

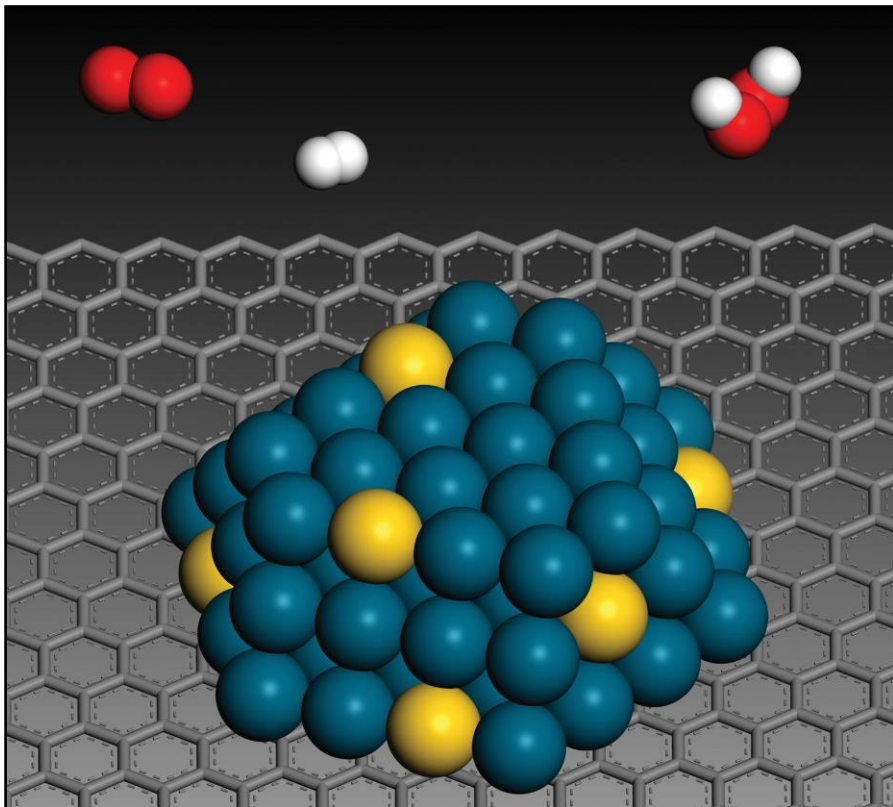


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# ***production processes***

## ***Nanoparticles***



## 1.1 Summary Strategies

Before studying the various nanoparticle synthesis processes necessary to say a few words on the criteria used for classes defined the various synthesis strategies.

There are two types of approaches to the production of nanoparticles which differ in their conceptually: there are top-down processes in which one starts from massive material and then obtain the nanoparticles and bottom-up processes in which the nanostructured materials are built "molecule by molecule". In other words, top-down approach we start from the bulk that worked in various ways from origin to nanoparticles while bottom-up approach is part of the basic constituents in order to obtain nanoparticles with special chemical processes and physicists.

### 1.1.1 Approach to the production of nanoparticles

As we told you can have two types of approach to production of nanoparticles can be from micro to get to the nano (top-down) or from the information to obtain nanostructures (Bottom-up)

#### 1.1.1.1 Top-Down Strategies

In this type of approach it is part from a raw material that is modified in shape and final size to reach the desired product.

This strategy is based on the gradual breakdown of a larger material. The crushing may take place by mechanical action in mills with high kinetic energy balls that lead to the formation of nanometric powders.

The advantage of these processes is the low operating temperature, in particular the absence of heat treatments. The powder of  $\gamma\text{-Al}_2\text{O}_3$  It can be treated in this way for the production of crystalline nanoparticles with high surface specific (about  $100 \text{ m}^2/\text{g}$ ).

#### 1.1.2 Bottom-Up Strategy

The bottom-up strategy is to build a product from the individual components. One of the advantages of this technique resides in the fact that you can minimize product losses and waste due to machining.

This strategy is most applied in technologies that lead to the production of nanoparticles from reagents that interact with each other chemically. Chemical reactions are typically productions of new compounds through a bottom-up strategy that aims at the construction of products atom by atom and molecule by molecule.

## 1.2 ! Production Methods

A second distinction of the various techniques of production can be made based on the nature of the process employed, it can be: physical, chemical, chemical-physical, mechanical or a combination of these.

### 1.2.1 ! Methods physicists

A physical process is what leads to the formation of a product only through the modification of the physical state of the system. For modification of the physical state is defined as the modification of the state of aggregation of matter which may occur by evaporation and condensation.

In this type of methods belong processes like PVD (Physical Vapor Deposition), laser ablation, sputtering and processes which provide for the rapid cooling of an oversaturated vapor by means of the use of a cold room or an inert.

### 1.2.2 ! chemical methods

The chemical methods are those that lead to the production of nanoparticles by chemical reaction. A typical case is the production of nanoparticles through a process of reaction and precipitation of an insoluble product.

Other examples of chemical methods are: Sol-Gel processes that lead to the transformation of a metal alkoxide corresponding oxide, processes hydrothermal and CVD processes (Chemical Vapor Deposition). The main difference between the chemical methods and those physicists lies in the nature of the process itself: in the first is of a chemical nature linked to the reactions that lead to the formation of products, in seconds instead of the product is obtained by physical state change of the material aggregation such example in the condensation.

### 1.2.3 ! biological methods

In nature, the nanostructures are made by means of biomineralization processes, ie the formation in vivo of inorganic crystals or amorphous particles in biological systems. In these cases l'accrescimento of the particles it is controlled by biological membranes constituted by proteins and / or polysaccharides which are capable of handling the supersaturation then going to influence the size and morphology of the crystals. There is also a process of producing crystalline nanoparticles which makes use of micelles or polymeric vesicles which behave as nanoreactors for the production of the same particles such as Pt, Pd, Rh, and Ir. This type of process is called Mimetic.

### 1.3 ! Renewable energy sources

We can distinguish in over the processes according to the sources of energy that are used: heat, chemical energy, plasma, laser, etc ... In the end we can make a distinction on the basis of the aggregation state of the components that take part in the process. The production of nanoparticles always passes through an energy consumption, this is to be expected given that, all systems tend to minimize their energy while the nanostructures because of their high surface specific tend to have a high free energy, so their production always requires the use of energy. From here the possibility of distinguishing the various production technologies by virtue of the type of energy source used.

The main energy sources that are used to produce the nanoparticles are: •

- Laser
- Plasma
- Heating Joule
- Electron Beam
- Microwave
- Freeze Drying
- Grinding mills with high kinetic energy
- Combustion
- Flame

In the end we can make a distinction depending on the state of aggregation in which the process takes place, in the specific we can be divided into processes that take place in:

- Solid Phase
- Phase Liquid
- Phase Gaseous

## 2.1 Synthesis in Liquid Phase

The synthesis in the liquid phase are those most used for the production of nanoparticles, provides for the preparation of solutions which must be well mixed before use. In this technology the critical stage of the process is generally carried out in the liquid phase. The generally used solvent is Water, but more often are used organic solvents or ionic liquids to reduce the agglomeration of the particles. The methods of synthesis in the liquid phase are the most efficient in the preparation of nanoparticles at low temperature.

Compared to the other synthesis in liquid phase techniques has the following advantages:

1. Scale-up of the simple process
2. easily controllable process with in-depth knowledge on the control of chemical reactions in the liquid phase
3. Lower operating temperature and atmospheric or slightly elevated pressure, with consequent advantage of costs in terms of process and equipment (non-complex and relatively inexpensive)
4. Control of the morphology and shape of the particles produced
5. Possibility of introducing into solution the agents that reduce particle agglomeration
6. Control of the particle size distribution by acting on the operating conditions of the process
7. high purity of the products

For all these reasons the synthesis in the liquid phase is adopted when the objectives to be pursued are: **high purity, dimensional uniformity, size and shape of the particles, crystallinity, with core-shell configurations, functional groups on the surface.**

The chemical synthesis in liquid phase are classified solely in the following manner:

1. controlled by chemical precipitation and co-precipitation reactions
2. Synthesis sol-gel
3. hydrothermal synthesis
4. Synthesis in microemulsions or reverse micelles
5. Synthesis in supercritical fluid
6. Synthesis in non-aqueous solutions high temperature
7. electrochemical Synthesis
8. Synthesis assisted by microwave and ultrasound

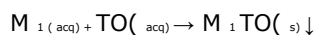
All these processes have in common the fact that they take place in the liquid phase and by means of chemical reactions which lead to the formation of the product.

## 2.1 ! The chemical precipitation and co-precipitation

The chemical precipitation is the production process more simple and widespread nanoparticles with regard to the production in the liquid phase.

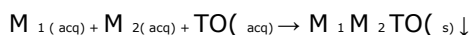
The precipitation occurs as a result of soprassaturazione induced by a chemical reaction whose product is insoluble in the liquid ( ***chemical precipitation in the term describes the phenomenon of separation of a solid substance from a solution***).

The latter takes place between the components of the solution,  $M_1$  and A, with the production of the compound which subsequently precipitates:



Where  $M_1$  It represents the cation (metallic) and A l'anione.

When more than one metal is involved in the precipitation you may have the precipitation of a second metal species according to the reaction:



where the reaction product is a mixed oxide of the two metals. The precipitation

process can be broken down into three stages:

- ***Nucleation***
- ***Grafting***
- ***Agglomeration***

The nucleation of solute consists in the formation of microcrystals, precisely of "nuclei" of crystallization, which tend to grow;

l'accrescimento consists instead

nell'ingrossamento of these to work of another solute crystals which surrounds the crystal and with it establishes electrostatic interactions. It is possible that due to a soprassaturazione, the nucleation prevails on growth, forming in this case a colloid, which is inseparable by ordinary means physicists from the rest of the solution. A colloidal solution is quite stable. The nuclei of solute formed all have the same charge and since repel prevent their growth. For this reason, it does not form an agglomeration of geometric shape de fi ned.

Next to the precipitation phenomenon there is also the annoying phenomenon of cooprecipitazione that determines an impurity of the precipitate, thus causing interference when analysis is performed. The cooprecipitazione can be done by:

- adsorption of foreign ions on the surface of the main precipitate
- for inclusion in the precipitate of foreign compounds
- Occlusion in cavities which are formed in the precipitate during l'accrescimento, of substances and foreign ions

A particular attention must be used to reduce l'agglomerazione that leads to the formation of aggregates (micrometer) of nanoparticles which are held together by electrostatic perhaps Van der Waals type.

To reduce l'agglomerazione can be added in solution of the chemical stabilizers such as: polyvinylpyrrolidone (PVP), plivinilalcohol (PVA) and polyacrylic acid (PAA). Even the type of solvent used can influence the morphology of the final product, in particular l'etilen glycol (EG) offers important advantages such as: high dielectric constant, which increases the solubility of inorganic salts and a high boiling point (about 195 ° C), which allows to operate in the liquid phase even at relatively high temperatures.

At an industrial level, the precipitation is a single operation of solid-liquid separation in the presence of a field of forces, which is carried out within precipitators. More precisely, if the field of responsible forces of separation is the force of gravity, one speaks of sedimentation or decantation, while if the field of electrostatic forces is, one speaks of electrostatic precipitation.

The following table shows some examples of production of nanoparticles by chemical precipitation

Nanparticelle	Characteristic values	Process	Applications
CrO <sub>2</sub>	4-5 nm Spherical, modisperse	room temperature addition of HNO <sub>3</sub> in solutions of NH <sub>4</sub>	Shift of Raman rays
ZnO	Particles of 1000 nm from agglomerating nanocrystals	Solutions of zinc acetate at pH = 9 with NH <sub>4</sub>	Pigments (red)
Fe <sub>2</sub> O <sub>3</sub>	spherical nanoparticles	Element Precipitating ammonium acetate	magnetic material
hydroxyapatite particles	particles of prismatic 2-10 nm	Reaction between calcium hydroxide and phosphoric acid T = 25-85 ° C	ceramic material for implants
SbO <sub>2</sub>	polycrystalline particles from 10 to 200 nm	Reaction among SbCl <sub>5</sub> and hydroalcoholic solutions	Sensitive material with optical properties all'umidità

## 2.2! Sol-Gel Process

In general, a sol-gel process involves the transition of a system from the state of a suspension of a solid in a liquid phase (sol), a condensed phase composed of a solid colloidal elastic material in which there are volumes of liquid (gel) . With the sol-gel term

therefore indicates a colloidal suspension able to gels fi ed

(Solid fi ed), forming a gel.

The starting materials for the process are generally organic salts of a metal, such as an alkoxide ( organic compound derived from an alcohol or a phenol to dell'ossidile atom replacement of hydrogen with a metal), dissolved in a water and alcohol solution. Water and alkoxide are immiscible due to the organic nature of the compound, so the presence of alcohol is needed to make miscible l'alcoosido same.

The process requires the presence of a catalyst which can be an acid or a base depending on whether the reaction is conducted in an acidic or in a basic environment. The sol-gel process normally consists nell'idorlisi alkoxide and in a condensation reaction.

### 2.2.1 ! Method of alkoxides

As is easily understood from the name, in this method, the starting reagents are the alkoxides; the most commonly used (which are those of silicon were also used in this work). The alkoxides are compounds with general formula  $M(OR)_x$  with  $R$  = alkyl or aryl radical; usually using an alcoholic solution using alkoxide

the alcohol

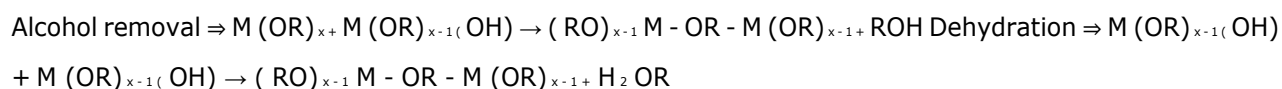
corresponding all'alcoosido chosen.

During the gels fi cation process, the solution the metal alkoxide is subjected to hydrolysis reactions:



Where  $R$  represents the alkyl chain. Hydrolysis is a chemical reaction in which the cleavage occurs in two or more parts of a molecule as a result of a molecule of water and can sometimes be regarded as the reverse reaction of the condensation reaction. The hydrolysis reactions are among the most varied; some are spontaneous, others have need of a catalyst, often an acid or a base.

The partially hydrolyzed species then undergoes condensation by dehydration or dealcoholation that occur simultaneously and their relative speed can be decisive for the quality of the end product:



The reactivity of alkoxides towards the fi nucleus substitution reactions is the in fl uenced by several factors:



- The percentage of ionic character of the MO bond, which depends on the difference in electronegativity between the metal and oxygen
- The nature of the R group which may amend the polarity of the MO bond, also the length and branchesfi cation of the R groups can in fl uence the solubility, the viscosity and volatility of the alkoxides and thus make it more or less easy the attack of an atom metallic molecule
- the metal's ability to increase its coordination number by binding, through dative bonds, the molecules of neighboring alkoxide

The condensation reactions can be controlled by acting on different process parameters such as:

- **The ratio  $r_w$** , which determines the degree of hydrolysis: low values for the crosslinking reaction is slow, are then formed preferably polymers linear and easy to evaporate the solvent is favored; such solutions are therefore more suited to the obtaining of fi bre and fi lm. For high values of  $r_w$  crosslinked structures are formed very quickly before the solvent evaporation stage with the consequent formation of extremely porous bodies. In addition, an excess of water could lead to undesired precipitation of hydroxides.
- **The solvent** It dilutes the reacting species and makes possible uniform hydrolysis and polymerization in the whole system.
- **The use of complexing agents** ( $\beta$ -diketones,  $\beta$ -ketoesters, glycols or acids organic) serves to slow the hydrolysis reaction, it is used to avoid the formation of precipitates and to facilitate the formation of homogeneous mixed systems.
- **The catalysts, acids or bases**, They are used to increase the reaction rate.

There are two different reaction mechanisms for the acidic and basic catalysis:

- An acid catalysis promotes hydrolysis
- A basic catalysis increases the condensation speed

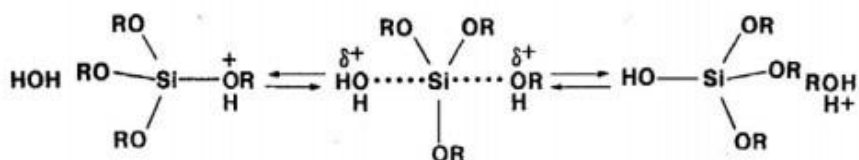
### 2.2.2 ! of the hydrolysis and condensation processes Chemistry

The hydrolysis is carried out for fi nucleus attack the water on organica molecule The rate of hydrolysis depends on several parameters: the molar ratio  $H_2O$  / alkoxide, the nature of the R groups (bulky substituents hinder hydrolysis), the effect inductive (important in the stabilization of the transition states involving the formation of negative or positive charges).

The kinetics of hydrolysis in a neutral environment is very slow, for this reason, it conducts the reaction in acidic or basic catalysis.

### 2.2.2.1 Hydrolysis in acid catalysis

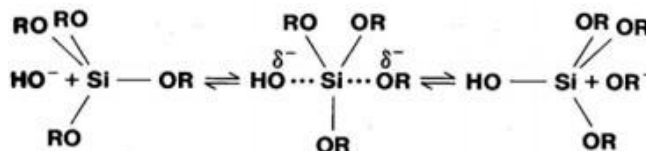
In the first stage of hydrolysis in acidic solution an oxygen of the alkoxide group is protonated making the electrophile molecule, and therefore more susceptible to attack the nucleophile by water. In acidic catalysis, the rate of hydrolysis is increased by substituents with little steric hindrance from substituents and with electron-donor effect that stabilize the formation of positive charges.



### 2.2.2.2 Hydrolysis in basic catalysis

Hydrolysis of silicon alkoxides in a basic environment proceeds, at the same concentration, with less speed than acid hydrolysis. The replacement of the alkoxide groups is always faster than which increases the number of substituted groups.

The hydrolysis reaction is an equilibrium reaction and as such may proceed in the opposite direction: in this case takes place reesterification.



### 2.2.2.3 Condensation in acid catalysis

The condensation reaction in an acid environment involves the protonation of the alkoxide hydrolyzate molecule, this makes the most electrophile molecule and therefore more prone to be attacked by the core. The groups that are protonated more easily are obviously those more basic.

The replacement of alkoxide groups (electron) with OH- groups (electron) tends to destabilize the formation of positive charges in the transition with the effect of resulting state of slowing down the condensation kinetics.

### 2.2.2.4 Condensation in basic catalysis

The maximum speed of condensation occurs in correspondence of pH = 7, when high concentrations of species and protonated and deprotonated species; the lowest speed is recorded at the isoelectric point.

### 2.2.2.5 In summary

To summarize what has been said, we can say that the sol-gel process passes through the following stages:

hydrolysis → polycondensation → nucleation → accretion

It has firstly the formation of a suspension "sol" which condenses in a three-dimensional network "gel" which can further condense to give a solid. The reactions leading to the formation of gel,

typically, they do not stop in

at the point of gelification as is present still an appreciable amount of oligomers able to diffuse and react. The properties of the gel evolve over time (over time of gelification) and depend on aging. Even after the gelification the number of bonds  $\equiv$  MOM  $\equiv$  continues to increase causing the contraction of the gel and the expulsion of the solvent from the pores (syneresis) so that the gel becomes more and more rigid.

During the aging process is verified structural reorganization processes of the network, variation of the diameter of the pores, precipitation of crystals and stiffening due to the formation of additional cross-links.

The factors which influence the hydrolysis and condensation reactions, and then the constituent microstructure of the sol-gel material are: pH, temperature, reaction time, concentration of reactants, the water / metal ratio, the nature of the catalyst and its concentration, the aging and the temperature and the drying time.

### 2.2.3 ! Drying

The thermal treatment of the final gel is required to obtain the compaction, thanks to the elimination of residual solvent, and to induce crystallization of the eventual product. Even the type of drying influences on the characteristics of the final product unavariata determining the porosity and homogeneity.

The step of drying the gel is the stage at which most probably tend to form cracks, this because to drying of the pores larger occurs more rapidly than smaller dei pori, due to the higher vapor pressure of the liquid present in them. So while the smaller pores are still filled with liquid and therefore subject to superficial tensions, the larger pores are already dry and no longer subject to such tensions.

The larger pores then act as microscopic defects that are transformed into macroscopic broken when the tension exerted by the smaller pores are sufficiently large to cause the rupture of the walls that separate the small from those large pores. To limit the formation of cracks is necessary that to drying occurs very slowly and, in case you wish to produce film, that it limits the thickness.

### 2.2.4 ! Advantages and application of the sol-gel method

The sol-gel process offers many advantages for the production of nanoparticles: low operating temperatures, ability to amend the final product by acting on the process parameters etc.

The validity of this method is in fact due to the excellent control it is possible to exert on the processes of hydrolysis and condensation.

The sol-gel processes at low temperature mainly produce amorphous material nanoparticles that require a further calcination to obtain crystalline powders. The sol-gel technique is very versatile and allows a wide range of applications among which we mention: Coating of super fine particles, nanoparticles, DSSC solar cells, catalysts. If we want a disadvantage of this method it is due to the high cost of alkoxides or of the starting compounds and in addition we have a slow process linked to the gelification speed.

The following table shows some examples of production of nanoparticles by sol-gel process

Nanoparticles	Feature of nanoparticles	Process description
SiO <sub>2</sub>	Nanoparticles monodisperse amorphous	hydrolysis catalyzed by ammonia and condensation with hydroalcoholic solutions
TiO <sub>2</sub>	Crystals of size 5-12 nm stabilized by isopropyl alcohol	hydrolysis of titanium hydroxypropyl
ZnO	Crystals of size 3-5 nm with the presence of agglomerations	Summary regarding diethylzinc, terraces butylalcohol, ethanol and water

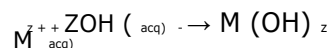
### 2.3 ! hydrothermal synthesis

The term "hydrothermal" comes directly from the Earth Sciences where it is used to describe a system of high pressure and temperature along with the presence of water. The hydrothermal synthesis refers to the treatment of aqueous solutions of metal salts or organometallic at elevated temperatures, generally comprised between 100 and 400 ° C and pressures of about 1 atm. Therefore, in this methodology ceramic powders can be produced through chemical reactions in aqueous solutions by the simultaneous application of heat and pressure, in the presence of an acid catalyst or alkaline. synthesis

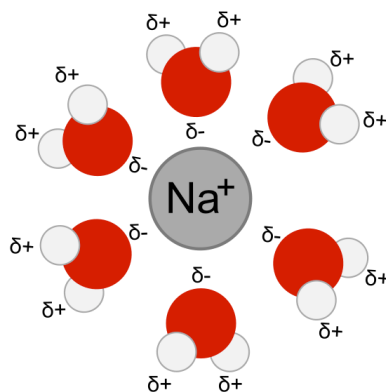
hydrothermal is generally carried out in a device that allows high pressures and temperatures, called an autoclave or bomb, and of which there are different types so as to cover different ranges of pressure, temperature and volume. By varying the characteristics of the initial solutions (pH, solvent, concentration of the ions), and the process conditions (temperature, duration, agitation mode) it is possible to effectively control the shape and the size of the nanoparticles and the crystal phases obtained. What happens it is that the metal salt reacts with the water hydrolyzing and forming a complex, a second stage of hydroxylation leads to the formation of n molecules of  $M(OH)_z$  which it is then decomposed into a molacola oxide and water.

#### 2.3.1 ! Process Chemistry

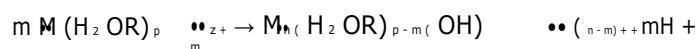
The equation for the hydroxylation of the metal ions is as follows:



The reaction mechanism is favored by solvation of the metal ion ( **for solvation refers to the interaction between the solute and solvent that carries the individual molecules of solute dissolved to surround solvent molecules. A solution in fact, differs from a generic dispersion because the solute is dispersed in the solvent at the level of individual molecules or ions and therefore does not have two phases**)



The reaction which leads to the oxide precipitation proceeds by deprotonation mechanism of the metal ion solvated:



The particularity of this process lies in the fact that under hydrothermal conditions the water can be regarded as a solvent even more efficient, which can also dissolve non-polar entity. These particular feature lowers the energy of activation is necessary for the formation of the final stages, which otherwise would be formed only if treated at high temperatures in the case of conventional solid state reactions. In operating conditions the solvent is able to maintain in solution the salts formed as a result of the reactions, with the release of pressure and temperature you have the variation of the solubility conditions generating a supersaturated solution which leads to the precipitation of the oxides.

At elevated temperatures forced hydrolysis occurs even without the presence of a base, then, fixing the initial pH, gradual l'elevazione temperature influence the hydroxylation reaction of the metal ion and the generation of the resulting complexes. The deprotonation of the metal ion solvated leads to a decrease of the pH ( $H^+$  ions in solution) then it is preferred to work at excessively low pH not just by virtue of ions generated during the process that tend to reduce the pH in the process. Most of the hydrothermal processes using as the solvent the water but you can also use other types of solvents when the situation requires. There are hydrolysis processes that occur in different liquid media such as polyols or hydroalcoholic solutions. The addition of alcohol

strongly influence the phenomena formation of particles (Nucleation and growth) and, therefore, the morphology of the particles themselves. In summary, forced hydrolysis requires an acidic solution of a metal salt at a given concentration, that is subjected to heating to produce hydroxides ties through deprotonation water.

A variant of this type of synthesis is constituted by solvothermal synthesis in which in addition to water, may be used various kinds of solvents including, for example, organic ones such as ethanol, methanol and the like. Although the hydrothermal method is extremely versatile for the production of ceramic nanopowders, one of its major drawbacks is constituted by the low reaction kinetics. In order to increase the kinetics of chemical reactions can be conducted using a heating source microwave.

### 2.3.2 ! Reduction of particle size distribution

The hydrothermal process can also be applied to standardize the particle size distribution of a sol-gel material. Thus, for example, a colloidal suspension of titanium dioxide to be used for coating is subjected to a hydrothermal process at approximately 200 °C for 2 hours. At the end of the process you are obtained a stable colloidal suspension of TiO<sub>2</sub> particles with size of several hundred nanometers.

In this case, the high temperature process leads to the disappearance of smaller particles and further growth of larger ones, thus eliminating the distribution and standardizing the size of the particles themselves.

To work with suspensions wherein the solvent has a boiling point lower than the operating temperature, it is necessary to adopt a reactor which works under pressure. For the case described above the operating temperature of 200 ° C in the reactor generates a pressure of about 20 ata.

## 2.4! Synthesis in microemulsions or reverse micelles

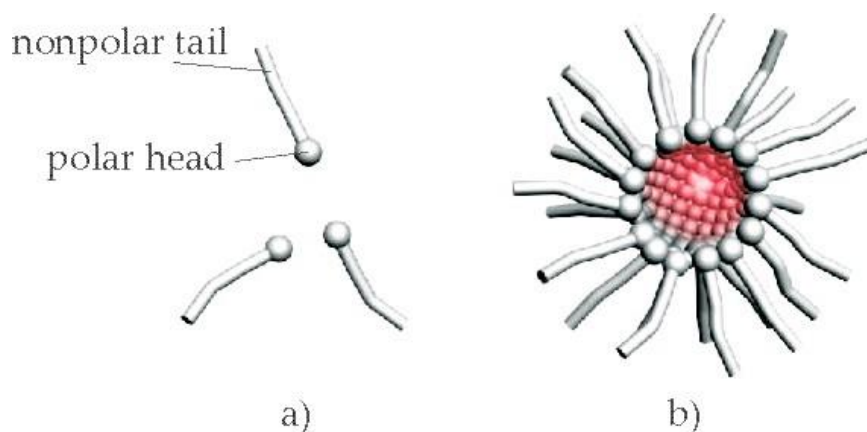
Among the chemical pathways for the preparation of semiconductor nanocrystals the use of microemulsion systems constitutes a simple and efficient method.

A microemulsion is a homogeneous dispersion of two liquids, between which are immiscible, mediated by a particular class of molecules known with the name of surfactants or surfactants which lower the interfacial tension so as to allow a spontaneous dispersion of two immiscible phases simply by thermal effect.

In first approximation, the microemulsions may be considered a scaled-down version of the emulsions, although they are typically formed by pseudospherical structure aggregates constituted by microdroplets of water in oil, with diameters that reach a maximum of 200 nm, approximately 100 times more than the size typical of classic emulsions.

Depending on whether the dispersing phase is the water or an organic solvent (typically a hydrocarbon or a halogen derivative of hydrocarbons) microemulsions are called oil-in-water or water-in-oil.

The microemulsions water-in-oil (water in oil) are constituted by so-called reverse micelles, spheroidal aggregates formed by the surfactant in an apolar medium. Unlike direct micelles, the polar heads (hydrophilic) of the surfactant molecules are directed towards the inside of the aggregate and form a polar core which can solubilize water (water-pool); the alkyl chain (hydrophobic) is instead exposed to the organic solvent.



These reverse micelles are extremely dynamic entities, and among them is configuration events breaking / formation with a rate even higher than 10 kHz. The collision, for example between two micelles, can give rise to a balance with a transient dimer thus allowing the exchange of material from the heart of the two polar micelles. The application of this technique is directed to produce nanoparticles of nanometric dimensions inside the micelles which play the role of nanoreactors. The operation key is to avoid the accretion of the particles due to micelles which serve as barriers and reduce the contact between the species present in the medium.



### 2.4.1 ! Process Dynamics

In microemulsion it is possible to obtain particle sizes of nanometric monodispersed, whether they consist of: semiconductors, metals or oxides using these systems as real microreactors. In general, the monodisperse particles prepared in microemulsion have the characteristic of possessing very small average size, a narrow size distribution and a high stability in the systems. Typically in a process of this type reagents, which may be metal salts or a precursor of the product that we want to achieve, are dissolved in the water pool of reverse micelles and may react through the micellar communication during the dynamic processes of collision, or coming into contact with another reagent in solution or in the form of gaseous stream, giving rise to phenomena of first nucleation and then growth inside of the micelles as the process advances. The nucleation process can take place exclusively in the water pool in the first stage of the precipitation, since the growth of nanoparticles is strictly limited by the strong adsorption of the surfactant. When a sufficient number of nuclei are generated so as to be able to absorb their growth with the oversaturation this can not take place any further nucleation process. This implies that the obtained particles are very small because the separation between nucleation and growth is ideally realized; it is therefore possible to obtain monodispersed particles. In addition the presence of the surfactant prevents the contact between the formed particles,

### 2.4.2 ! Benefits from the use of reverse micelles

This synthesis technique offers numerous advantages: small particles can be obtained and sufficiently monodisperse; the size of the particles by varying the experimental parameters of the microemulsion (in the literature is reported, for "water-in-oil" ternary systems, a dependency of the particle size by the diameter of the aqueous pool) can modulate.

The use of reverse micelles constitutes a "soft" technique because it does not require particularly drastic conditions of pressure and temperature and allows to realize. The preparation in these systems microheterogeneous then allows the use of nanoparticles obtained either directly in the micellar solution, which represents an ideal medium for those types of applications that require compartmentalized systems (photodegradation water and production of hydrogen) and after their subsequent isolation. One disadvantage of this technique may be the low productivity due to the fact that, when the supersaturation within the micelle falls below the critical value, the nucleation phenomenon stops and does not generate more particles.

In the final reverse micelles serve as microreactors batch of leading to a discontinuous nucleation process.

The process is influenced by temperature, concentration of surfactants and ratio water / oil, in particular a high amount of surfactants can significantly influence the morphology of the particles

With this technique it is possible to obtain monodispersed metallic particles of: Pt, Rh and Pd size of 3-5 nm reducing its salts by treatment with hydrazine or hydrogen gas.

Another example is the production of nanoparticles of magnetite ( $\text{Fe}_3\text{O}_4$ ) by treating aqueous solutions of ferrous and ferric ions, dispersed in microemulsions W / O with ammonia. The microemulsions are also advantageously used to produce the composite nanoparticles, for example enzymes encapsulated in silicon oxide, used for drug-delivery of medicines.

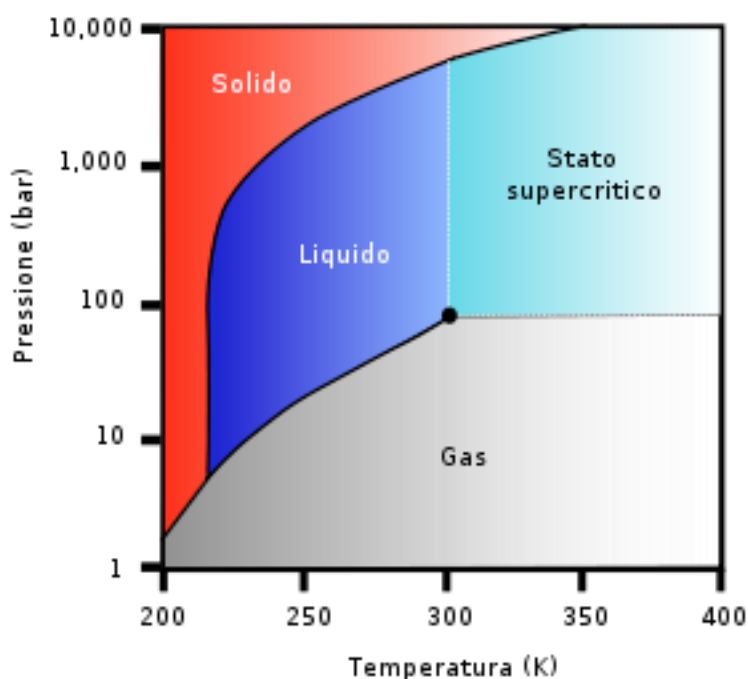
The following table shows some examples of production of nanoparticles by synthesis in microemulsions

Nanoparticle	Features	Process
$\text{SiO}_2$	30-70nm monodispersion	Hydrolysis of TEOS in microemulsions of water in the polyoxymethylene, NP5, cyclohexane, $\text{NH}_4\text{OH}$
$\text{ZrO}_2$	amorphous particles	Microemulsion reverse water-cyclohexane-hexanol, Triton (dispersant)
$\text{TiO}_2$ OR $\text{Fe}_3\text{O}_4$	Amorphous 2-4 nm	Hydrolysis of aluminum isopropoxide in octane / mixture of water and acetonitrile
$\text{TiO}_2$	Nanoparticles in phase Anatase and Rutile	Hydrolysis of tetrabutyltitanate with microemulsions of water in the presence of Span-Tween 80 surfactant

## 2.5! Synthesis in Supercritical fl uid

The fl uid supercritical can be used to produce inorganic nanoparticles, by means of new synthesis reactions based processes.

A fl uid is said supercritical when it is in conditions of temperature and pressure higher than the critical one. Under these conditions the properties of the fl uid are partly similar to those of a liquid (eg density) and partly similar to those of a gas (eg viscosity).



The fluid in the supercritical state are used as industrial solvents, replacing the organic ones. In particular, the supercritical carbon dioxide is widely used. In general terms, the supercritical fluid have properties intermediate between those of a gas and a liquid. In addition, there is no superficial tension in a supercritical fluid, given the absence of liquid / gas bonds.

By changing the pressure and the temperature of the fluid, the characteristic properties can be approached to those of the fluid or gas. One of the most important properties is that the solubility of a material in the fluid. In a supercritical fluid the solubility tends to increase with the density of the fluid (at constant temperature). Since the density increases with pressure, then the solubility tends to increase with the pressure.

The advantages of adopting such technologies are: a great efficiency in the production of nanoparticles, the ability to control size and morphology of the particles by varying temperature, pressure and atmosphere (oxidizing or reducing) by the introduction of gas or components Extra equipment ( $O_2$ ,  $H_2$ ,  $H_2O_2$ ).

The fluid used as supercritical solvents are  $H_2O$  and  $CO_2$ . In the first case the technique is known as supercritical hydrothermal process.

### 2.5.1 ! Techniques used

The techniques used for the production of nanoparticles that employ the use of supercritical solvents are different, among which we mention:

- Precipitation supercritical solvent (SAS)
- Rapid expansion of supercritical solutions (RESS)

#### *SAS technology*

The supercritical antisolvent precipitation is a process that provides for the rapid dissolution of a solution in a supercritical fluid where it is produced a little soluble compound. The precipitation of the compound finally occurs as a result of chemical processes in which a reaction within the fluid forms a slightly soluble compound which precipitates.

#### *RESS Technique*

This technique provides a rapid expansion of supercritical solutions, is used to produce nanoparticles of PbS. It can be implemented by performing the rapid expansion of a supercritical fluid in a liquid solution, or by making occur a reaction between a reagent in the supercritical fluid and the other one in the critical solution

### 2.5.2 ! Process with supercritical water

In case of using water in supercritical conditions there is a strong reduction of the dielectric constant when operating conditions exceed the critical point ( $T_c = 374^\circ\text{C}$ ,  $P_c = 221\text{ bar}$ ). The reduction of the dielectric constant has the advantage of increasing greatly the kinetics of the hydrothermal reaction,

Moreover, the solubility of the salts inorganic in condition supercritical is very much reduced while increases that of organic compounds. The reduction of solubility, leads, at the same concentration of salts, to a sharp increase of the supersaturation at which nucleation phenomenon and follows the accrescimento of the particles. The increase of the solubility of organic compounds makes, then, can be maintained in solution, organic anti-caking additives.

In this case, therefore, the process consists in putting in solution the reagents and then bring the solution under supercritical conditions so as to favor the nucleation, the solvent is then removed by means of expansion (thus bringing in gaseous conditions).

### 2.5.2 ! Process with supercritical carbon dioxide

Another fluid is the anhydride widely used supercritical carbon dioxide ( $\text{CO}_2$ )

### 3.1 Gas-phase Synthesis

The synthesis in the gas phase is a synthesis method that is widely used if it is intended to produce monodisperse particles, the element of the process is critical to drive the flow and collection of the particles after their formation.

The synthesis in the gaseous phase provides ease of control of the process parameters such as gas composition, the pressure, the temperature and the gaseous flows. In this category of processes energy sources are very diverse, they go from strength ovens, laser, plasma up to electron beams.

The advantages of the synthesis in the gas phase are: versatility, speed of the process, ease of obtaining products with high purity and high specificity of the products obtained. The disadvantages are represented by: high production costs, low yields, difficulty of scale-up and the possibility of unwanted reactions with the heat source. The vapor phase techniques can proceed with different both chemical mechanisms that physicists, in particular can exploit :

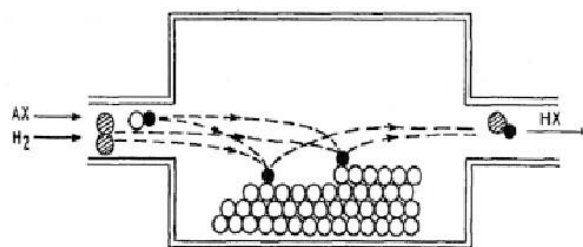
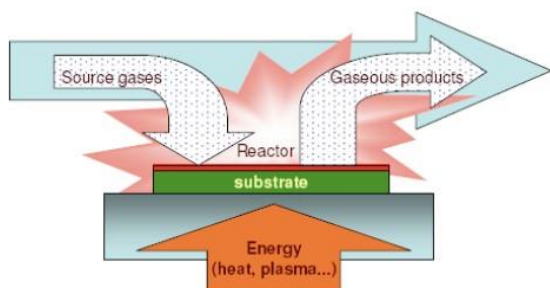
- Evaporation of a target and subsequent vapor deposition
- Formation of plasmas with deposition of the desired species
- Deposition of the material as a result of a chemical reaction in the vapor phase

The production techniques of nanoparticles by a gas is then divided into two categories:

1. Deposition of a solid from a condensing steam
2. Chemical reaction in the vapor phase

#### 3.1.1 Chemical Vapor Deposition CVD

This technique consists in a chemical reaction between two or more gaseous molecules and the subsequent deposition of the material produced. The transport of the precursor takes place through the use of a gas (oxygen, argon, hydrogen, nitrogen, ...), thanks to which are then removed from the system all of gaseous decomposition products that desorb from the surface of the film.



In general, the CVD technique involves a reactor, of the reactants in gaseous phase and an activator of the chemical reaction, a kind of catalyst (heat, laser beam); with this technique may present two different situations, homogeneous or heterogeneous nucleation, that is, the reaction can take place on a surface extraneous (example bubbles

steam on the surface of a pot), or happens in the same gas (air bubbles in the water of the pot); the homogeneous nucleation is much more hindered and then usually takes a heterogeneous nucleation phenomenon, which can as the case may lead to the formation of nanoparticles or film. Typical reactions taking place in a CVD process are:

- Adsorption
- Oxidoreduction
- Pyrolysis
- Formation of compounds

When using an oven for the CVD process the starting material is often a metal chloride. The reaction leading to the formation of the ceramic material is by oxidation of the precursor in the presence of oxygen:



More generally, the precursors used in this type of process are typically of organometallic, compounds that contain at least one metal-carbon bond, where the term "metal" is the broadest sense also comprising the alkali metals and alkaline earth metals, metalloids and properly said metals.

These compounds are highly reactive and can give reactions:

- **Oxidation:** are strong reducing agents which tend to react strongly with oxidizing materials
- **π nucleophilic attack:** are particularly reactive towards, for example, the π addition to the nucleus to a - (C = O) -
- **Deprotonation (hydrogen removal):** the more thermally unstable organic metal, such as those of the heavy elements of p, after heating unit undergo a displacement with a decomposition reaction of hydrogen in the β position as it passes to the metal

The CVD reactors can be hot-wall or cold wall, with the disadvantage that with the hot wall there might be a deposition also on the walls leading to a lower deposition rate; the cold-wall reactor is not an oven but a reactor to seal in which the sample is placed on a sample holder so heated does not involve the walls to the reaction, in this case, however, has the problem of the presence of internal thermal gradients to the chamber and then of deposition gradients which involve a non-homogeneous growth.

### 3.1.1 Kinetics of CVD process

The kinetic model that describes the process can be divided into two phases: the first due to the transport of matter via convection, ie The Contribution of reactants through a carrier gas, this phase is in fact governed by the transport phenomena in forced convection conditions, second phase instead regards the consumption of reagents to effect the chemical reaction that leads to the formation of products of interest, in this case the laws that govern the stadium are kinetics, then linked to the kinetics of the reaction.

#### 3.1.1.1 Phase Convective

During convective write the following relationship:

$$F_G = h_G (C_G - C_s)$$

In which with  $F_G$  we mean the flow of incoming gas while  $C_G$  is the concentration of the reagent in the gaseous phase,  $C_s$  is the concentration of the component interface with the surface (can also be ideal) on which the reaction takes place and  $h_G$  It is the coefficient of transport of matter which can be determined empirically based on the motion conditions inside the chamber.

It can be shown that the phenomenon of the exchange of matter is fully described in the case of forced convection by a power law of the following dimensionless groups: Reynolds number, Schmidt number and Sherwood number. The relationship between them was determined experimentally:

$$Sh = 0,023 \cdot Re^{0.8} Sc^{0.33}$$

This relationship is valid for turbulent motions ( $Re > 2100$ ), and from it we can obtain the value of the coefficient of mass transfer:

$$h_G = \frac{Sh \cdot D_{ab}}{L}$$

where is it  $D_{ab}$  It represents the diffusivity in the middle and  $L$  It is the characteristic dimension of the process. In this way we are able to calculate the flow of matter that reaches the surface on which the chemical reaction takes place.

#### 3.1.1.2 Reaction Phase

In this phase instead we are studied the reaction phenomena and therefore the kinetics of the process can be described by the following relation:

$$F_R = k_S C_{Sn}$$

production of nanoparticles



Where is it  $F_R$  is the flow of matter that is consumed during the reaction,  $k_s$  It is the constant kinetics of the same reaction and  $C_s$  is the concentration of the reactants on the surface of reaction. L'apice  $n$  instead indicates the order of reaction that can be determined from experimental tests.

### 3.1.1.3 Matter of Balance

In the case of said stationary conditions the incoming flow must be equal to the flow outgoing from which it follows that, going to make the balance of the two flows described above, we can find an expression of  $C_s$  which turns out to be a function of the kinetic constant and the coefficient of exchange of matter:

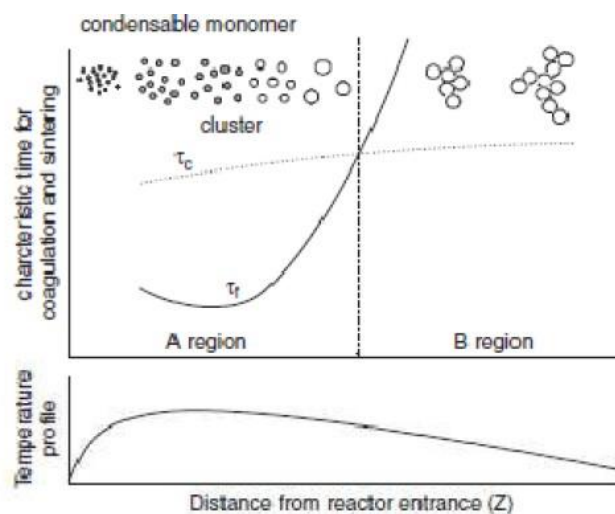
$$C_s = C_G \frac{h_G}{1 + k_s h_G}$$

and in addition we can write the growth rate as a function of the parameters described above by dividing the total flow to the number of moles of the gas component that have reacted.

In particular, if we consider the mole fractions we can write the following reaction:

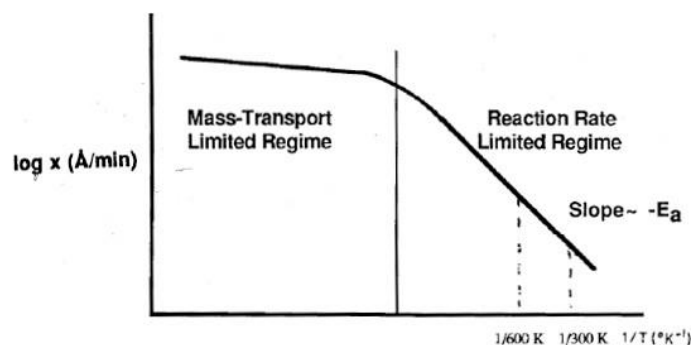
$$v = \frac{F}{N_1} = \frac{k_s h_G C_G Y}{(k_s + h_G) N_1}$$

It follows therefore that the speed of the process depends on how fast the reaction takes place on the surface and how quickly these species are transported toward the surface.



If  $h_G \ll k_s$  the reaction proceeds faster than the reagent arrives on the surface, it follows that the controlling stage is that due to the convective

transport of matter. In this case we must intervene by increasing the coefficient of exchange of matter going to act on the motion conditions. If  $h_G \gg k_s$  the reaction proceeds slowly and therefore it has a reagent accumulation on the surface of contact, this indicates that the parent stage is responsive. In this case increase the coefficient of exchange does not lead to any benefit, on the contrary, it causes wastage due to the fact that the gaseous stream carries away part of the unreacted reactive.



### 3.1.3 ! Classification of CVD techniques

The CVD techniques can in turn be distinguished as a function of different parameters such as: the presence of plasma, the temperature of the reactor walls, pressure of the reaction chamber, the presence of energy sources such as laser, etc. type of reagents. Below is a classification of the various techniques:

- **APCVD:** CVD at atmospheric pressure;
- **LPCVD:** CVD at low pressure;
- **MOCVD:** Metal-organic CVD (gas with metal molecules linked with organic molecules);
- **OMCVD:** CVD organo-metallic (gas with organic molecules attached with metals), lower temperatures;
- **PECVD:** Plasma enhanced CVD;
- **HDPCVD:** CVD plasma high density;
- **LACVD:** Laser-assisted CVD.

### 3.1.4 Advantages and disadvantages of CVD techniques

The main advantages of this process are:

- high production capacity with production of pure materials
- film uniform Productions with good adhesion and repeatability
- Control of the crystal structures, the morphology of the surface by means of control of the process parameters
- deposition rate adjusted instantly
- reasonable costs for the conventional technique of CVD;

- Flexibility of use thanks to the wide range of chemical precursors such as halides, hydrides, metal-organic that allow the deposition of a wide spectrum of materials including, metals, carbides, nitrides, oxides, sulfides
- It allows the deposition of refractory materials to a temperature lower than the melting point.

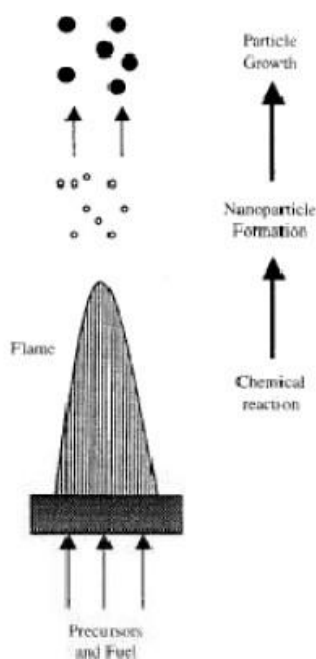
The main disadvantages are:

- High activation temperature of the reactions that leads to high deposition temperatures
- security risks caused by the use of toxic, corrosive, flammable and explosive in
- Difficulty of depositing multicomponent materials with stoichiometric ratios controlled using multi-source precursors, because different precursors have different evaporation rates

### 3.2.1 Synthesis in flame

In this process the gaseous reactants are fed to a flame that is the medium in which the reaction takes place. The flame contains both molecules that fuel combustion, typically methane and air (but may vary depending on the heat power necessary for it), which by a highly exothermic oxidation reaction generates energy (heat) necessary for the sustenance of the reaction.

The chemical precursor is vaporized within the flame in which the reaction takes place (usually oxidation), the reaction gives rise to the formation of products with low vapor tension that tend to nucleate to generate particles. At a sufficiently high temperature (the temperature of the flame goes from 1200 to 2500 K), the particles coalesce with each other giving rise to the primary particles that, subsequently, in the course of cooling give rise to very resistant aggregates which have dimensions ranging from a few nm up to a maximum of about 500nm. With this technique it is possible to produce ceramic oxides such as  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ .



The production in this field is of the order of several million cubic meters per year, while the quality of the product is strongly influenced by the mixing between the reactants resulting determinant on the temperature of the flame and of all the results of the process such as: composition of the product, size of the particles, aggregation etc.. The advantages of the synthesis in flame are: the production of ceramic nanoparticles composed of very hard oxides, very short residence times, simple scale-up and high purity of the products.

The disadvantages include the formation of agglomerates difficult to break, temperatures and residence times uneven, and difficulty in the production process of nitrides and borides.

### 3.3 ! Physical Vapor Deposition PVD

The techniques of this type involve the condensation of a gas or a vapor to obtain a solid particulate. In most cases the energy for generating the steam can be supplied by: an electrical resistance, laser, plasma, electron bombardment, or an arc discharge.

Depending on different parameters we can have a wide range of techniques that are based on the principle of evaporation physical, more in particular we can distinguish different methods of condensation of the vapors as well as the different sources of energy. As for the condensation methods we have for example:

1. Evaporation of the starting material in a vacuum chamber in the presence of inert gas.  
The evaporated material condenses on a cold wall.
2. Condensation of the material as a result of contact with a cold substance rather than on the wall (of the isolated matrix method).
3. Method of the gas flow and the cold trap: the vapor of an organic is sent in a stream of inert gas which transports the particles, the current is then sent in a chamber cooled with a liquid nitrogen jacket.
4. Method of gas flow in a cold trap in which there is a solution: the gaseous stream with the nanoparticles is sent in a trap in which there is a solution of an organic compound, for example ethanol, precooled between -30 and -140 °C depending on the type of organic.

#### 3.3.1 ! Process Dynamics

The process of formation of nanoparticles for physical evaporation of a material is essentially based on three fundamental steps:

1. **Evaporation:** the material to be deposited is evaporated from the "target"
2. **Transport:** the evaporated material is transported towards the surface condensing
3. **Condensation:** the material from the target nucleates and grows according to the mechanisms seen previously.

As has been mentioned energy sources available to easily evaporate the target can be different, typically one can distinguish the technique in accordance with the vapor created:

- **Direct evaporation**, based on the heating and subsequent evaporation of the material with which I want to coat the substrate;
- **Electron gun**, in which an electron beam affects the material and makes it evaporate by thermal transfer;
- **arc deposition**, in which it is easy to evaporate is produced by a direct electric discharge on the material.

- **Laser**, in which the energy required thermal evaporation of the target is supplied by a laser beam. production of nanoparticles

### 3.3.2 ! Evaporation in vacuum

It became a PVD process in which the material is thermally vaporized from a source, usually a filament, which produces heat by the Joule effect. In the simplest form a remarkable intensity current passes through a metallic crucible with high melting temperature (eg Tungsten, Molybdenum), shaped to accommodate the material to be evaporated. Alternatively, the crucible is heated by means of a ceramic material or radiatively if the metal is immersed in the crucible. The basic stages of the process are as follows:

- Sublimazione of a solid or evaporation of a liquid to form a gaseous species
- Transportation of the particles from the source to the substrate
- Condensation of the particles on the substrate

Thanks to the vacuum produced in the chamber, the evaporated material reaches the substrate with few or no collisions with residual gas molecules present between the source and the sample. Usually the condensation stage takes place at a pressure between  $10^{-3}$  Pa and  $10^{-6}$  Pa depending on the level of contamination that can be tolerated. During their stay in the gaseous phase, the particles travel in a straight line if they do not collide with a residual gas molecule; then enters the mean free path in the gas, which is the higher, the lower is the pressure.

In the majority of deposition systems for thermal and electron gun evaporation, the distance between source and substrate is of the order of a few tens of centimeters, the distance to the air at ambient temperature and at pressures of the order of  $10^{-5}$

mbar is comparable to the mean free path of the particles that make up the starting material, in general, therefore, the overall vaporization slopes is small. In the case where it is easy to evaporate occurs by the Joule effect, the current passing through a melting pot of conductive materials (metal coils or various types of metal sheets) with a given resistance, dissipates power as set by heating the material.

The room required for the deposition is characterized by a distance, relatively large, between the source and the substrate; this minimizes the radial from the heating source itself.

Defects of this method are often due to contamination of the heated crucible, moreover, the small size of the crucible limits the total amount of material that it is possible to evaporate.

### 3.3.3 ! electron gun

In the situation of use of a flow of electrons, instead, the energy is supplied by thermal particle beam that impacts the surface of the material to be evaporated contained in a water-cooled cavity.

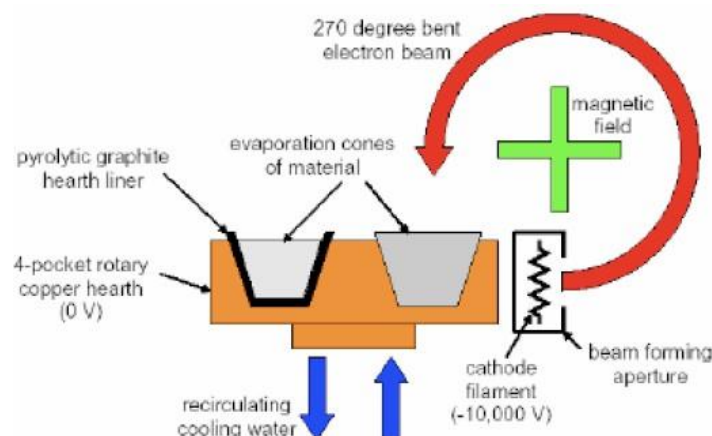
The operation is as follows: a hot filament generates a large electron current, even a few amperes, the beam is

accelerated between the filament and the anode at a high

production of nanoparticles



voltage (between 3 kV and 30 kV). The electron beam is typically deflected by  $270^\circ$ , by means of a suitable magnetic field, so as to avoid that the filament that emits electrons is exposed to the material to be evaporated. The crucible in which is contained the material to be evaporated is typically graphite which is the known material with the highest melting temperature. In turn the graphite crucible is contained in a copper heat sink. The electrons dissipate their kinetic energy in the material and cause heating and subsequent evaporation.



With this technique one can achieve also higher growth speed, the deposited materials are less contaminated than in the case of thermal evaporation, this method has the advantage of concentrating the energy only at the point to vaporize ( $3000^\circ\text{C}$ ) so as to be able to vary in a wide range of the vaporization speed ( $1\text{--}10\text{ nm/s}$ ) and to avoid reactions, so contamination arising from the crucible. The material melts locally and the crucibles are maintained at a relatively low temperature. The real disadvantage of this technique is in the X-rays produced by the incident electron beam that can damage parts of devices already present in the substrates.

### 3.3.5 Advantages of PVD methods

The advantages of this method are:

- ultra fine particles (in the presence of inert gas)
- Cleaning the surface of the particles
- applicability of the technique to metals, alloys, semiconductors
- flexibility in the control of crystallinity

### 3.4! Synthesis by Aerosol

In a process by aerosol the starting material is a homogeneous liquid which is converted into an aerosol. An aerosol is a type of colloid in which a liquid or a solid are dispersed in a gas, the diameter of the particles is normally between 1 and 100 nm, but in the case where there are turbulent motions may be included as particles

larger. Subsequently, the aerosol is converted into a gaseous suspension of solid particles.

### 3.4.1 ! Process Steps

This type of process consists of vaporizing the liquid present in a container by passing through it, air, nitrogen or a gaseous mixture. The size of the droplets thus generated are dependent on the liquid from the gas used and the type of aerosol generator. The process steps are:

- Initially there is a solution containing the precursor of the material that we have to produce
- The solution is sprayed by means of a run inert gas (sometimes it can also be reactive)
- Subsequently the aerosol enters into a furnace inside which the liquid evaporates and the particles produced are concentrated on the bottom
- The particles are sent to a collection zone where they are cooled by a cold gas and separated by a filter

The size of the produced nanoparticles depends on the degree of dispersion of the aerosol, the more the liquid is dispersed in the aerosol particles produced are smaller. The aerosol process advantages are the purity of the products, the obtaining of spherical particles and a modest agglomeration.

The disadvantages are the wide particle size distribution of the particles produced, the need for large gas flow rates for dilution in order to reduce the agglomeration and aggregation, a low production capacity and the difficulty to perform the scale-up.

### 3.4.2 ! Morphology and particle size

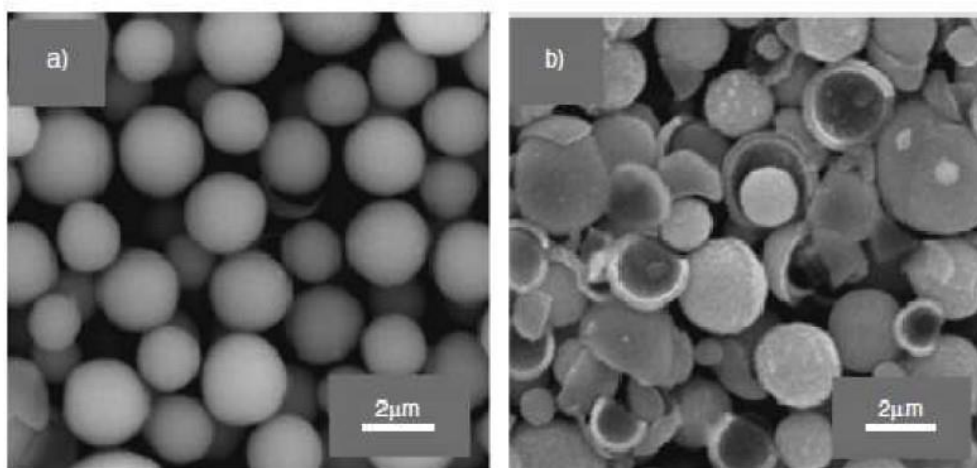
The size and morphology of the particles produced is also determined by the concentration and velocity of the droplets generated from the atomizer. It should be borne in mind that with this technique it is possible to obtain compact particles, porous or hollow. The final configuration depends on two characteristic times: the evaporation of the solvent,  $\tau_{sv}$  and that of the solute diffusion  $\tau_{sl}$ .

In the case of low speeds of heating or reduced size of the drops, easy to evaporate the solution and crystallization proceed slowly, thus producing polycrystalline particles with a significant overall size or monocrystals. At temperatures equal to about the melting temperature of the material or higher are obtained dense particles next to the spherical morphology. You can also get planar morphology particles, when there is a precise orientation in the accretion of crystalline solid during the formation.

In the case, instead, of high-speed heating or large dimensions of the drops are obtained porous materials. This morphology is not very suitable for many

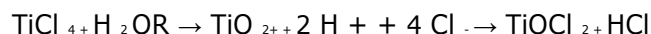
applications structural type, but it may be interesting pre production  
catalizzatori high surface specific.

If the heating rate is high in the first phase of the process, easy to evaporate it occurs quickly on the surface of the droplets, so that the concentration of the solute in the drop is no longer uniform and the outer part of the droplet can already present a solid film marked cation when the inner part is still liquid. In this situation, the steam that is generated in the central part of the drop tends to create cracks in the solid peripheral or a vacuum in the central part of the particle. The aerosol flame technique consists in bringing the flame aerosol to be burned. This technique is preferable to that of simple pyrolysis for greater scalability and a minor agglomeration of the particles. In figure shows the particles of  $ZrO_2$  prepared by spray pyrolysis.



### 3.4.3 Preparation of barium titanate particles

For the preparation of barium titanate the first step for a good yield of the process is to prepare a homogeneous solution using, for example, titanium tetrachloride and barium chloride, or  $TiCl_4$  and  $Ba(NO_3)_2$  in a hydroalcoholic mixture. The titanium chloride has a strong tendency to be hydrolyzed in accordance with the following reaction:



In the furnace it is then carried out hydrolysis of titanium monoxide  $TiO_2$  that after further heating above  $380^\circ C$  assumes the anatase phase. If there is the  $Ba(NO_3)_2$  the reaction takes place which leads to  $BaCl_2$  due to the presence of  $HCl$  and then to barium titanate at  $540-650^\circ C$ :



Then the aerosol process has the advantage of preparing the reagents in solution with good fi of ease of preparation there, reduction of toxic vapors etc. and the reaction takes place in phase spray, then Finely dispersed, thanks to the activation by the heat.

## 4. Solid Phase Synthesis

The solid-phase synthesis are interested in those processes that have as starting materials solid materials. Most of these methods follow a top-down approach that includes the traditional mechanical grinding and solid state reactions.

### 4.1 ! Grinding high energy content

The easiest method to produce a material in the form of nanoparticles, starting from a solid is grinding using mechanical energy that breaks the bonds between atoms and molecules of the original solid. The grinding process can be applied not only on a natural solid material, but also on a material obtained by chemical synthesis. Despite the grinding is a very old process, it is not yet clear what is the correlation between the entity of the fracture phenomena and the particle size subjected to fracture.

The achievement of size up to 100 nm is possible today only by means of an assisted grinding to a liquid or a gas.

The grinding is carried out in special mills such equipment. They may be very different from passing macinazioni mild that produce micrometric materials to grinding to obtain ultra ironwa it.

#### 4.1.1 ! Ball Mill

A ball mill is a device used in grinding cylindrical ca (or mixing) to produce materials such as minerals, chemicals, ceramic raw materials and paints. The ball mills rotate around a horizontal axis, they are partially filled with the material to be treated more organs for grinding which are usually of the steel balls or high hardness ceramic material. An internal cascading effect reduces the powder material fi nissima kinetic transferring the energy of the spheres on the shattering fi no material to nanometric dimensions.



The higher the quality of the most finely spheres is ground material, high quality spheres are potentially very expensive but it can grind fine particles to 5 nm greatly increasing the surface specification and the dust reaction speed. The grinding, or grinding, it is based on the principle of critical speed. The critical velocity can be understood as that speed beyond which the steel balls (which are responsible for the grinding of the particles) begin to rotate along the direction of the cylindrically shaped device, so as to avoid any further grinding.

There are many types of grinding media suitable for use in a ball mill, each material has the specific properties and advantages.

The key properties of grinding media are size, density, hardness and composition.

- **Dimensions:** the smaller the size of the spheres, the smaller the particle size of the final product. At the same time, the grinding balls should be substantially larger than the largest of the pieces of material to be milled.
- **Density:** the spheres should be more dense material to be ground. If the means of grinding floats on top of the material to be ground the efficiency of grinding is drastically reduced
- **Hardness:** The grinding means must be strong enough to grind the material, in fact, the hardness of the balls must be greater than that of the material to prevent crushing of the same.
- **Composition:** if special requirements of the material finished can be used of different material spheres. Some of these requirements are based on the fact that some of the grinding media will be in the finished product. Others are based on how the means react with the material. Some materials, such as iron, can react with corrosive substances. For this reason, when the corrosive substances are present during the grinding operation should use balls of inert material such as stainless steel and ceramic materials.

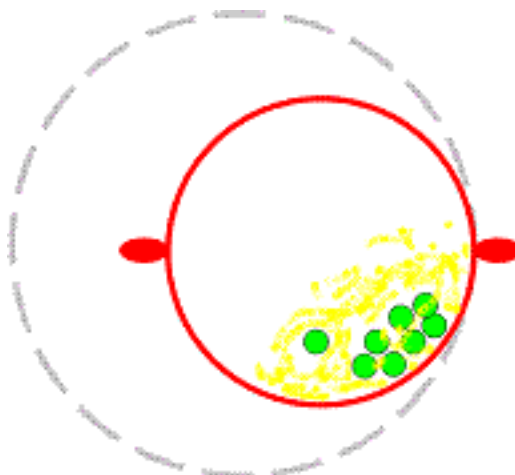
#### 4.1.2 ! planetary Mill

In addition to the common ball mills there is a second type of mill called planetary mill. The planetary ball mills are smaller mills common spheres and is mainly used in laboratories for grinding material fine to very small dimensions, about 5 nm. A planetary mill consists of at least one grinding jar, which is disposed eccentrically on a so-called sun wheel. The sense of the movement of the sun wheel is opposite to that of the jars (ratio: 1: 1 or -2: -1).

The grinding balls in jars are subjected to rotational movements of superimposed, generating the so-called Coriolis forces. The speed difference between the balls and jars produces an interaction between the forces of friction and impact, which liberates high dynamic energy.

The high energy transfer due to the superposition of all the forces at play in the grinding jars makes it possible to produce materials with dimensions in nanometer level

very small apparatus compared to conventional mills, this leads to high levels of clutter and advantages of production.



During the grinding nanometric particles are formed which can easily riagglomerarsi by virtue of their super fi cial energy, you can take, however, the speci fi c measures us how the introduction of gases or liquids. For this reason often it operates grinding doing, the communication in the presence of

liquid

(Wet grinding). The wet grinding mills therefore are assuming an increasingly important role, they are made with an agitator inside so as to circulate the suspension during the grinding process.

The grinding performance depend on the time of the process and the diameter of the balls, in fact the impact frequency between the bead and the material is inversely proportional to the diameter of the same, in fact, the smaller the diameter of the spheres, the smaller the size of the produced nanopowder. It should however take into account the fact that the energy of impact can lead to changes of the fi no crystalline structure to bring the material to the amorphous phase.

In the course of grinding the size of the particles produced is reduced to a minimum value, at which riaumenta for a phenomenon that is called reverse grinding me. The minimum dimension obtainable is chamiata " **equilibrium value of the milling** ".

It has also examined the effect of the centrifugal force supplied from the mill to the single ball on the fi nal particle size and it is seen that when this force increases the final size fi powder grows with it, then the use of an excessive d'impatti force can be harmful.



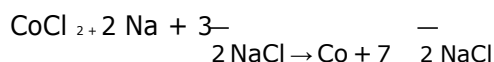
#### 4.1.3 ! The mechanochemical

When different sized particles are subjected to grinding their size decreases, consequently it increases their surface specific, which translates into an increase in the reactivity of the particles. Due to the high surface-active surface area of contact, they are induced at the interface solid state reactions that lead to the separation of new surfaces which in turn are affected by new at the molecular level reactions for which the material that forms is of nanometric nature.

The particles produced in this way have an amorphous structure due to the plastic deformations induced bumps which increase the density of dislocations within the material resulting in grain crystalline destruction, only then, after tempering heat treatments, it regains the typical crystalline structure of the material of departure.

This technique is called "mechanochemical process" as it not only involves the reduction of the material, but also The Contribution during the grinding energy required to start the chemical reaction between two or more reactants.

An example of a reaction that can occur in a mechanochemical process is the production of metallic materials upon reaction with chlorides. In this, as in other cases, the reaction is exothermic and involves the development of heat that must be removed by means of a diluting agent, still solid. An example is the reaction:



in this case the diluent substance is sodium chloride. It also plays the role of reducing the agglomeration formed of metal particles.

At the end of the process chlorine compounds they are eliminated by washing with water and you will get nanoparticles of a size of approximately 10-20 nm.

The mechanochemical is a process that affects the production of oxides and metal sulphides, in fact using special devices such as very fine starting material and medium-sized spheres was possible to obtain, for example, cadmium sulfide nanoparticles of very small size and nanoparticles of barium titanate from barium carbonate and titanium dioxide in saturated NaCl environment.

In the synthesis by mechanochemical can activate chemical reactions between solid at room temperature, reactions that would otherwise require very high temperatures, this is possible thanks to the high energy transferred during impacts that allows the reaction to occur even at relatively low temperatures. When

It makes use of additional components for temperature control and to avoid the aggregation of the particles, it is necessary to subject the end product to a washing, which on the one hand entails a high consumption of water and the other can generate agglomeration between the particles.

The advantage of this technique is the simplicity of its application and investments not very high, on the other hand

there may be contamination of the material by the working environment and a low controllability of the size and the final shape.

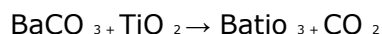
## 4.2 Solid State Synthesis

This is the most traditional and simple process for obtaining many ceramic powders, it implies a mild grinding and mixing of solid reagents, after which the solid mixture is subjected to calcination. For the production of  $\text{BaTiO}_3$  the calcination is carried out between 900 and 1200 °C, in general, the temperatures of these processes are very high due to the high thermal stability of the ceramic materials which involves extremely high melting temperature. The calcination process takes place through diffusion phenomena that lead to the recombination of the crystalline structures of a solid interdiffusion with another. The diffusive phenomena are phenomena of migration of atoms or molecules within the material. In solids

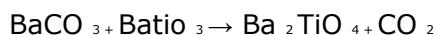
the

atomic migrations are very slow (hampered by bonds), but present. The presence of holidays eases the movement of atoms in the crystal. The energy of activation (sufficient to trigger the diffusion process) depends on the availability of the atoms of space to move. In the compact structures we need a greater quantity of energy where there is an appreciable diffusion process. The energy of activation in the case of solid state synthesis is provided in the form of heat. In the case of  $\text{BaTiO}_3$  the production process for the calcination takes place in the following stages:

1. Reaction to the interface by diffusion of Ba to the  $\text{TiO}_2$  to form a layer of  $\text{BaTiO}_3$  surrounding the  $\text{TiO}_2$



2. Formation of a phase orthotitanale



3. Reaction of Education



The high temperature is necessary to promote the diffusion of the barium and titanium, which gives life to the solid phase reaction.

The efforts aimed at further optimize this process are aimed at minimizing the distance to be covered by diffusion in the solid state by means of a more intense grinding, thereby it is possible to reduce significantly the calcination temperature (100-200 °C). The grinding high temperature inevitably promotes the agglomeration and the growth of the particles, and then a lower reaction temperature allows to obtain more dispersed particles and then smaller. Probably evolution technique will reduce the size of the particles up to 300 nm, but it certainly will not be able to get to smaller than 100 nm.

### 4.3! Process sintering of solid particles

The sintering process is a densification of a compact of powders, below the melting temperature, with removal of interstitial porosity, coalescence and development of strong bonds between adjacent particles.

The process can be applied to all classes of materials (metals, ceramics and polymers) and occurs as a result of different diffusion mechanisms.

The temperature that must be reached in order to obtain the sintering process is about 0.7 and 0.9 times the melting temperature. The procedure consists in the removal of porosity between the particles of the starting powder, in the growth of the particles, in the formation of robust connections (necks) between the latter and in the withdrawal of the components. The characteristic of a component is made by sintering the extreme hardness of the surface of work, combined with the relative cheapness in producing it in series.

By the term "compact" refers to the generally pressed initial powders prior to heat treatment. In the case of perfectly spherical particles of the same diameter and maximum achievable packing is 74%, often not used in reality powders with a precise dimension, as mixtures of different sized granules; such arrangement allows to increase the powders packing, this is because the smaller particles can fit in the interstices left by the combination of larger particles, with an improvement in the degree of what in technical jargon compactness is called the "green" or the artifact before the sintering heat treatment. The compact can be achieved by:

- Strong pressure impressed by high frequency vibrators, presses or mills which exert compressive forces with a minimum range of 100N / mm<sup>2</sup> and maximum range of 1400N / mm<sup>2</sup> depending on the desired density to be obtained and the different plasticity
- A gun that shoots the powder against a surface fixed or rotating according to the procedure for realizing the bisque in hollow pieces, from sedimented powder: the powder suspension liquid is absorbed by the porous region of the mold thereby obtaining the metal bodies.
- With an explosion in a water tank that allows contributions of great density by exploiting the high pressures involved
- Using the binders during pouring powders

The first effect of sintering is the **densification**, which it is measured as the reduction of **ratio surface / volume** (high for a compact powder) resulting in free energy reduction system (remember that the atoms to surface have a chemical bond does not fully balanced, so we need to provide energy to move the atoms from the inside of a solid, where the chemical bonds are balanced, towards the surface; the same energy is released when the surface is eliminated).

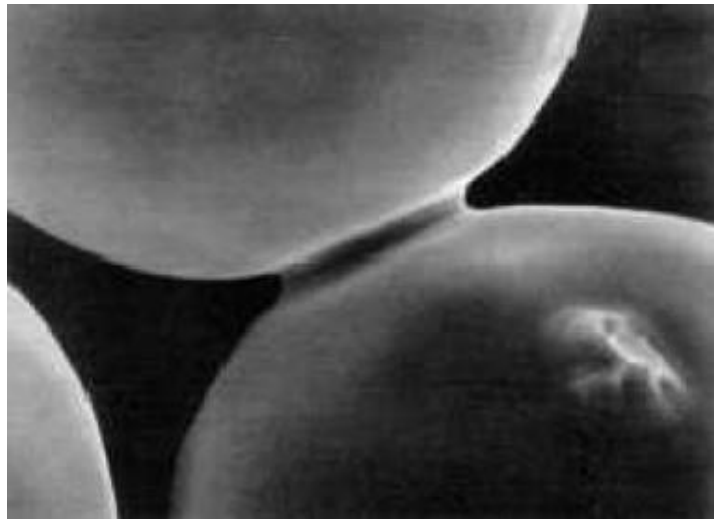
The sintering mechanisms distinguished by The absence or the formation of a liquid phase at the time of heating of

the pressed powders.

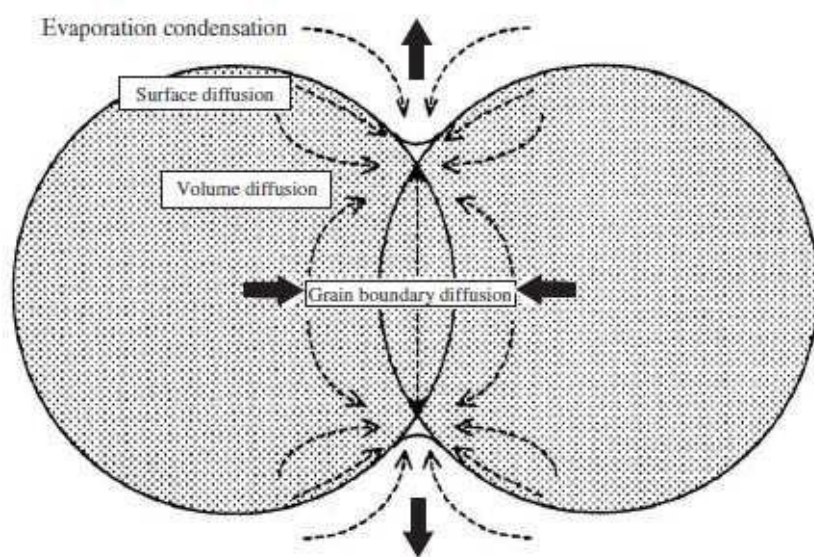
production of nanoparticles

When the particles are in a high temperature flow (still below their melting temperature) atoms acquire mobility and spread into other particles to reduce their surface specific area. In this way the smaller particles go to swell larger ones which interact with each other form strong cohesion bonds. As a result of the strong chemical bonds that occur between the particles and depending on the mechanism which develops, the pores are eliminated and the solid is densified. Since the pushing force of sintering is the reduction of the surface specific area of the particles, in the case of materials of nanometric dimensions this process is favored by the high activity of their surface, it follows that the sintering ability is high.

The diffusion of atoms from one particle to another leads to the formation of stable bridges that represent the point of contact between them (necks or "neck").

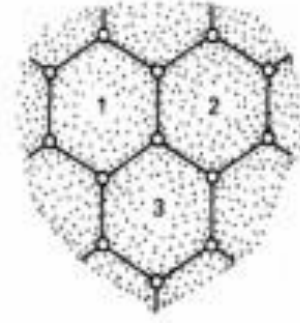
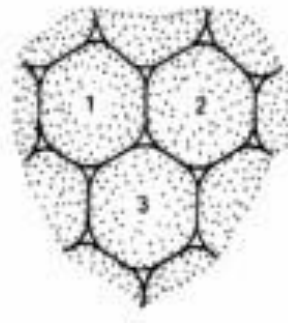
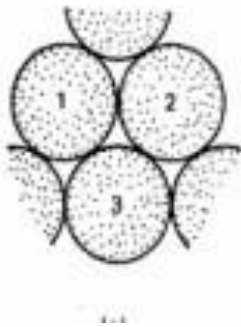


In the sintering of the mass transport it takes place by evaporation-condensation, superficial spreading, diffusion to the grain boundary and diffusion within the solid.



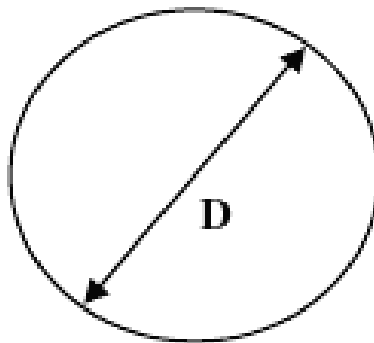
In general, the sintering process is divided into three stages:

- Early stage (up to 5% of the withdrawal)
- intermediate Stage
- Stadium fi nal (last 10% of shrinkage)



#### 4.3.1 ! Mechanisms of the sintering process

The guiding concept that underlies the sintering process is the energy of the surface. For powders, the energy of the surface per unit volume is greater the smaller the grains. This means that if a grain of metal powder is joined to another there is an increase in volume, but decreased surface and a consequent decrease in energy. The process is therefore energetically favored. Consider a simple geometric model with spheres of a diameter  $D$ .



$$V = \frac{4}{3} \pi R^3 = \frac{\pi D^3}{6}$$

$$A = \pi D^2$$

The sphere is formed by  $n$  atoms each volume  $\Omega$  (it follows that  $V = n\Omega$ ).

If the sphere experiences an increase in number of atoms  $dn$  it will vary its volume and its surface. For the volume we can write:

$$V = n \Omega = n \frac{4}{3} \pi D^3$$

$$\begin{aligned} dV &= dn \Omega = n \frac{4}{3} \pi \cdot 3 D^2 dD \\ &= 4 \pi n D^2 dD \end{aligned}$$

Similarly, for surface we can write:

$$\frac{dA}{dn} = \frac{4 \pi D^2 dD}{dn} = 4 \pi D$$

Now the chemical potential difference relative to the change in surface energy due to the addition of new atoms ( $dn$  atoms) will be proportional to this variation of area:

$$\frac{\Delta U}{dn} = \gamma \frac{dA}{dn} = \gamma 4 \pi D$$

This equation relates the variation of internal energy with the size of the particles and is seen as it decreases with increasing diameter of the same. At this point we can introduce the following parameters:

- Neck size ratio: the ratio between  $x$  (width of the neck) and  $D$  (particle diameter)
- Shrinkage: variation in the size of the object with a consequent increase of the density.

As mentioned the sintering process consists of three phases. In the first stage the adjacent particles are connected forming "necks" of sintering that at the end of the treatment correspond to the grain boundaries. The mechanism of formation of the neck is tied to the diffusion phenomena in place due to the different concentration of atoms between neighboring particles, this gradient can be generated by the presence of point defects such as holidays and interstitial atoms, the different concentration of such defects leads to the migration of atoms superficial in the interstitial areas formed by the particles. The formation of the neck does not lead to an effective approach of the centers of the grains, or is not a phenomenon which in itself constitutes a "densification" of the grains. Each agent diffusive mechanism on the surface of the particles does not involve an actual removal of porosity; the densification is produced instead by displacement of material from the inside of the grains and dislocations moving in the crystal lattice, these last movements lead to a deformation of the grains, which can clog, so efficiently.

The second sintering stage is characterized by the complete deformation of the crystal grains of departure. The porosity is concentrated at the grain boundaries, thus constituting, for the diffusion of the channels.



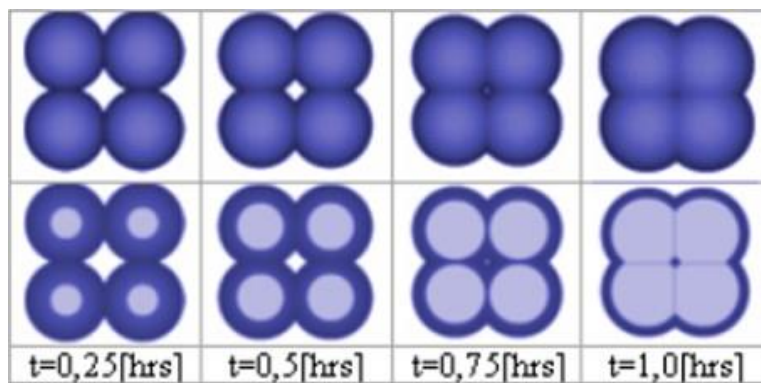
Under these conditions, the porosity  $P$  residual follows a logarithmic dependence with respect to the sintering time.

$$P = -C \log(t)$$

The model applies to what a final porosity remains interconnected, namely when the channels network remains defined. When the pores are no longer communicating it is verification beginning of the third stage of densification.

The final stage of sintering corresponds to isolated pores, mostly at the meeting points between four grains.

The absorption of such residual porosity is difficultly moldable and generally requires a very long time for the densification.



At this point, however, one can verify another phenomenon which is that abnormal grain growth which can lead to the inability to complete the sintering. abnormal grain growth of the crystal grain size can be drastically limited by the introduction of specific additives there as MgO and alumina, which act as "pinning" function, that is to anchor the grain boundaries so as to slow down the growth.

#### 4.3.1.1 The coarsening of the solid-state particles

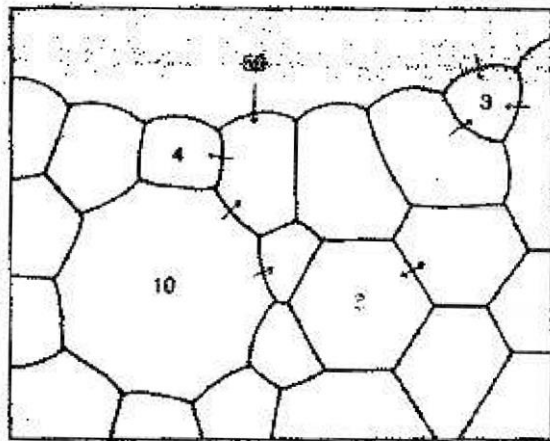
Geometrically a polyhedron of six flat sides is a polycrystal in a minimum energy level.



Grains large (usually more than 6 sides) tend to incorporate the grains smaller leading to a decrease of free energy, from which it follows a more stable situation.

This behavior is favored by the decrease of the surface specific ca. Recall that at each surface corresponds to a certain energy content because of unexpressed ties, it follows that the grain size further reduce the ratio surface / volume with the consequent reduction of the free energy of the system. We can summarize:

- Particles with less than 6 sides have concave edges
- The granules grow or will withdraw depending on the number of sides, those with more than 6 sides grow, those with less will withdraw
- The grains grow to more than smaller expenses



Another parameter that influence the dense fi cation is the presence of gas in the environment of sintering. If the gas enclosed in the pores remains trapped inside the material, the dense fi cation can not be completed as part of the volume of the material is occupied by the gas particles that increase the porosity of the material.

Oxides sintered in air dif fi cult to reach 98% of the theoretical density, but often their degree of dense fi cation is in the range 92-96%.

#### 4.3.1.2 Time-Temperature Performance

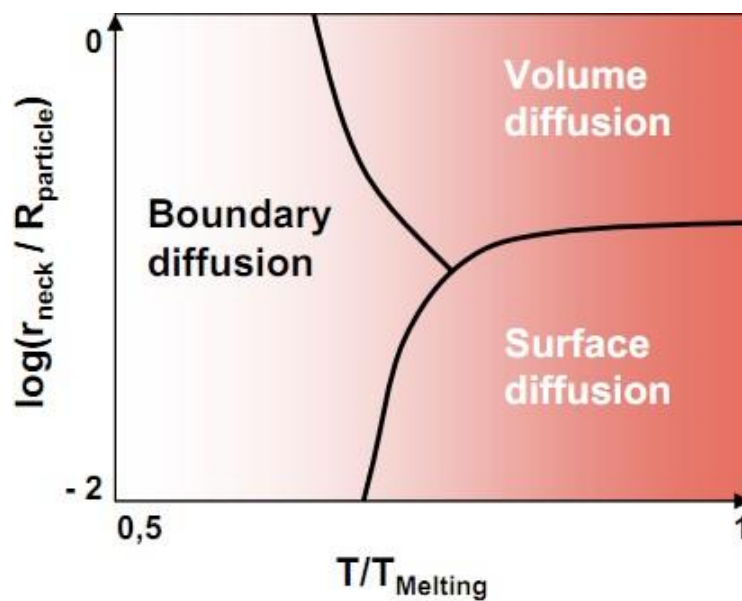
The sintering proceeds in time with increasing temperature. As previously indicated the smaller the size of the grain, easier is sintering, that is, the required temperature is lower precisely by virtue of the high specific surface of the particles which implies a high surface free energy and a consequent reduction of energy activation. So the great advantage to operate with nanoparticles is to reduce the sintering temperature and consequently the energy required.

L'ef fi ciency of sintering can be increased through the application of simultaneous pressure and temperature (hot pressing). The speed of dense fi cation is governed by the equation:

$$\frac{d\rho}{dt} = \frac{4\sigma V_m}{RT} \cdot \dots$$

$$dt = C \cdot r_{0n}$$

production of nanoparticles



#### 4.3.2 sintering Models

Depending on the type and characteristics of the process of densification we can distinguish four types of sintering:

- **Sintering in the solid state:** wherein the densification and compaction occur below the melting point of all the possible liquid phases. Sintering is accompanied by the change in the form of grains
- **Sintering in the liquid phase:** in which the formation of the liquid phase does not totally eliminate the porosity; the full densification is reached by reaction of the solid phase.
- **Reactive Sintering:** the compact powder chemically reacts with liquid and gaseous phases
- **Glazing densification:** with formation of a liquid phase and the consequent elimination of the gaseous phase and intergranular pores. The driving force for the full densification is represented by the reduction of superficial consequent elimination of pores / bubbles.

#### 4.3.2.1 Sintering in the solid state

The solid state sintering to evaporation-condensing It is the mechanism prevalent for solids with high vapor pressure, such as alkali halides (poorly interesting to fi engineering ni), in which the material transfer is carried out for switching to external and subsequent gas phase condensation.

#### 4.3.2.2 Sintering in the liquid phase

In the liquid phase sintering with training; powders to be sintered substance containing additives suitable to the formation of a liquid phase, for a content not exceeding 5%. The liquid phase "lubricates" the grains in the sense that makes the mutual sliding possible, act to reduce porosity, and at the same time partially dissolves the base material (the result is a material transport through the liquid phase amending the grain geometry, allowing a more favorable mutual adaptation); it is the sintering mechanism found important for ceramic materials "technical", such as alumina  $\text{Al}_2\text{O}_3$  (added with  $\text{MgO}$  and  $\text{SiO}_2$ ), the silicon nitride  $\text{Si}_3\text{N}_4$  (added with  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$   $\text{Y}_2\text{O}_3$ ). The liquid phase, solidified as glass, or as amorphous phase, it is a weak point in high temperature applications, when leaving softens "disconnected" the crystal grains. The negative effect of secondary phase may be reduced: in some cases (for example in the sintering of  $\text{Si}_3\text{N}_4$  admixed with  $\text{Al}_2\text{O}_3$  and other oxides of bi- and trivalent metals, with the development of an oxy-nitride glass as a secondary phase). In some cases, the amorphous phase can be crystallized by means of a suitable heat treatment; in other cases, the same morphology of the granules limits the mutual sliding (very elongated crystalline grains and interconnected are hardly mobile for a "mutual friction effect": it is the case of siliceous refractory materials, or even of  $\text{Si}_3\text{N}_4$  or of ceramic  $\text{SiAlON}$ ).

The partial dissolution and homogeneous distribution of the liquid phase conditions are of course can only be reached in conditions of high "wettability" between liquid and powder to densify. Finally, a sintering particular case with the liquid phase is represented by reactive sintering in step (Reaction bonding). Components in  $\text{Si}_3\text{N}_4$  and  $\text{SiC}$  can be produced from powders

It infiltrated liquid, which reacts, respectively, with nitrogen (from the atmosphere) or with graphite (inserted into fine powder, between the  $\text{SiC}$  grains).

#### 4.3.2.3 Sintering for fi cation glazing or sintering viscose

The sintering for vitrification or sintering viscose It is a part of the raw materials gives rise, in "cooking", in a vitreous liquid phase, particularly viscose, also in contents above 20%; the liquid phase is so abundant as to infiltrate, to creep, in the pores, deleting them. This is a typical mechanism of silicate raw materials, used for example in the manufacture of traditional ceramic products with compact paste such as stoneware and

porcelain; the glass sintering represents the limit case, when

production of nanoparticles

the whole mass coincides with the viscous liquid phase. The equation that governs the densification, according to this mechanism, is the equation of Frenkel:

$$\frac{\Delta V}{V_0} = \frac{94 \cdot \gamma \cdot t}{\eta \cdot r_0}$$

where  $V_0$  is the volume of the compact of powders prior to sintering,  $V$  is the volumetric shrinkage from the compact to the sintered product, the surface energy  $\gamma$ ,  $r_0$  the curvature radius of the particles,  $t$  the holding time and  $\eta$  the viscosity of the glassy phase at the selected sintering temperature. This law applies, strictly speaking, in the cases of spherical particles, or in any case of homogeneous size, and interconnected porosity, which is determined by the interstices between the granules, open. When the sintering proceeds and the porosity consists of pores blocks the equation of Frenkel loses its meaning.