired optical properties, such as refraction index, transparency, etc. The obtained double layered hollow tubes, are an intermediated product, which can be submitted to further thermal treatments, by hot extrusion in order to obtain optical fibers. This posterior thermal process proceeds in graphite tubular furnaces, in order to render the necessary plasticity for extrusion of the double layered solid tubes, described above.

As a result of the scientific and technological progress, this method has been further improved, converting to plasma assisted deposition, two years later **[163]**. The modified version of this deposition technology is based on presence of plasma, obtained by ionisation of the ventilation gases (in this case oxygen - argon mixture). The advantage of this improved method is obvious taking in account that the plasma can be formed by ionization of only one gaseous precursor, unlike the combustion process which requires at least one oxidant and reducer (i.e. combustible). Thus, apart the fact that almost the same processes occur in both the basic and the improved deposition methods, the latter is much faster, since the already formed plasma occupies entire surface area of the quartz cylinder, in form of ring, on the internal surface of the quartz tube walls, surrounding the nozzle. Supplemental advantage of this modified deposition approach is that it does not require any tube rotation, since the plasma occupies the entire diametrical surface of the tube, near the nozzle. Hence, the burner here is substituted by a metallic ring, which is charged by a high frequency AC generator, supplying AC currents with 4.5 MHz of frequency. The length of this ring predetermines the length of the high temperature treatment zone of the tube.



FIGURE 4.44

Improved microwave plasma assisted IVPO- process 1- tubular furnace; 2- tubular quartz substrate, 4- plasma ingnition ring; 5- microwave plasma, 6. precursor supply nozzle

Thus, the high frequency of the electrical charge current induces microwave electric field, necessary for the high temperature required for the gas ionization. Because the area occupied by the plasma is fixed and predetermined by the external metallic ring, a white smut layer forms, which thickness is predetermined by the solid internal surface of the quartz tube, the gases imparting the plasma (e.g. the vapors of metallic halogenides, the ionized plasma forming gas, etc.) Several processes occur in the plasma occupied zone: gas ionization, heterogeneous oxidation and gas transport, resultant solid fraction deposition, superficial diffusion, and layer densification, heat exchange phenomena. After the crossing the high temperature zone, the gases are being evacuated by a vacuum pump, mounted at the opposite of the gas feeding face of the quartz tube. This improved technological approach results in removal of additional combustion and the respective combustible demand, and denser layer deposition with uniform thickness distribution. The elevated density and uniform thickness of the obtained by this manner films are result of the equal radial distribution of high temperature area. In addition, the plasma assisted version enables much higher productivity, since the high temperature zone is not fixed on located areas of the quartz tube surface, combined with lower energy demands, because it demands neither tube rotation mechanisms, nor combustible expense. This modified technological approach is followed

by the same posterior high temperature extrusion processes, in order to obtain initially thinner double layered dense glass sticks, and afterwards subsequently extruded optical fibers.

These methods appear to be difficult for continuous industrial production regime, resulting in limitations of the production amount in general terms.

External Vapor Phase Oxidation

This method known as "Outside Vapor Phase Oxidation Deposition" (OVPO) **[164, 165]** can be considered as alternative to the described in the previous section internal vapor phase oxidation for production of double layered tubular details, by layer deposition on the exterior surfaces of the tube walls. The chemical reactions occurring during the process can be described as follows:

$$MeX_{2n+}n/2O_{2} \rightarrow MeO_{n} + nX_{2}$$
(16)

By technical point of view, this method can be described as combination between spin coating and chemical vapor deposition. **Fig. 4.45** shows schematically the corresponding equipment:



FIGURE 4.45

Improved Schematic Illustration of the External Vapor Phase Oxidation – (EVPO) 1. – bearings, 2. – burner, 3. – spray nozzle, 4. – nozzle moving mechanism, 5. – tubular substrate, 6. – already deposited layer

This method enables also film application on dense cylindrical bodies, when the burner is mounted beneath the cylindrical substrate. Besides, this approach enables additional temperature control by change of the distance between the substrate surface and the burner flame.

Crystal growth by layer-by-layer mono-crystal deposition (Method of Fritsch)

This method is developed by Fritsch at 1935, **[166]** and carries the name of its inventor. Although the method is elaborated for monocrystal growth via gradual layer-by-layer deposition of ZnO from Zn metallic vapors and preliminary heated oxygen, it allows to be adopted for thin layer deposition. Variations of this method have intensively developed during the 1960th years, after the discovery of the piezoelectric properties, possessed by this oxide. This method has been developed as a response to the difficulties, related to mono-crystalline ZnO formation, especially in presence of Fe

and Mn contaminants in the composition of the initial Zn precursors. These additional elements deteriorate significantly the structural ordering and the resulting properties of the produced ZnO crystals, limiting their application in the industrial practice. The entire technological cycle includes two basic synthesis stages – which can be simultaneously performed, if these are apart in separated work-spaces. In the former furnace, metallic zinc is submitted to evaporation at 750 °C, and inert gaseous medium, whereas in the latter one, a chemical conversion reaction proceeds between the Zn vapors and the preliminary heated oxygen at 1350°C, combined with solid ZnO fraction deposition on the substrate surface.

The layer deposition coincides its crystallization on the substrate surface (in the classical case – the ZnO crystal nucleus) or the already deposited layers of the same material. In this case, the crystal nucleus surface serves crystal growth base, since each new layer completes the incomplete superficial elemental cells, or creates new ones. Hence, the obtained mono-crystal possesses the same orientation axel as the initial nucleus. This approach is also often called *"film deposition by epytaxial layer growth"*. In other words, the nucleus predetermines the orientation of the resulting mono-crystal, because the crystalline lattice geometry serves as a matrix for each consecutive deposited layer formation during the crystal growth. Hence, the structure of every layer is predetermined by the previous one, and on its turn defines the next layers structure.

Chemically the layer deposition can be described by the following equation:

$$2Zn(g) + O_2(g) \rightarrow 2ZnO(s). \tag{17}$$

This reaction is endothermical and coincides the phase transition from the gaseous precursors to solid state product. It is a typical example for oxidadtion/reduction process, where:

$$2Zn^{\circ} - 4e \rightarrow 2Zn^{2+} \qquad \text{is the reducer} \qquad (18)$$
$$O_2^{\circ} + 4e \rightarrow 2O^{2-} \qquad \text{is the oxidant} \qquad (19)$$

The temperature required for the melting, evaporation or direct sublimation of the inicial metallic Zn precursor is provided by electrical resistance heaters. In order to prevent any undesirable deposition on the internal surface of the connector tube between the furnaces, a supplemental electrical heater is mounted. Since this tube is thinner than the chambers, that it connects its surface is relatively larger for unit of volume, and loses more heat due to the heat exchange with its surrounds. That is the reason for the additional heater demand. The entire ZnO synthesis/deposition system is depicted in **Fig 4.46**. It can be inferred that the entire technological process comprises four composing processes:

- 1. precursor evaporation,
- 2. vapor oxidation,
- 3. deposition, and
- 4. crystalline film growth.

The latter three processes occur on the substrate surface, whereas the precursor evaporation and the preliminary oxidant heating proceed in other work spaces, before them.

Since all the processes described above proceed subsequently, the evaporation of the solid Zn metallic precursor appears the rate limiting stage for the overall deposition process. It depends on several factors, such the precursor inherence (e.g. its melting point, exposed active surface area,

etc), as well as on its environment conditions (i.e. gas flow temperature, pressure and speed). These conditions inside the precursor evaporation chamber can be regulated by the inert carrier Ar gas current speed. It can be efficiently driven by vacuum pumps connected to the exhaust gas tube. The oxygen flow minimal value depends on the Zn evaporation intensity, in order to obtain stoichiometric ZnO crystals. The method described here enables modifications allowing deposition of pure metals in inert gas media, semiconductor crystals with induced ion deficient point defects (by variation of the ratio between the metal vapors and the oxygen quantity) and production of various semi-conductors such as PbS, using S-vapors, SO₃, N₂, or NO₂, J₂, F₂, Cl₂ alone, or in gas mixtures. The method allows various optimizations and modifications, for instance use of mixed metals precursors, various gaseous mixtures, alternative heat sources (such as plasma, lasers, etc.).



FIGURE 4.46

Scheme of chemical oxidation accompanied ZnO crystal growth by method of Fritsch

1– exhaust gas tube, 2– reaction/deposition furnace; 3– reaction chamber; 4– Zn – O_2 gas/vapor mixing chamber; 5– additional electric heater; 6– Zn-precursor evaporation chamber; 7- Evaporation furnace; 8- preliminary gas heating chamber; 9- inert Ar-carrier gas inlet; 10- Zn melting crucible; 11- crystal nucleus

Chemical vapor synthesis of fine dispersed powder materials

An alternative manner for vapor involved synthesis of powder like silicon nitride Si_3N_4 is represented in **Fig 4.47.** This is an example for synthesis by preliminary passing of gaseous precursor through a liquid fusion with posterior chemical conversion reaction. Thus, one of the precursors (i.e. SiF_4) enters in the reactor via blowing through a liquid of metallic silicon fusion. By that manner, this precursor promotes elevation of silicon vapor content inside the reactor. Thus, the resulting gaseous mixture consisted of SiF_4 , abundant by Si vapors, enters in direct reaction with gaseous ammonia, resulting in formation of Si_3N_4 powder which falls on the reactor bottom.

In order to intensify the synthesis process, the reactor is designed by such a manner that provides opposite directions of the gaseous precursors, which collide between them, forming a reaction front at given zone of the reactor, elevating by this manner the reactor production capability. In these conditions, the chemical conversion synthesis reaction rate reaches 2.9 to 0.9 seconds per mol. The role of the additional inert carrier gas is to facilitate the maintenance of the technological

regime conditions. The reaction temperature is about \approx 1300 °C. At this temperature, the synthesis process proceeds with simultaneous ammonia decomposition, necessary to supply the nitrogen precursor. The reactor illustrated in **Fig 4.47**, enables coincident desired product fraction separation from the exhaust gases, since the former drops on the apparatus bottom, under the force of its own weight.



FIGURE 4.47

Scheme of reactor for powder materials synthesis by interaction between gases and metallic vapors 1 - generator of Si- vapor enriched SiF₄, 2 - graphite reactor, 3 - Zone of thermal decomposition, 4 - gas fraction transport tubes, 5 - Internal tubular workspace, 6 - External tube (reactor body)

Besides, the hot exhaust gases pass through the space, enclosed between the internal and the external cylinders (composed by SiC /A_{I2}O₃ ceramic composite) prior to leave the reactor, providing a partial recuperation of the heat energy, expensed for their heating, increasing the production process energetic efficiency. When Si metal-organic compounds are used as precursors, the respective obtained products of this method are in form of fine dispersive spherical particles, composed by Si3N₄ + SiC (SiC_xN_yH_z). The work temperature can vary in the range between 1100 and 1300 $^{\circ}$ C, depending of the synthesis reaction, and the precursors involved. In general, the Vapor Phase Oxidation (VPO) based technologies are very convenient for production of amorphous oxide powders for the needs of the hi-tech ceramic industry **[167, 168]**.

Typical features of the vapor deposition methods

Advantages

Possibility for layer deposition with uniform distribution thickness, density, structure, and composition.

Disadvantages

Impossibility for application in continuous production regime, limiting the production amounts of the respective products.

Hazards, related to implosion in the case of classical bell vacuum installations.

Demands for specialized equipment (vacuum pumps, etc.).

Hydrothermal and solvothermal methods for nanomaterial synthesis at high pressures

Basic concepts

When a liquid is submitted to a gradual temperature rising, it becomes evaporate intensively, until reaching of a temperature at which it becomes to boil. This temperature is known as "boiling point", and possesses specific value for each liquid substance, or solution. Although at atmospheric pressure, the boiling point owes a constant value, predetermined by inherent nature of the corresponding liquid substance, each liquid is able to boil at lower or higher temperatures, depending on the pressure of the gaseous phase above its surface. Thus, when water is exposed to higher than the atmospheric pressure it can remain liquid at higher temperatures, than 100 °C. At such conditions of very high temperature and pressure dissolution of principally insoluble compounds becomes possible. This phenomenon is well known from the geological sciences [169], and explains the existence of various crystalline rocks and minerals, formed by exposition to hot water at very high pressure. Thus, the synthesis of solid materials by precursor exposure to liquids at very high pressure, known as "solvothermal" or "hydrothermal" method is widely used for growth of massive monocrystalline materials, such as quartz crystals for high performance optical devices. Indeed, the dissolution of quartz in water is observed by Zhang et al. [170] at 374 °C and 23 MPa. In order to intensify the quartz dissolution in aqueous medium, other authors have preferred to apply even harder conditions: temperature range between 500 and 900 °C, and pressures from 100 MPa, up to 1 GPa [171]. Such conditions are possible inside thick wall, hermetically encapsulated reactors, known as "autoclaves". Figure 4.48 illustrates such an autoclave for industrial application.

Obviously, the stirring enables intensification of the dissolution process, but it is related to technical inconveniences, originated from the necessity to assemble electric motors in rather severe conditions. In the classical variants, the liquid flowing inside the autoclave is supported by temperature gradient inside the liquid bulk. This gradient appears when the electrical resistance heater is mounted near the autoclave bottom and additional coolers are mounted near the autoclave walls. By this manner, the liquid surrounding the heater creates upward flow, and when it reaches the liquid surface it inverts its direction being pushed by new quantities of hot stream, and pressed by the vapors above the liquid surface. Afterwards, this stream spoils the relatively cooler internal surface of the autoclave walls, forming downward cool stream. Namely, these phenomena are successfully used for mono-crystal growth of quartz [172 - 174], titanates [175], oxides of rare Earth elements [176], etc. In the case of crystal growth, the autoclaves require loading by special crystal nuclei, near the liquid surface, in order to initiate controlled crystal growth.



FIGURE 4.48

Schematic illustration of industrial autoclave

1. – autoclave bonnet, 2. – autoclave body, 3. – sealing gasket, 4. – exterior thermal insulation, 5. – internal protective layer; 6. – temperature controlling serpentine, 7. – liquid solution, 8. – electrical heater, 9. – initial precursor sediment

Recently, alternative applications of the hydrothermal/solvothermal synthesis have been elaborated. In this sense, Nazarkovsky and co. **[177, 178]** has successfully implemented this method for nanoparticle synthesis of doped titania/silica photocatalysts. Besides, the solvothermal method is also proposed **[179 - 181]** for thin layer kesterite deposition for solar light based alternative energy sources.

Typical features of the hydrothermal methods

Advantages

Possibility for synthesis of materials with uniform structural and compositional distribution Possibility for production of massive mono-crystals

Disadvantages

Impossibility for application in continuous production regime, limiting the production amounts of the respective products.

Potential explosion hazards, related to the high pressure demands of the method. Besides, at too high temperatures, the water molecules in the vapor phase are able to decompose, enhancing the possibility for chemical explosion.

Nanomaterials synthesis via high temperature treatment of sol-gel derived materials

Basic concepts

This group of methods is not a typical representative of the high temperature methods, since a large variety of low temperature products can be produced via sol-gel method. Nevertheless, these methods can be used in conjunction with posterior high temperature treatments, in order to obtain sol-gel derived ceramic nanomaterials. The gels can be described as colloids, composed by polymeric matrix with equally distributed liquid phase in its bulk **[1]**.

All technologies that comprise gel formation as intermediate or finishing stage can be considered as "sol-gel technologies". Despite the relatively large history of the research activities on the sol-gel methods and corresponding gel materials [182], the sol-gel methods have become object of greater interest during the recent decades. The main reason for the undervaluation of the sol-gel methods during decades originates from the peculiar difficulties, related to the obtaining of massive monolithic bodies and thick films, as consequence of the gel cracking during the gel drying process. However, the recently increased interest to the sol-gel synthesis of various materials has been promoted by the significantly extended diversity of metal-organic hybrid precursors, and additives, such as detergents, surfactants and other chemical compounds, provided by the nowadays chemical industry. Another favoring factor for the increased interest on this group of methods is the tremendous variety of the possible nanosized materials able to be obtained in laboratory conditions by the sol-gel road. Indeed, the sol-gel method has enabled the synthesis of entire new generations of organically modified inorganic materials and completely hybrid materials, as was mentioned in the introduction of the present Chapter. The great variety of these substances has imposed the need to be classified as entire self standing classes, as is mentioned by Haas and Rose [3]. Mackenzie and Bescher [183] mention that these new classes of materials have been initially named "Organically Modified Silicates", (ORMOSIL) by Shmidt (1983) [184] and Wilkes (1984) [185]. These materials are the first representatives of much larger class of materials, named "Organically Modified Ceramics", (ORMOCER) [3, 186 - 188], including in-situ synthesized composites and nano-composites [5, 80 – 83]. Examples for successful synthesis of amorphous (vitreous) materials also can be found in the literature [190 – 195]. In this sense, Gaur et al. [196] remark the undoubted advantages of the sol-gel method for preparation of modified titania products, especially the possibility for addition by large diversity of dopants, which can be successfully added to the basic O - Ti – O matrix, and the simple equipment demand. Indeed, the remarkable variety of TiO₂ derived nano-materials is demonstrated in the literature [152] and shown in the next Figure:



FIGURE 4.49 Natural and artificial titanium dioxide solids [152]

The synthesis of titania based materials via the sol-gel method, from metallic alkoxides comprises two main processes: hydrolysis of the initial Ti-precursors, and subsequent polymerization of the hydrolyzed radicals, as is proposed by Samuneva et al. [197]. These processes can be described as follows:

- Hydrolysis:

 $\begin{array}{ccc} \text{Ti}(\text{OC}_4\text{H}_9)_4 + 4\text{H}_2\text{O} & \rightarrow & \text{Ti}(\text{OH})_4 & + & 4\text{C}_4\text{H}_9\text{OH} \\ \text{Tetrabuthyloxytitanate} & & \text{tetrahydroxititanate} & & \text{buthanol} \end{array}$ (20)

- Polymerization:

$$nTi(OH)_4 \rightarrow (TiO_2)n + nH_2O$$
(21)
titanate ceramics

As can be inferred from the review papers, **[197 - 202]**, the authors of the majority of publications devoted on sol-gel synthesis from metallic alkoxides preferred to use Si-alkoxides in order to obtain silica containing hybrid materials, since there is a large variety of silicon metal organic hybrid precursors, because the organic moieties of the Si-precursors enable to control and modify the composition and structure of the obtained hybrid metal organic polymeric matrixes **[201, 203 - 205]**.

$$OR - Si - OR + H^{O} + H^{O} OR + H^{O} OR + OR - Si - OH + ROH^{(22)}$$



Alternative manner to manipulate the resulting solids is possible by formation of composite structure, via in-situ involvement of solid powder ingredients in the initial sols **[3, 80 – 82, 206]**. That is the manner for preparation of composite materials with remarkably extended mechanical and wear strength, since the involved powder material serves as reinforcing phase. Besides, the addition of powder materials to the sol-gel system enables gel cracking suppression during the gel drying process. Another direction for development of new generations of sol-gel derived materials is the addition of detergents and surfactants to the initial systems, in order to manipulate the particle ordering in the initial sols, predetermining by this manner both the structure and the morphology of the obtained products.

Besides Ti- and Si- derived materials, a great number of inorganic and hybrid materials can be obtained by variation of the metallic cations of the initial metallic organic precursors. Indeed, more than 40 elements included in the compositions of various sol-gel derived products are listed by

Dislish [207]. Nevertheless, recently the number of the elements suitable for new material elaboration has been restricted by the environmental restrictions [115, 116], predetermining the actual trends in the material selection for sol-gel precursors. Besides the already mentioned Ti and Si metal organic compounds, Ce and Zr become an object of increasing interest. Especially the cerium containing substances has been examined as an efficient substitute of the apparently toxic Cr(VI) compounds [80 – 82, 208, 209] as an active corrosion protective ingredient of sol-gel derived coatings. Furthermore, Ce-compounds encounters extending interest for potential application for sensor elements [127 – 129, 210 - 215], alternative energy sources [216 - 223], etc. The interest to the cerium compounds as ingredients of various sol-gel derived materials will undoubtedly increase, because of its beneficial effect, on the polymerizing processes established by Suegama et al. [224]. The inherence of this positive effect can be explained taking in account the additional densification of the obtained gels, due to the chelating capability of the metallic ions, as is proposed elsewhere [225] (fig. 4.50).



FIGURE 4.50

Schematic presentation of metallic chelating bridging among the polymer chains **[225] M** – means whatever metallic ions

Finally, it is worth to mention that that the the addition of $Ce(NO_3)_3$ or $Ce(NO_3)_4$ [129, 213, 215] remarkably decreases the initial sol pH values, so that these precursors combine two functions: as Ce(III)/CeCe(IV) providers and acidic hydrolysis catalysts. Later, the same authors have established similar effect for diammonium hexanitrocerate $(NH_4)_2Ce(NO_3)_6$ [128], as well.

Another factor of great importance for the sol-gel derived materials is the composition of the organic moieties of the metallic alkoxides used, since it renders a great impact on both the composition and structure of the obtained materials, predetermining their properties. The organic radical's length influences the flexibility and the elasticity of the obtained gels **[203]**, as well as the porosity of the resulting products after sintering **[204 - 206]**. The use of metal organic precursors with relatively larger organic chain length allows overcoming the gel cracking problems during the drying process, enabling preparation of materials with uniform and regular structural distribution. Besides, when the aim is the synthesis of nano-sized fine dispersive products, the organic moieties of the alkoxide precursors define the resulting powder particle size **[227 - 229]**.

When the organic moieties have active groups, such as -COOH -HCO, $-NH_2$, etc, the polymerization process can be performed by chemical bonding among these active groups, as is proposed in the literature **[223, 227 - 230]**. The most famous example for gel formation by polymerization of organic compound is the so called "citrate method". It is developed by Pechini on the basis of

polyesterification of citric acid and ethylene glycol **[231]**. Finally, it worth to note, that prior to undertake any experimental activities, the researchers should consider the environmental restrictions **[117]** corresponding to the use of volatile organic compounds.

Technological aspects

As was mentioned in the previous section, the sol-gel methods are based on conjunction between precursor hydrolysis for obtaining of sols, and subsequent polymerization of the already hydrolyzed free radicals, resulting in gel formation. Since these processes occur almost simultaneously, considerable difficulties usually appear, related to formation of products with desirable properties and uniform structural and compositional distribution. Sometimes, undesirable precipitation of some of the precursors is observable at defined medium pH values. Nevertheless, this phenomenon could possess a beneficial effect, because the controlled partial precipitation can be efficiently used for in-situ composite material formation during the sol-gel synthesis. Indeed, the precipitation of metallic alkoxides is described in the literature as a room temperature method of synthesis [232]. Also, Hayakawa et al. [192] have demonstrated that the controlled precipitation of some of the ingredients during the sol-gel synthesis is able to be successfully implicated for modification of the optical properties of the obtained products. Other problems relied to gel cracking during the subsequent drying arise, as well. In order to avoid the production of strongly ruptured products, the drying should be performed at moderate conditions, demanding usually a large time extending of the drying process. However, the gel cracking could possess also beneficial effect, when fine dispersed nano-materials are desired. Even direct combustion of freshly prepared gels is also proposed in the literature. Another example for positive effect of gel film cracking is described in the literature [127, 129, 213, 215]. In these cases, the film cracks provide appropriated conditions for enhanced humidity adsorption, and subsequent capillary water condensation, improving remarkably the obtained humidity sensor properties.



The sol-gel process includes several main stages, as is shown in the next figure:

FIGURE 4.51

Schematic presentation of the basic stages of the sol-gel synthesis process 1. – Initial gel formation, 2. – gel drying, 3. – finishing high temperature treatment The entire production process via sol-gel synthesis method can be divided into three main stages:

- 1. Initial gel formation,
- 2. gel drying,
- 3. finishing high temperature treatment.

The practical execution of the sol-gel synthesis process requires fine control of various process parameters, such as:

- (i). Chemical composition of the liquid medium;
- (ii) chemical composition of the precursors (alkoxides)
- (iii) Molar factor (ratio between the alcohol, and the alkoxides);
- (iv) pH of the medium;
- (v) Presence of additives (such as free metallic ions, detergents, etc.);
- (vi) Temperature (in both stages gel formation and posterior gel drying);

(vii) - Pressure and chemical composition of the gaseous medium over the gelling system during the dry (annealing) process.

One of the basic trends in the sol-gel synthesis is the simultaneous structural, compositional and morphological modification of the sol-gel derived products via coincident presence of more than one alkoxide. This approach allows self assembling of the respective ingredients, manipulation of the product porosity after sintering (by alkoxides with different aliphatic chains, which burn or decompose during this stage), or by coincident hydrolysis of alkoxides of different metals. When two or more alkoxides are submitted to hydrolysis, always the difference between their hydrolysis rates should be considered, as is mentioned by Lopez et al **[225]**.





Schematic presentation of the sol gel process at coincident occurrence of two alkoxides [225]

Typical features of the sol-gel synthesis method

Advantages:

Versatility – A great variance of products can be created via sol-gel method, including biocompatible products **[233, 234].** This method stays on the basis of the synthesis of entire generations of new products, such as ORMOSILs and ORMOCERs.

Possibility for great structural, compositional and morphological modifications, since various factors can be varied, predetermining the features of the obtained products.

Disadvantages:

- Great time expense for correct gel formation

- Difficulties related to the control of the synthesis parameters, resulting in the repeatability of the obtained products properties.

- Difficulties corresponding to the obtaining of crack free products. The drying of the obtained gels should be performed at moderate conditions, with control of the gaseous medium composition and pressure.

Conclusions

The performance of every industrial product is directly related to the characteristics of the respective composing materials. These characteristics predetermine the entire performance of each material at the corresponding conditions of its exploitation. Thus, the conjunction between the exploitation conditions and the properties of the respective materials predetermine their durability, resulting in the reliability of the corresponding industrial product. Thus, each material is able to reveal its mechanical, magnetic, electrical, optical, etc. properties, only when it is submitted to the appropriated conditions (such as mechanical tensions, magnetic fields, electrical charge, or illumination, as well as the environmental composition temperature and pressure). On the other hand, both the combination of properties possessed by given material, and its capability to remain them unchanged for large periods of exploitation (i.e. its ageing resistance) are entirely predetermined by the technological regime applied for its production. Namely, the technology applied completely predetermines the structural (crystallinity, porosity, etc.), compositional (organic, inorganic, hybrid, etc.), and morphological (roughness thickness, etc.) features of the obtained products. The industrial production technologies may be considered as specific conjunctions of production methods and conditions. In this sense, the present chapter is an attempt for brief description of the basic classical and modern high temperature nano-material production methods with industrial large scale production capability. Besides, the description of each method is supported by examples from the literature. Here, it is worth to note that there is inherent difference between the laboratory research activities, based on examination of the properties of newly elaborated materials, and the scale-up activities related to development of respective suitable technology with optimal efficiency, and production capability. Thus, the advanced material development and the elaboration of optimized technological regimes for efficient industrial production are completely different aspects of the nowadays R&D activities. The difference between these aspects often imposes the need for collaboration among specialists from different scientific and engineering fields, who have sometime, completely different competences about the material inherent features and the nature of the physical, chemical and the mechanical processes involved in the material production and subsequent product exploitation. Nevertheless,

recently common trends have arisen, related to general material and energy spends reduction, decrease of the number of intermediated production stages, and also the time, materials and energy employed in a unit of final product (e.g. mobile telephones, computers, etc.). These trends are further favored by the permanent endeavor for life quality improvement by extension of the economical accessibility to high tech products, by lowering of the economical expenses for their production, and increase the production capability of the respective industrial plants. Besides, the constant rise of the human population imposes new challenges for the modern industry, because the sustainable community development obviously demands sharp reduction of the energy consumption, combined by environmental restrictions regarding the implication of some heavy metal elements, and volatile organic contaminants. Hence, although the tremendous variety of chemical precursors supplied by the modern industry their number is going to be restricted due to environmental considerations. These considerations lead to extended research activities on compounds of Si, Ti, Ce, Zr, C, etc, in order to substitute other elements as Pb, Cd, Co, or Cr. The same trend is established in the field of the organic substances, where toxic compounds are being intensively replaced by biocompatible ones. Finally, it is expectable that the further trends in the technological regime improvement will be related to invention of combined high temperature methods of synthesis, comprised by simultaneous implication laser radiation, gas charge plasma, magnetic fields, sharp pressure and temperature changes, etc, enabling the coincident proceeding of several process in the same work-space, decreasing the time, energy and material expenses for unit of final product.

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