Chapter 2: Synthesizing methods of nanomaterials

1- Nanomaterial synthesis methods

Depending on the desired physical properties, the size, shape and organization of nanoobjects are important parameters to control.

The various techniques for developing nano-objects are conventionally classified into two categories: the top-down approach and the bottom-up approach.

In this chapter we briefly present these two approaches and some of the methods for developing nano-objects used today, specifying their specificities and their limits. Nano-objects and nanomaterials can be synthesized using two different approaches:

The bottom-up approach and the top-down approach.

- The “bottom-up” approach consists of building nano-objects and nanomaterials atom by atom, molecule by molecule or aggregate by aggregate. The assembly or positioning of atoms, molecules or aggregates is carried out in a precise and controlled manner, thus allowing the development of functional materials whose structure is completely controlled.
- The "top-down" approach consists of miniaturizing current systems by optimizing existing industrial technologies. Devices or structures are thus gradually undersized or fractionated until they reach nanometric dimensions

The two approaches tend to converge in terms of the dimension of the nanoscale domains. The “bottom up” approach seems richer in terms of type of material, diversity of architectures and control of the nanometric state (size, size dispersion, positioning of molecules, phases). The "top down" approach makes it possible to obtain larger quantities of materials but the control of the nanometric state is more delicate (size dispersion, structural defects, non-equilibrium phases).

The manufacture of nanomaterials according to the "bottom up" approach consists in the construction of structures atom by atom or molecule by molecule. This concerns metals, ceramics, semiconductors, polymers, fullerenes and nanotubes. These structures are then used directly (e.g. catalysis: substance that increases the rate of the reaction) or serve as elementary bricks for the construction of nanostructure architectures of varying complexity. These architectures form "naturally" by self-organizing in liquid media, polymers (hybrid materials) or are controlled by sets of transformation operations: mixing of nanopowders, or with other systems (e.g. polymers, nanotubes).

The direct manipulation of atoms or molecules is more complex. The “top-down” approach aims to produce nanomaterials from successive fractionations of a "classic" microstructured material. These "top down" methods are essentially based on the application of so-called "severe" mechanical stresses: violent shocks, strong deformations. We find in these techniques mechanical grinding and the effect of alloying by mechanical stress (mechanical alloying) which can be followed by heat treatments, consolidation or chemical reactions.

2- Physical methods:

2.1- Evaporation / Condensation

This method consists of evaporating a metal by heating then condensing the metal vapor in order to obtain nanopowders formed of dispersed nanometric particles. The type of heating depends on the vapor pressure of the metal, ie its ability to evaporate but also on the surface state (oxidation). Fe, Ni, Co, Cu, Pd, Pt, produce sufficient steam by radiative (1200°C) and inductive (2000°C) heating. Oxygen-hungry metals (Al, Cr, Ti, Zr) and refractory metals (very low vapor pressure (Mo, Hf, Ta, W) require more powerful heating methods: heating by electronic bombardment (3,000°C) heating by inductive plasma or/and coupled with the electric arc (3,000°C to 14,000°C).

If the metal particles are placed in a reactive atmosphere, generally oxygen, after formation, the nanoparticles obtained are then the oxide of the initial metal after the oxidation reaction. Figure 3 presents the "historical" process. It consists of evaporating a material in a partial atmosphere and collecting the nano-aggregates on a cold finger.

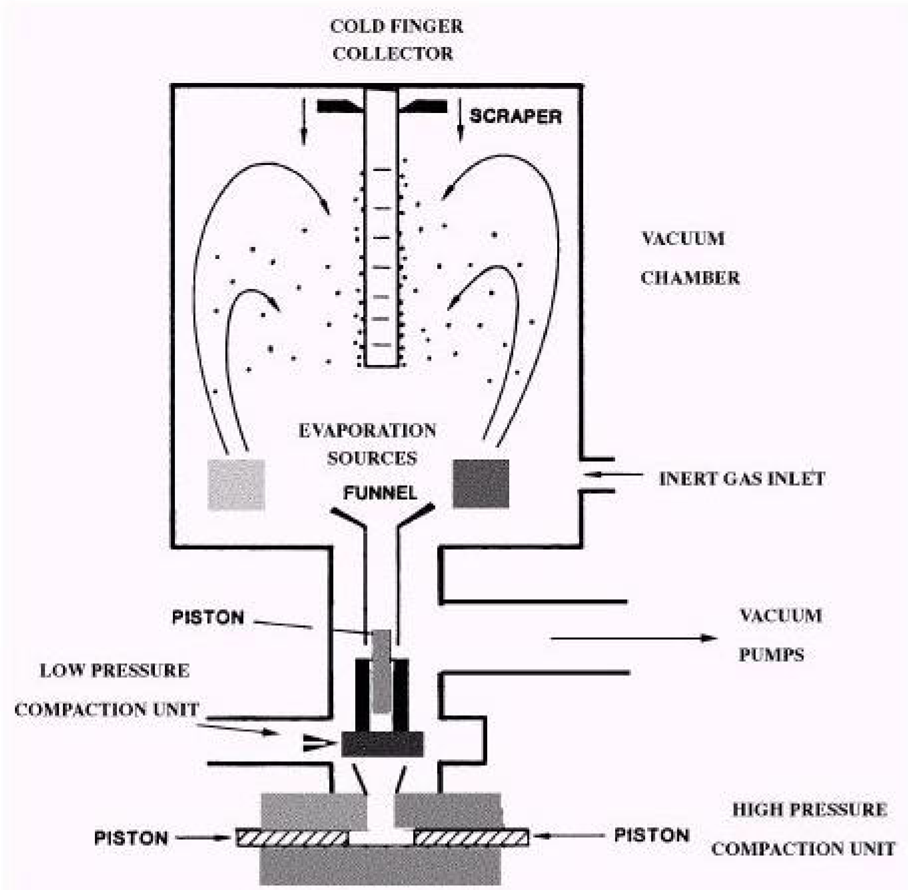


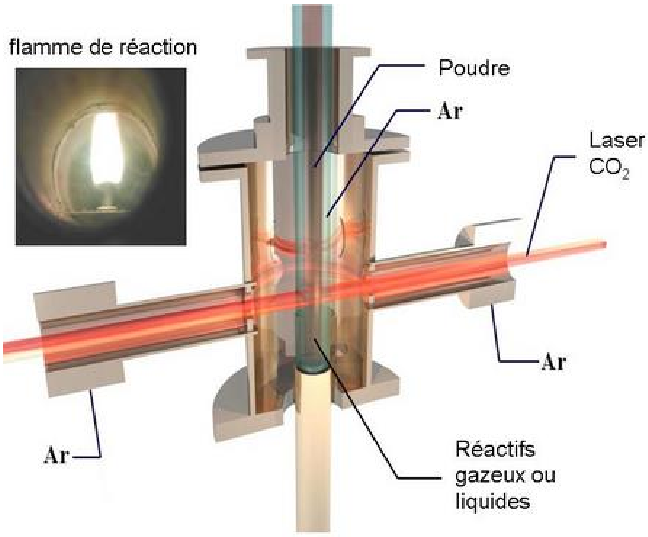
Figure1: Evaporation / condensation process

2.2- LASER Pyrolysis

Laser pyrolysis is a flexible and efficient method for synthesizing nanoscale powders. It is based on the interaction in crossed jets between the emission of a CO2 laser and a flow of reagents. The resonant energy transfer causes a rapid rise in temperature in the reaction zone by excitation of the vibrational levels of the molecules, the precursors are dissociated and a flame appears in which the nanoparticles are formed which then undergo a quenching effect on exiting the flame. The powders are entrained by a gas flow in an area where they will be collected. This method makes it possible to easily synthesize particles of 15 to 20 nm. Among the advantages of this method, we can mention:

- A high chemical purity of the products, essentially limited by the purity of the reagents. Good physical and chemical homogeneity.
- A fast quenching speeds.
- Good flexibility of use.

Depending on the mixtures of precursors introduced into the reactor, a wide variety of powders have been synthesized: Si, SiC, SiCN, SiCNAlY, SiCO, Si3N4, TiC, TiO2, fullerenes, etc.).



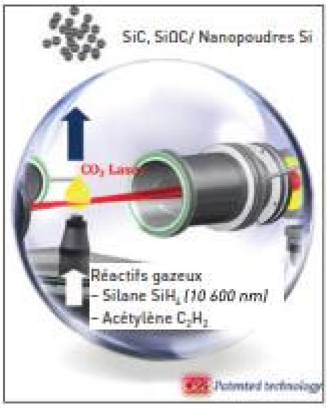
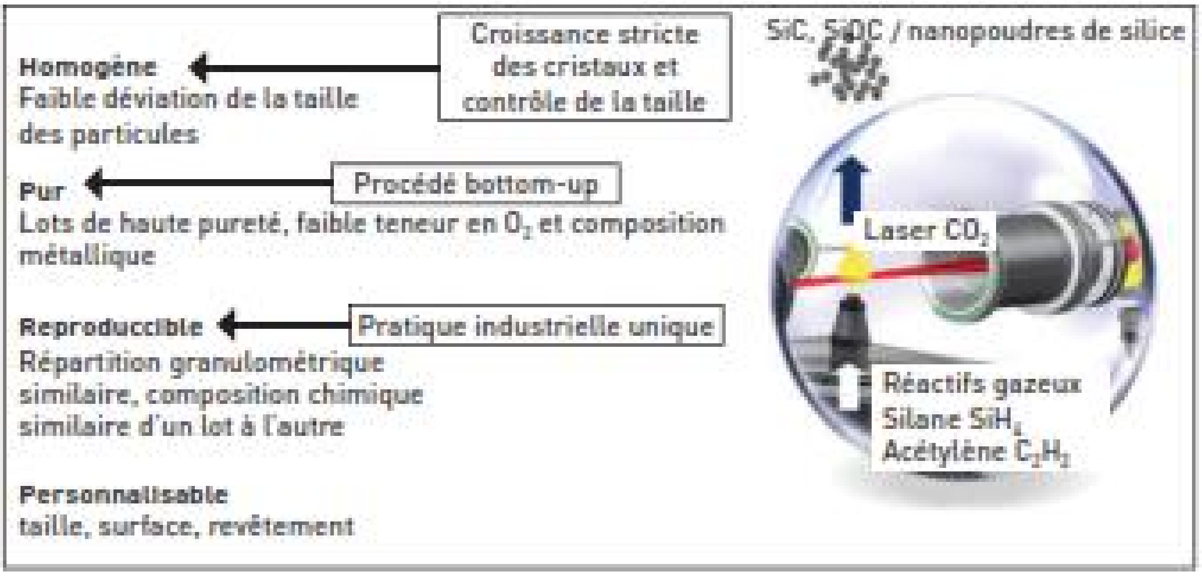


Figure 2: Operating principle of laser pyrolysis, allowing atoms to be obtained from gaseous molecules.

A flow of “process gas” made up of gaseous molecules (in practice hydrides) which contain, depending on the purpose, silicon or carbon. The flow is crossed by the light of a laser which comes to break the molecules, leaving on one side the hydrogen which is eliminated, and on the other the atoms of silicon and carbon which combine in different ways to form either silicon carbide, or pure silicon, or carbon-coated silicon. Depending on process gas conditions. After the molecules break, the solid matter aggregates and grows into crystals. At the desired point, we stop (we "quench" a chemical reaction means stopping it with the help of a chemical species, called a deactivator or quencher (extinguisher in English).) the crystal growth reaction to control very strictly the size of the particles. This control is one of the fundamental advantages of the process. This makes it possible to obtain particles of very homogeneous sizes. Processes are nominally set to 35-40 or 75 nm.

The produced products

- silicon carbide, used for mechanical reinforcement
- silicon or carbon-coated silicon used for battery applications.



It can be had in different forms, either in the form of loose powder (reactor outlet) with a low bulk density and a very high dustiness, thus forming a very light powder. It can also be put in the form of a compacted powder, which increases its bulk density by about a factor of ten and greatly reduces the dustiness (by two or three orders of magnitude) allowing much safer handling conditions for operators. Incidentally, the lower volumes also generate lower transport costs. Finally for certain specific applications.

The advantages of the laser pyrolysis synthesis process are as follows:

- the homogeneity of the size thanks to a very strict control of the growth of the crystal;
- high chemical purity of the product. This is a consequence of the “bottom up” process, since the starting reagents are strictly controlled;
- very high product stability.

2-Chemical methods

2.1- Sol-gel technique:

Sol-gel techniques make it possible to produce nanomaterials from alkoxide solutions or colloidal solutions. The materials are produced in the form of monoliths, nanopowders or thin layers. These are techniques based on inorganic polymerization reactions.

The sol-gel process consists of:

- the development of a stable suspension (sol) from chemical precursors in solution.
- obtaining the (gel): following interactions between the species in suspension and the solvent, these "sols" will be transformed into a three-dimensional solid network expanded through the liquid medium. The system is then in the “freeze” state.
- -These gels are then transformed into amorphous dry matter by evacuation of the solvents.

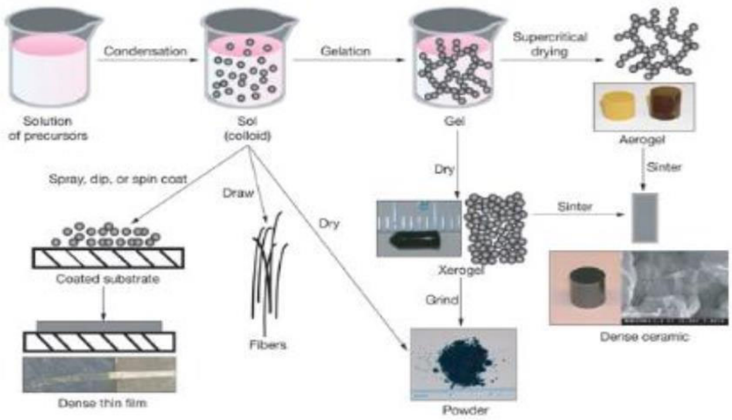


Figure 3 : Sol-gel techniques

3- Mechanical methods

3-1 Mechanical synthesis:

Mechanical synthesis consists of:

- Grind micrometric powders (1 to 50 mm)
- The powders are introduced into a sealed container, accompanied by steel or tungsten balls.
- The assembly is strongly agitated, which will allow plastic deformation accompanied by high-energy mechanical wear.
- The material is then continuously refined until a nanometric size is obtained.
- The temperature required in mechanical synthesis is low, which allows a slow magnification of the particles formed.

3-1 Principle of mechanical grinding

A Benjamin innovation in the 1960s, mechanical grinding was first used to produce Ni-based superalloys containing oxide dispersions.

- It has been extended to a variety of alloys
- Mechanical grinding is a non-equilibrium process that allows the production of nanostructures.
- The repeated phenomena of fracture, welding and resoldering lead to severe plastic deformation of the powder particles.

A refinement of the size of the crystallites the introduction of a high density of structural defects (gaps, interstices, dislocations, grain boundaries, etc.). The formation of solid solutions, amorphous phases, intermetallic phases, stable and metastable phases, etc.

3-2 High energy mechanical grinding

High-energy mechanical milling is a non-equilibrium process that allows the production of nanostructures. The repeated phenomena of fracture, welding and re-welding lead to a refinement of the size of the crystallites and the introduction of a high density of structural defects (gaps, interstices, dislocations, grain boundaries, etc.). The formation of solid solutions, amorphous phases, metastable phases, intermetallic, etc. is due to the interdiffusion of the elements through severe plastic deformation.