

Techniques for synthesis of nanomaterials (II)

Lecture 12

MTX9100
Nanomaterials

OUTLINE

- What are advantages of liquid phase synthesis?
- How to produce nanostructures by mechanical methods?
- Summary of the methods.

Liquid phase synthesis

Precipitating nanoparticles from a solution of chemical compounds can be classified into five major categories:

- (1) colloidal methods;
- (2) sol - gel processing;
- (3) water - oil microemulsions method;
- (4) hydrothermal synthesis; and
- (5) polyol method.

Solution precipitation relies on the precipitation of nanometer-sized particles within a continuous fluid solvent. An inorganic metal salt, such as chloride, nitride and so on, is dissolved in water. Metal cations exist in the form of metal hydrate species, for example, $\text{Al}(\text{H}_2\text{O})_3^+$ or $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. These hydrates are added with basic solutions, such as NaOH or Na₄OH. The hydrolyzed species condense and then washed, filtered, dried and calcined in order to obtain the final product.

Colloidal methods

Colloidal methods are simple and well established wet chemistry precipitation processes in which solutions of the different ions are mixed under controlled temperature and pressure to form insoluble precipitates.

For metal nanoparticles the basic principles of colloidal preparation were known since antiquity. E.g. gold colloids used for high quality red and purple stained glass from medieval times to date.

However, proper scientific investigations of colloidal preparation methods started only in 1857 when Faraday has published results of his experiments with gold. He prepared gold colloids by reduction of HAuCl_4 with phosphorus.

Today, colloidal processes are widely used to produce such nanomaterials like metals, metal oxides, organics, and pharmaceuticals.

Sol-gel technique

Sol-gel technology is a well-established **colloidal chemistry technology**, which offers possibility to produce various materials with novel, predefined properties in a simple process and at relatively low process cost.

The sol is a name of a *colloidal solution* made of solid particles few hundred nm in diameter, suspended in a liquid phase.

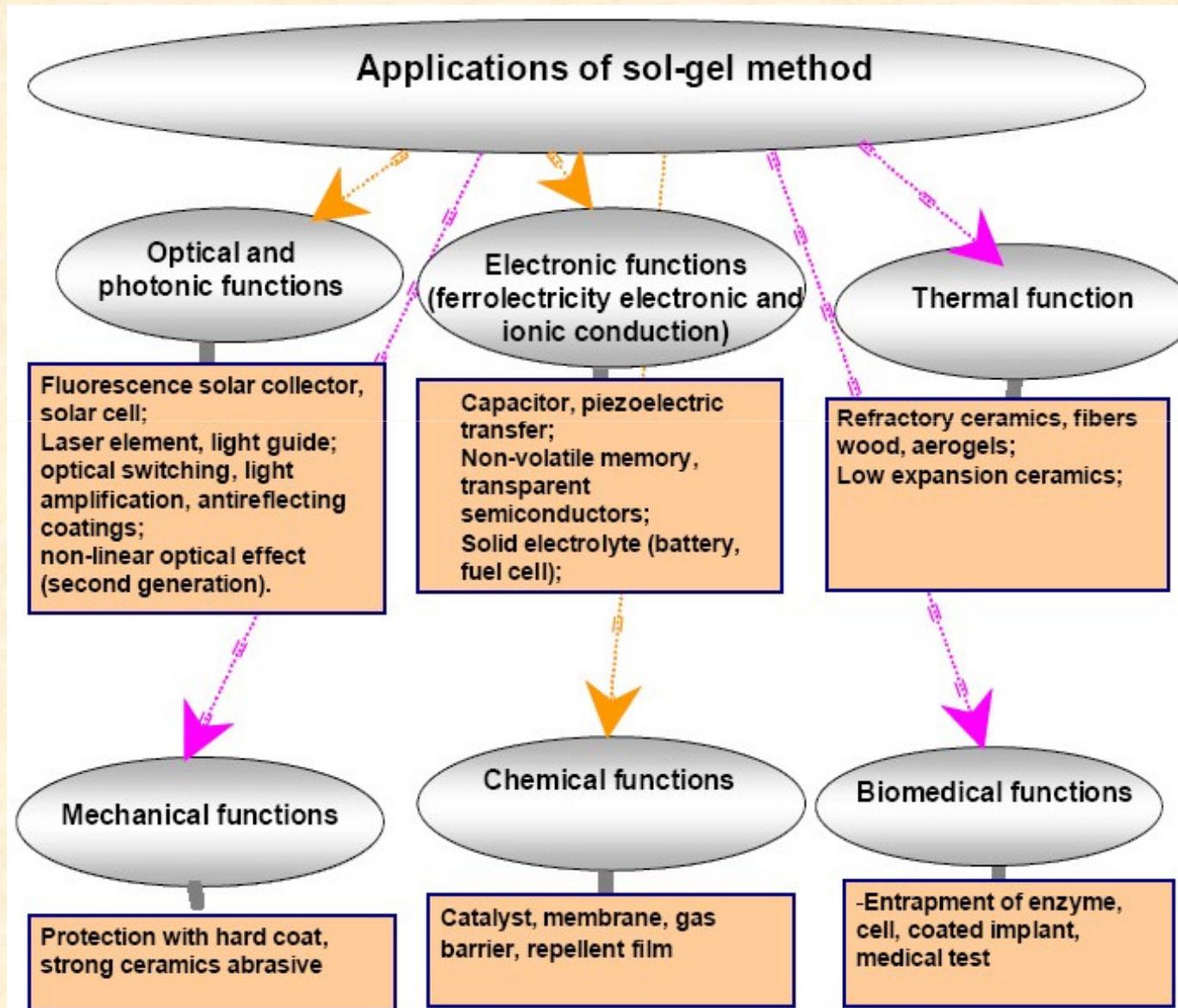
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The gel can be considered as a solid macromolecule immersed in a solvent.

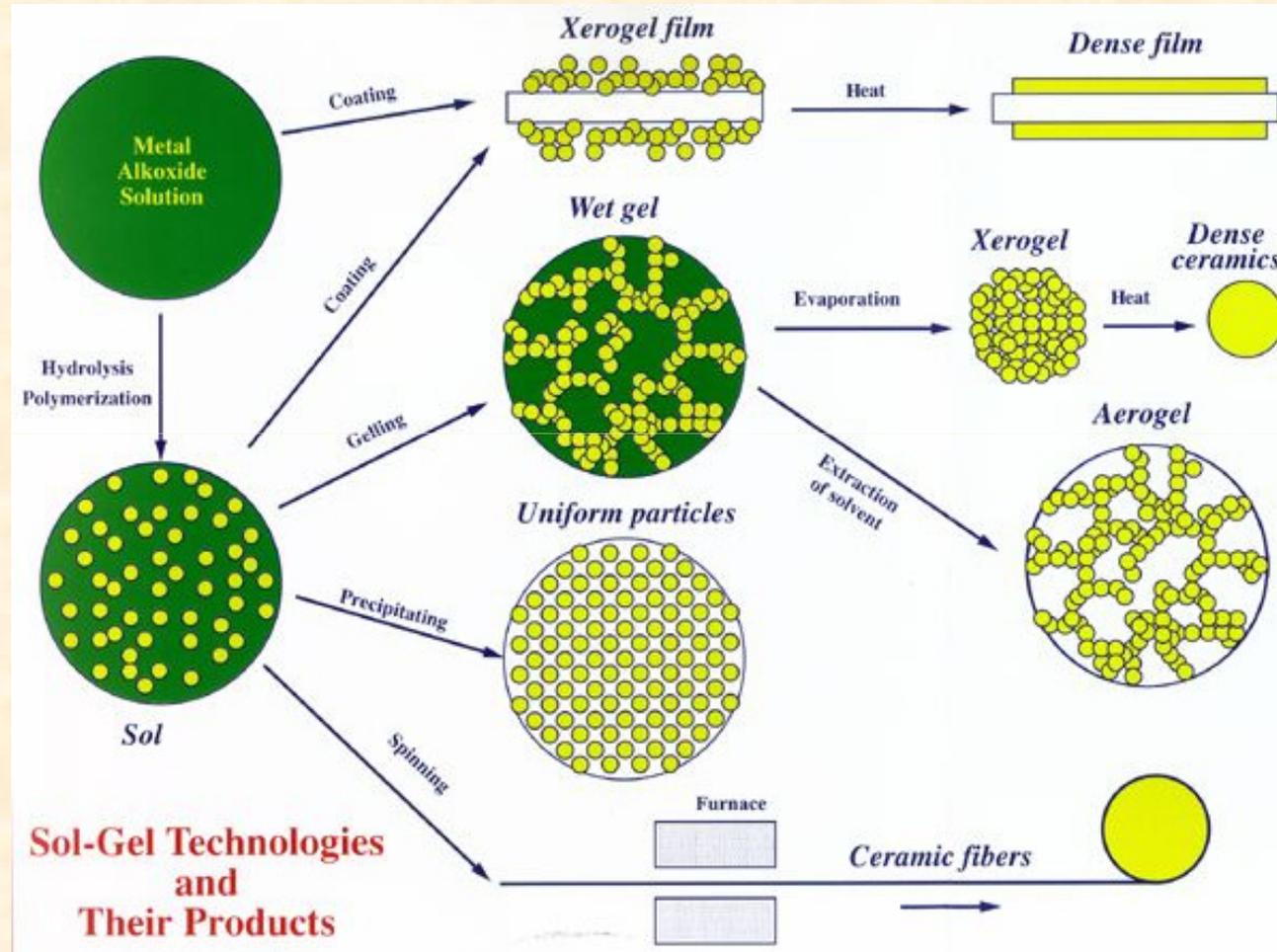
Sol-gel process consists in the **chemical transformation** of a liquid (the sol) into a gel state and with subsequent post-treatment and transition into solid oxide material.

The main **benefits** of sol-gel processing are the high purity and uniform nanostructure achievable at low temperatures.

Applications of sol - gel



Sol - gel process



Start with precursor

Form Solution (e.g., hydrolysis)

Form Gel (e.g., dehydration)

Then form final product

Aerogel (rapid drying)

Thin-films (spin/dip)

Sol – gel for ceramics

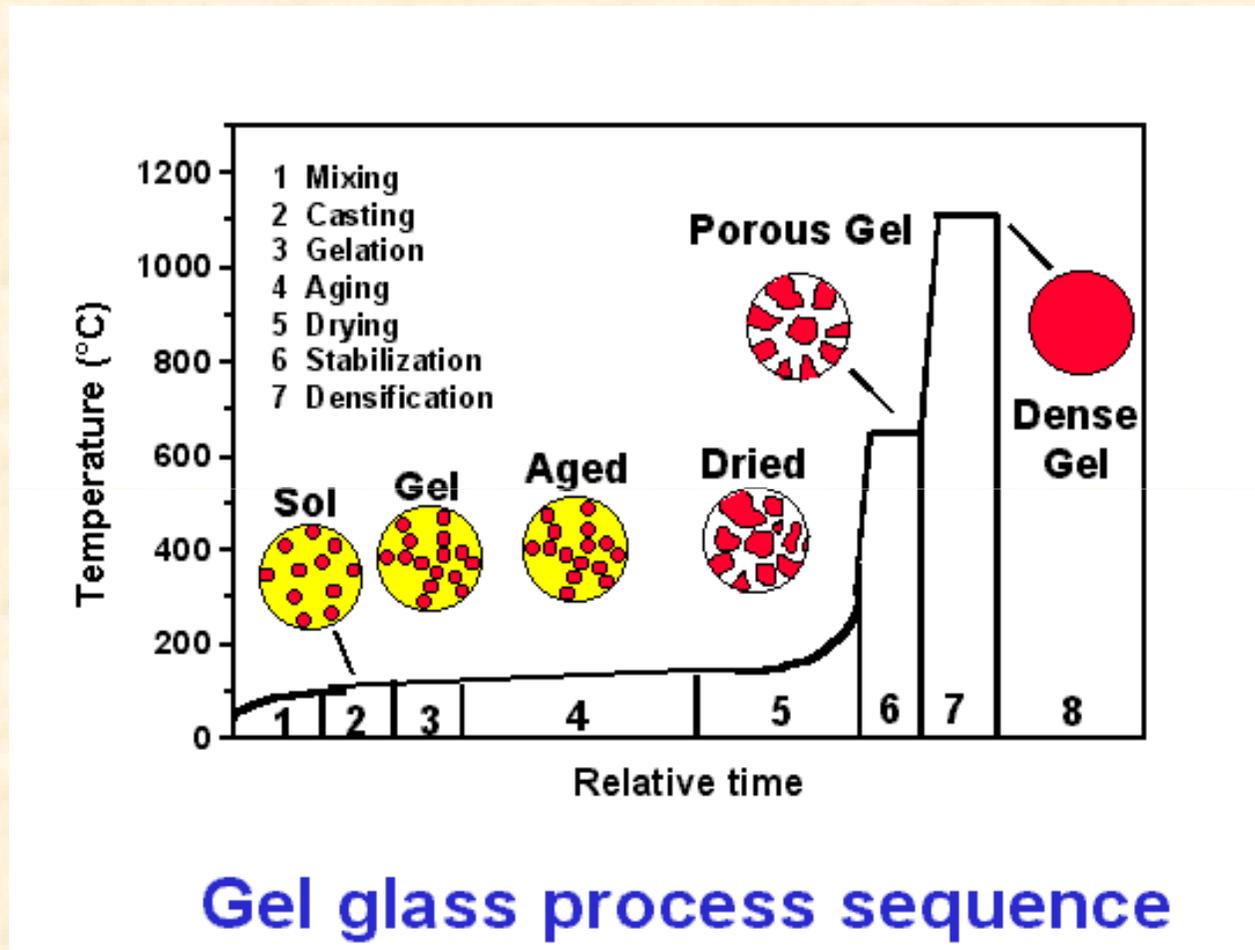
The Sol-Gel process allows to synthesize ceramic materials of high **purity and homogeneity** by means of preparation techniques different from the traditional process of fusion of oxides.

This process occurs in liquid solution of organometallic precursors (TMOS, TEOS, Zr(IV)-Propoxide, Ti(IV)-Butoxide, etc.), which, by means of hydrolysis and condensation reactions, lead to the formation of a new phase (SOL).



(M = Si, Zr, Ti)

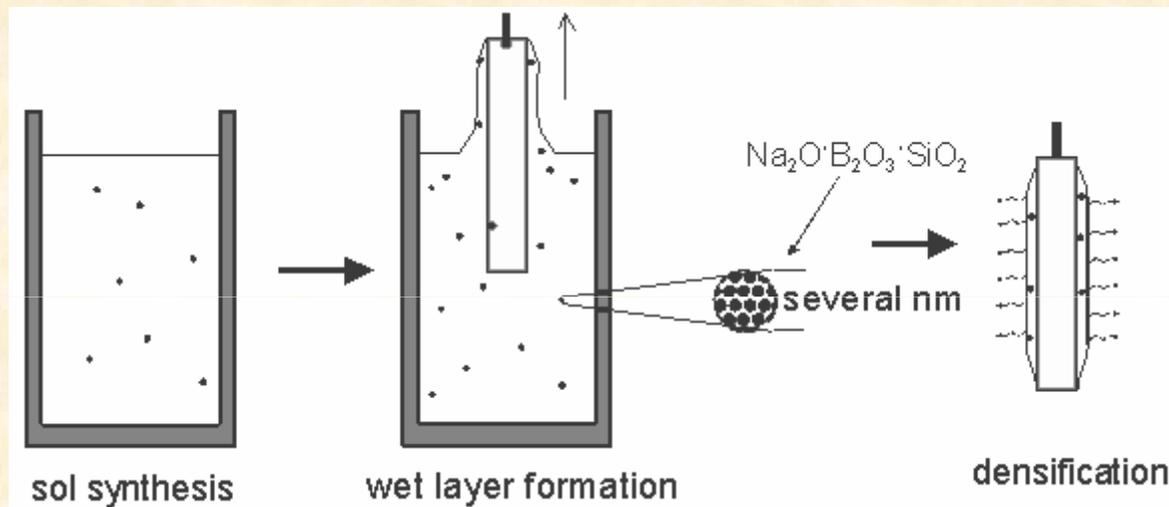
Schematic of Sol-gel



The fundamental property of the sol-gel process is that it is possible to generate ceramic material at a temperature close to room temperature.

Sol – gel for coatings

The most common application of sol-gel process is fabrication of various coatings and films

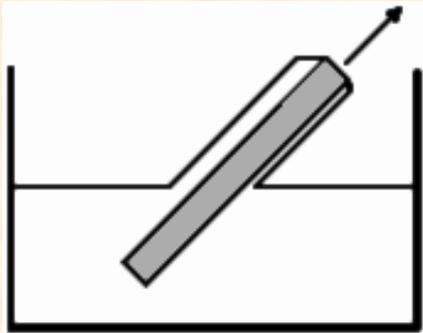


In the *dip coating process* the substrate is immersed into a sol and then withdrawn with a well-defined speed under controlled temperature and atmospheric conditions.

The sol left on substrate forms a film with thickness mainly defined by the withdrawal speed, the solid content and the viscosity of the liquid.

Next stage is a gelation (densification) of the layer by solvent evaporation and finally annealing to obtain the oxide coating.

Sol – gel for coatings (2)



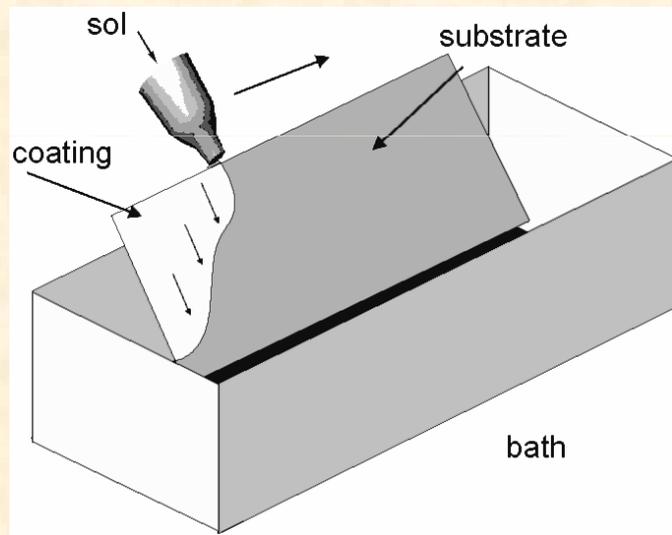
In an *angle-dependent dip coating* process the coating thickness is dependant also on the angle between the substrate and the liquid surface, so different layer thickness can be obtained on the top and bottom side of the substrate.

Spin coating is used for making a thin coating on relatively flat substrates . The material to be made into coating is dissolved or dispersed into a solvent, and then deposited onto the surface and spun off to leave a uniform layer for subsequent processing stages and ultimate



Flow coating process

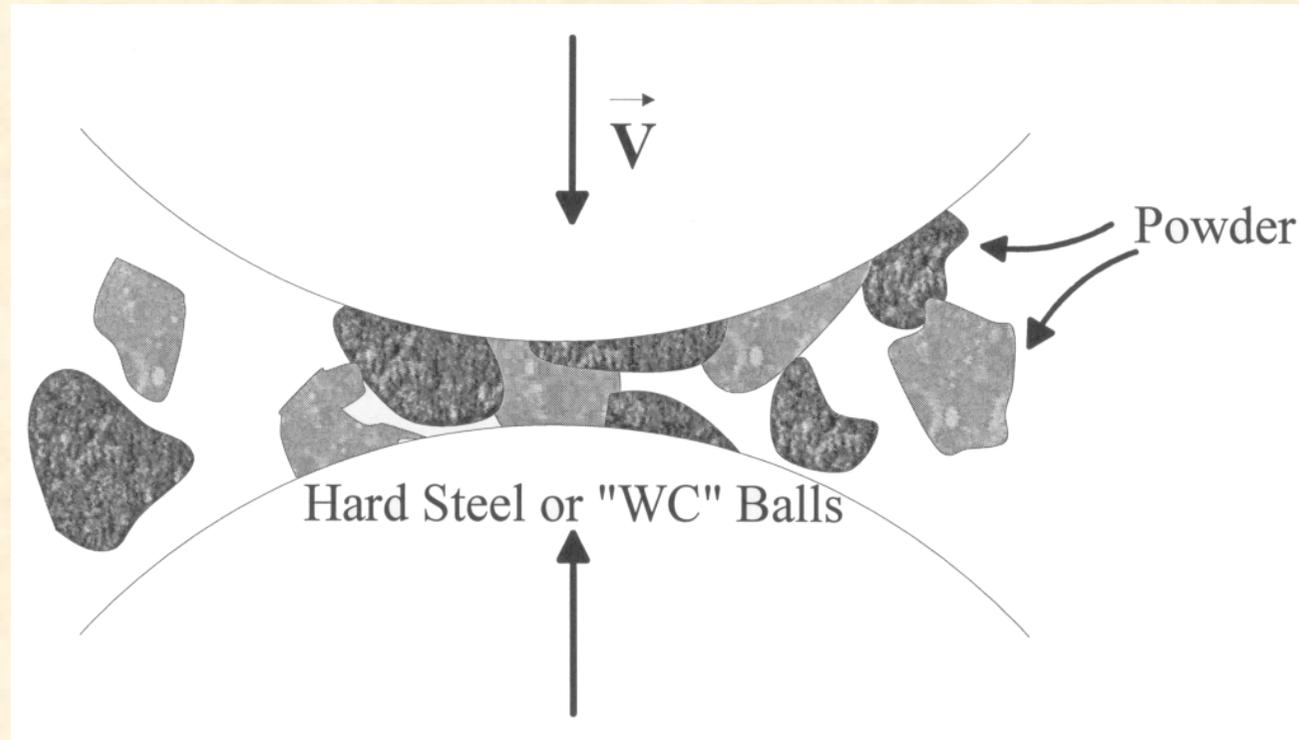
In the *flow coating process* the liquid coating system is poured over the substrate to be coated.



The coating thickness depends on the angle of inclination of the substrate, the liquid viscosity and the solvent evaporation rate.

The advantage of the flow-coating process is that non-planar large substrates can be coated rather easily.

Solid – state phase synthesis



Mechanical attrition methods give **very high production rates** (up to tones per hour) and are widely used for industrial production of clay, coal and metal powders.

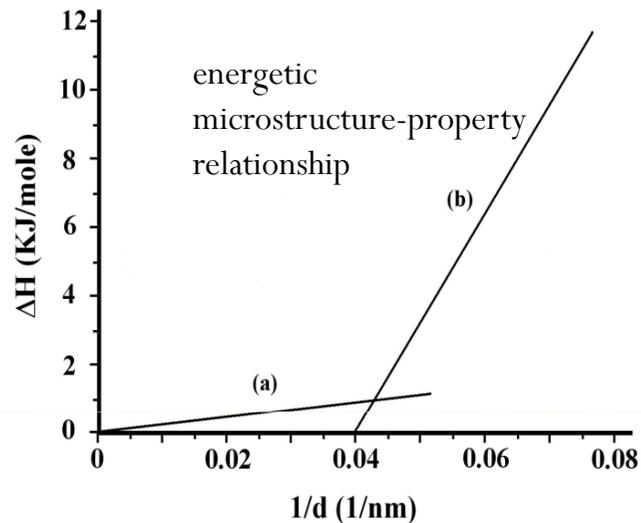
High-energy milling

In the 1980s, the method of *high-energy milling* gained a lot of attention as a non-equilibrium solid-state process resulting in materials with nanoscale microstructures.

- Deformation localization in shear bands containing a high dislocation density
- Annihilation/recombination/rearrangement of dislocation to form cell/sub-grain structure with finer dimension
- Random orientation of grains, i.e., low angle grain boundary → high angle grain boundary → grain boundary sliding rotation



Mechanical milling



The stored enthalpy H as function of reciprocal grain size $1/d$ of Fe at different levels of mechanical attrition.

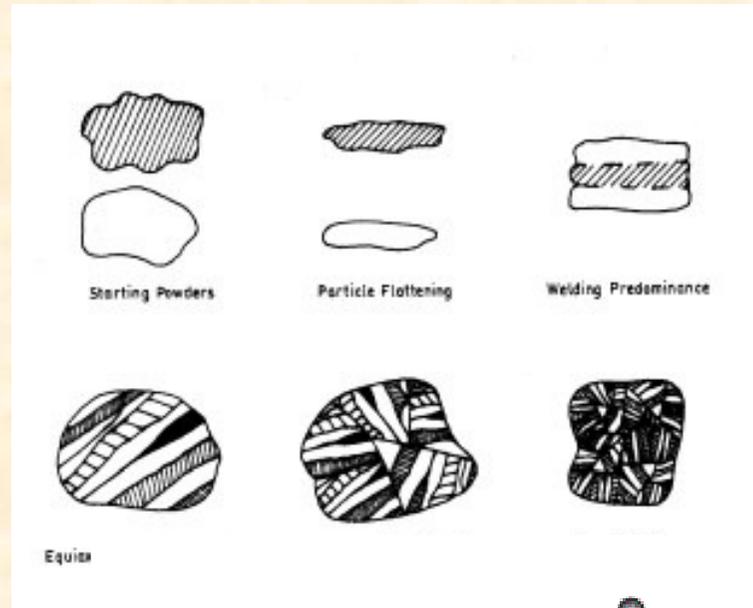
The stored enthalpy, ΔH , in attrited Fe powder is shown as a function of average reciprocal grain size, $1/d$, since $1/d$ scales also with the volume density of grain boundaries in the nanocrystalline material. Two different regimes can be clearly distinguished:

(a) - the stored enthalpy shows only a weak grain size dependence typical for dislocation controlled deformation processes for small grain size decrease at the early stages of mechanical attrition;

(b) - an energy storage becomes more efficient when the average domain size is reduced below $d^* = 30-40 \text{ nm}$.

The critical grain size, d^* , corresponds to the size of nanograins which are formed within the shear bands. Therefore, for domain with size $d < d^*$ deformation is controlled by the properties of the low and, later, high angle grain boundaries which are developing in stages (b).

Mechanical alloying and amorphization

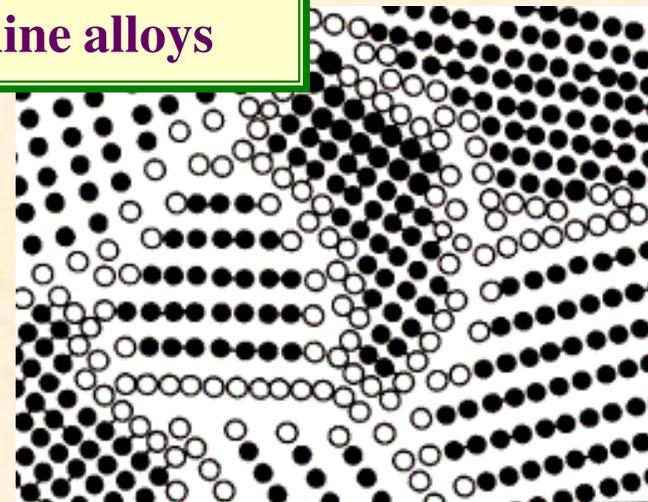
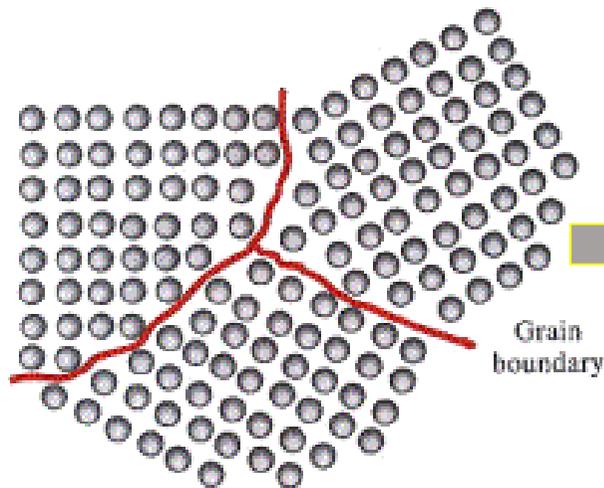


Repetitive cold welding and fracture

Alloying

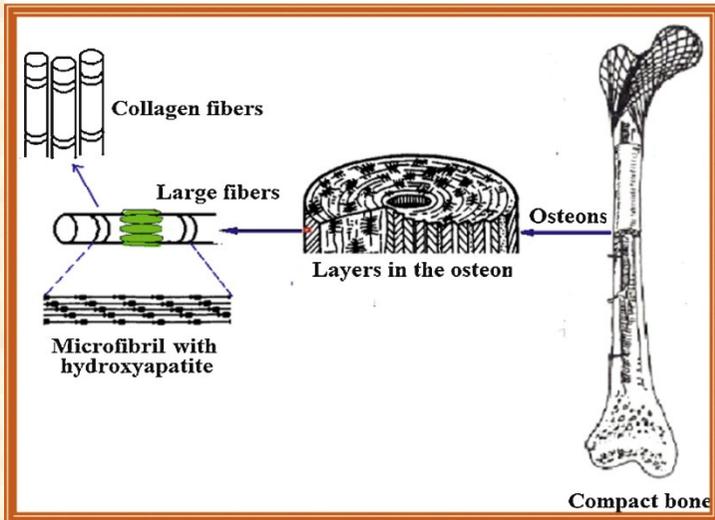
Amorphization

Defect induced disordering of the crystalline alloys

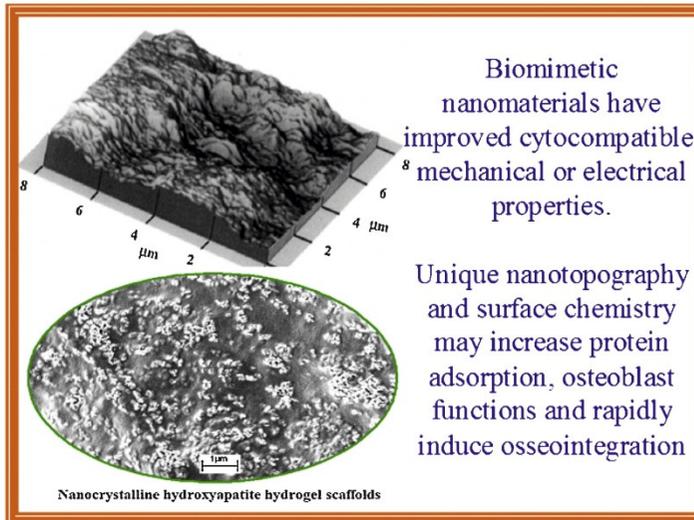


Nanocrystalline structure

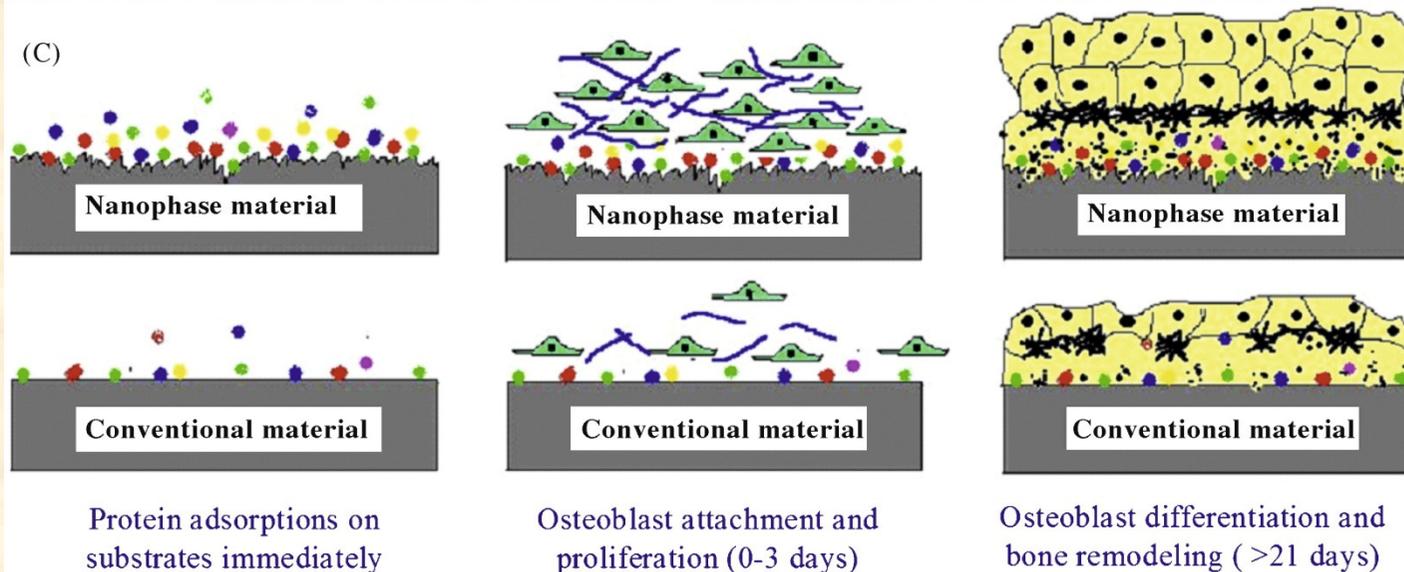
(A) **Nanostructured bone**



(B) **Nanomaterials**



(C)



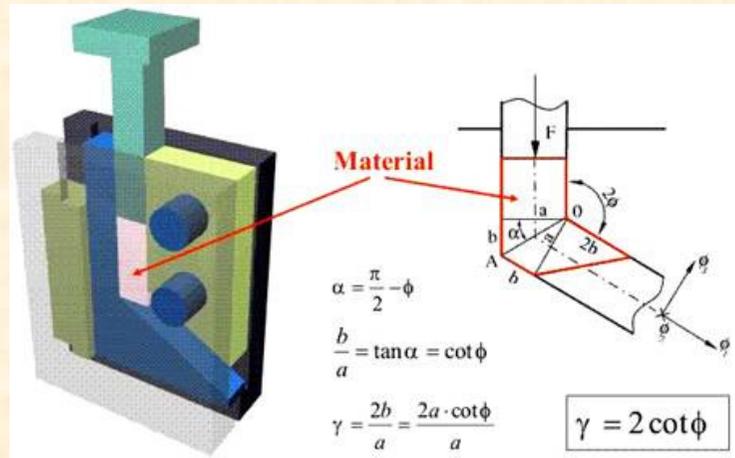
Severe plastic deformation

Severe plastic deformation (SPD) processing, in which materials are subjected to the imposition of **very large strains** without the introduction of concomitant changes in cross-sectional dimensions of the samples, is one of the most successful **top-down** approaches.

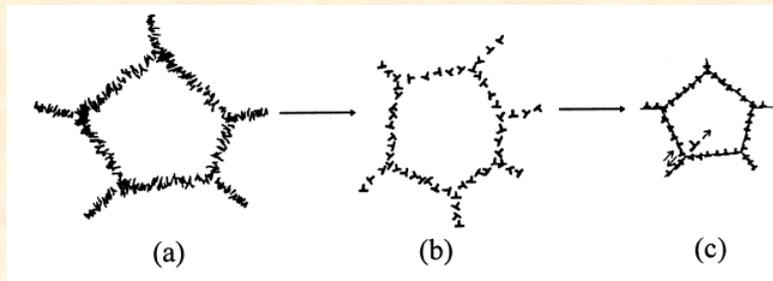
Materials produced by SPD techniques have **grain sizes** in the range of 50-1000 nm. However, they have sub-grain structures, which are often much smaller than 100 nm.

Now there are several SPD processing available:
*equal-channel angular pressing (ECAP),
high-pressure torsion,
accumulative roll-bonding,
repetitive corrugation
and friction stir processing.*

Severe plastic deformation: ECAP



Sketch of an ECAP tool and materials deformation



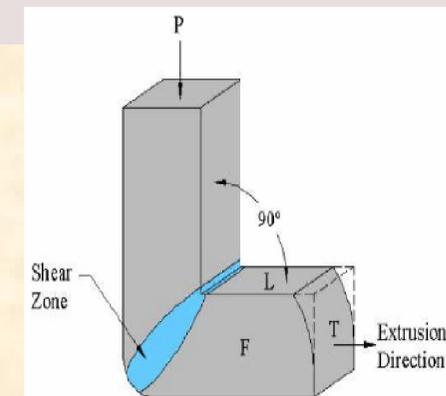
Schematic model of dislocation structure evolution at different stages during severe plastic deformation (adapted from R.Z. Valiev, R.K. Islamgaliev, I. Alexandrov.

18 nanostructured materials from severe plastic deformation, *Progress in Mat. Sci.*, 2000, v. 45, 103–189)

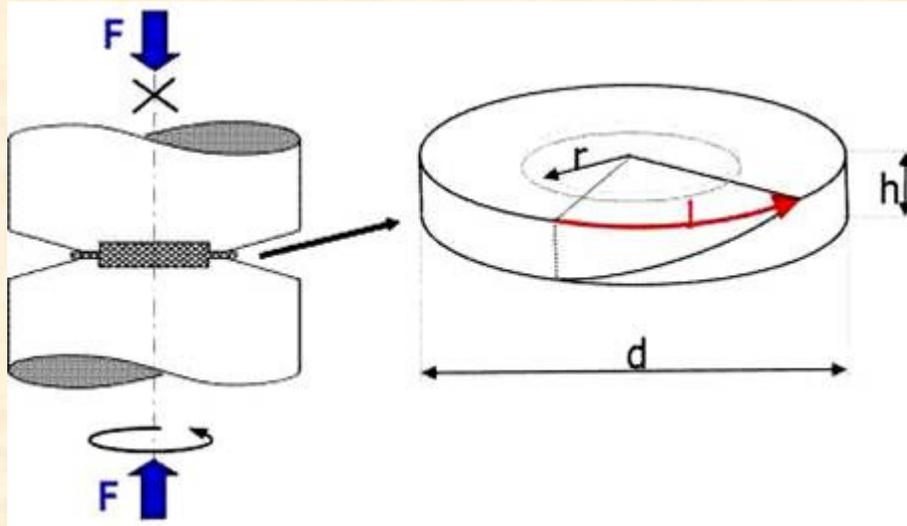
During ECA pressing a billet of material is multiple pressed through a special die. The angle of two channels intersection is usually 90° , however, in the case of a hard-to-deform material, the angle may be changed.

Moreover, for processing of hardly deformed materials, ECA pressing can be conducted at elevated temperatures.

During ECAP the direction and number of billet passes through the channels are very important parameter for microstructure development.



Severe plastic deformation: Torsion

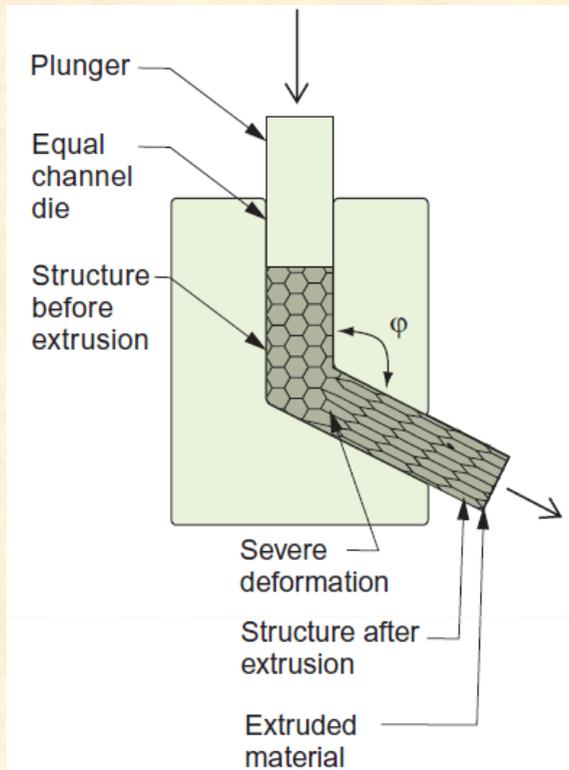


Severe torsion straining can be successfully used not only for the refinement of a microstructure but also for the *consolidation of powders*. During torsion straining at room temperature, high pressure can provide a rather high density that may be close to 100% in the processed disk sample.

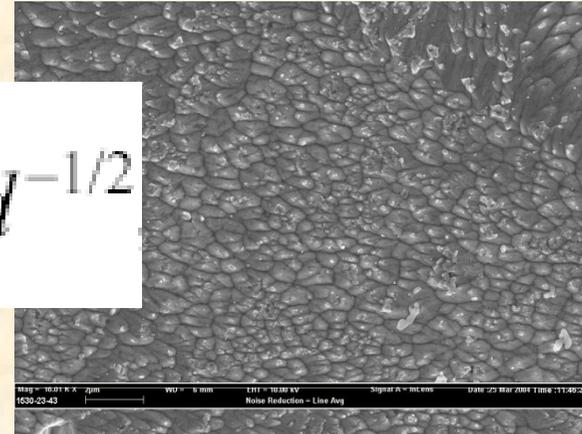
A method of **torsion straining** under high pressure can be used for fabrication of disk type samples. An ingot is held between anvils and strained in torsion under the applied pressure of several GPa. A lower holder rotates and surface friction forces deform the ingot by shear. Due to the specific geometric shape of the sample, the main volume of the material is strained in conditions of quasi-hydrostatic compression under the applied pressure and the pressure of sample outer layers.

As a result, in spite of large strain values, the deformed sample is not destroyed.

Properties of nano- materials



$$\sigma = \sigma_0 + kd^{-1/2}$$



| Properties | Materials | Value | |
|---|-------------------|-----------------------|-----------------------|
| | | nc | cg |
| Curie temperature, K | Ni | 595 | 631 |
| Saturation magnetization, Am ² /kg | Ni | 38.1 | 56.2 |
| Debye temperature, K | Fe | 240 | 467 |
| Diffusion coefficient, m ² /s | Cu in Ni | 1 x 10 ⁻¹⁴ | 1 x 10 ⁻²⁰ |
| Ultimate solubility at 293 K, % | C in α -Fe | 1.2 | 0.06 |
| Young's modulus, GPa | Cu | 115 | 128 |

Sintering of nanoparticles

Thermodynamically, **nanopowders** are highly **unstable**. The **sintering process** is driven by the tendency to reduce the **excessively large surface area per unit volume**.

Example:

1 kg of copper spherical particles of 5 nm in radius has a total surface area of around 75000 m², while the same amount of particles of radius 50 microns will have the surface area of 15 m².

Problem

Usually, the surface energy is assumed to be isotropic. For nanocrystals, the **anisotropy problem** becomes critical. First, sintering starts at a lower temperature. In this case, the effects of surface energy anisotropy are more pronounced. The highly anisotropic behavior of nanoparticle surfaces may be responsible for the crystallographic alignment, which has been often observed.

The extra energy of a surface with a radius of curvature, R , may be calculated as a stress (σ) in a **Laplace equation**

$$\sigma = \gamma / R$$

where γ is the surface energy.

In nanomaterials, this sintering stress may reach very high values.

Example:

the sintering stress may be as large as 300 MPa in 10 nm particles compared to only 3 MPa for 1 μm particles, if γ has a typical value of 1.5 J/m².

Sintering: Compaction

The **first step** of powder consolidation is *compaction of nanopowders*. To produce a so-called green body, process goes at relatively low or moderate temperatures. Most sintering defects may be related to the microstructure of such green body.

Inhomogeneities in density, packing, and particle size in green compact will limit the final sintered density.

Such an example is the crack generation in ceramics upon sintering inhomogeneous cold compacts. Generally, nanocrystalline powders are more sensible to defects in green compacts compared to conventional powders.

Why conventional compaction routes do not work?

Due to Hall – Petch relationship between yield stress and particle size, the cold compaction of nanoparticles requires stresses in **gigapascal range**.

On the nano-scale, **mechanical friction** becomes substantial due to many interparticle contacts. These forces are a result of mechanical, electrostatic, van der Waals, and surface adsorption phenomena that are much more significant when particle size decreases down to nanometers. Friction limits particles motion and rearrangement and may cause a lower density green body formation.

Principles of sintering

Sintering process starts when powder is packed together and heated to high temperatures, typically about $2T_{\text{melt}}/3$.

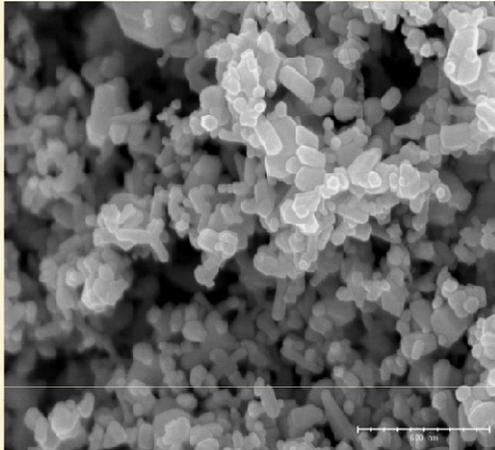
At this stage, **diffusion** becomes significant.

The densification process consists of solid particle bonding or neck formation followed by continuous closing of pores from a largely open porosity to a pore-free body.

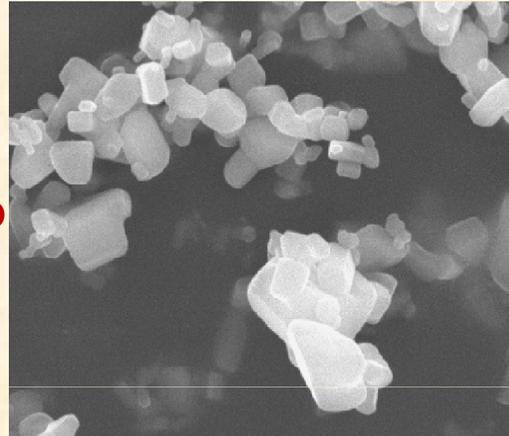
Full densification of different powders.

| Material | Particle size, nm | Temperature, K | Percentage of densification |
|------------------|-------------------|----------------|-----------------------------|
| TiC | 140–170 | 1900 | 91 |
| TiC | 5000 | 3070 | 91 |
| ZrO ₂ | nano sized | 1745 | 100 |
| ZrO ₂ | conventional | > 1975 | 100 |
| TiO ₂ | 12–14 | 1300 | 100 |
| TiO ₂ | 1300 | >1630 | 100 |
| TiN | nano sized | 1823 | 100 |
| TiN | conventional | 1823 | 63 |

Sintering parameters



ZnO



48 nm average particle size
30 m²/g specific surface area

790 nm average particle size
3.2 m²/g specific surface area

The general relationship between sintering parameters

$$\frac{dp}{dt} \sim \frac{1}{d^n} \exp\left(-\frac{Q}{RT}\right)$$

where n is a constant, p is the density, Q is the activation energy for sintering and d is the mean powder particle diameter. The n is usually about 3 and Q is considered to be equal to the activation energy for grain boundary diffusion.

| Material | Particle Size (nm) | T, K | T/T _m |
|------------------|--------------------|---------|------------------|
| TiO ₂ | 40 | 950 | 0.46 |
| TiO ₂ | 13 | 823 | 0.4 |
| ZrO ₂ | 70 | 1370 | ~0.5 |
| ZrO ₂ | 8–9 | 870–920 | ~0.3 |
| Fe | 2000 | ~900 | 0.5 |
| Fe | 30 | 393 | 0.21 |

Powder densification

Problem: the elimination of large pores that originate from the green compact. This elimination requires high temperatures upon subsequent sintering, thereby, promoting unwanted grain growth and losing the desired nanosize features.

pores fraction

$$\frac{1}{\rho(t)(1-\rho(t))} \cdot \frac{d\rho}{dt} \sim \frac{1}{r_p(t)} \cdot \frac{1}{d^n} \exp\left(-\frac{Q}{RT}\right)$$

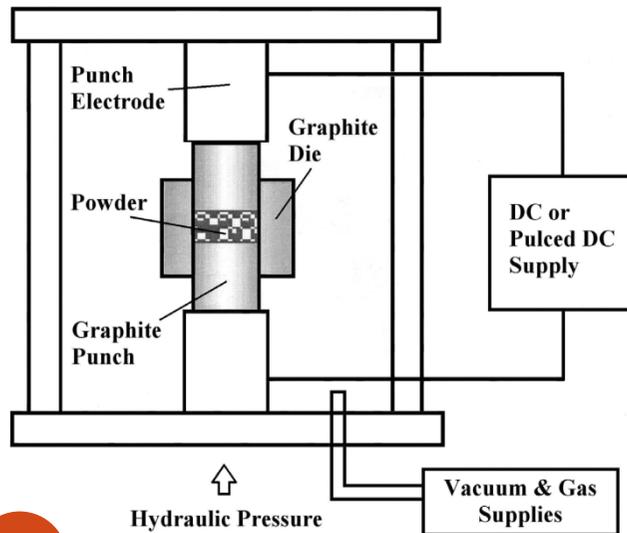
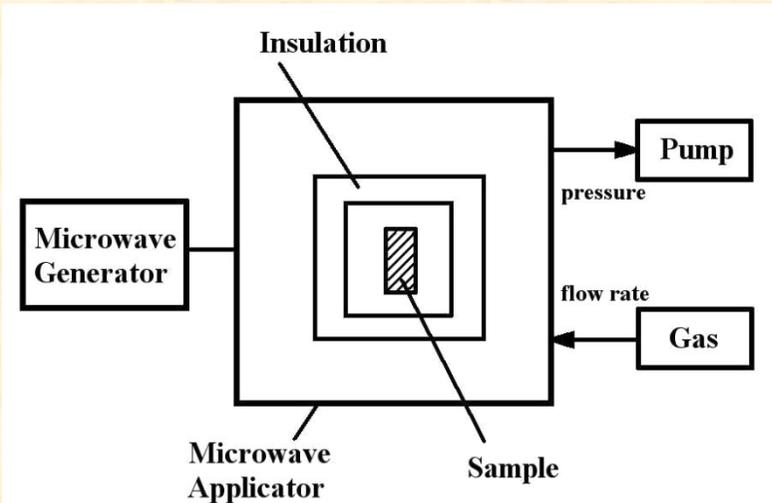
where $\rho(t)$ and $r_p(t)$ are the instantaneous density and pore radius, respectively.

The **success in nanopowder consolidation** is intimately related to the control of the competition between densification and coarsening. The driving force for densification is largely due to the excess of surface energy. As sintering progresses and grain boundaries are created, the driving force for mass transport may be expressed as a Gibbs-Thomson effect:

$$\Delta p = \frac{2\gamma_b}{d} + \frac{2\gamma}{r}$$

Special methods of sintering

Microwave sintering has a rapid processing time, two to fifty times faster than conventional heating. There is also an acceleration of sintering and diffusion in the material because of high electrical fields; thus densification can occur at lower temperatures.



One of the most interesting and promising methods of powder consolidation is **field-assisted sintering (FAS)**. Electric FAS is an emerging technology for the fabrication of metals, ceramics and their composites starting from powders. FAS often referred as spark plasma sintering (SPS) or pulsed electric current sintering (PECS). All these methods are essentially identical in the application of a pulsed discharge and subsequent or simultaneous resistance sintering.

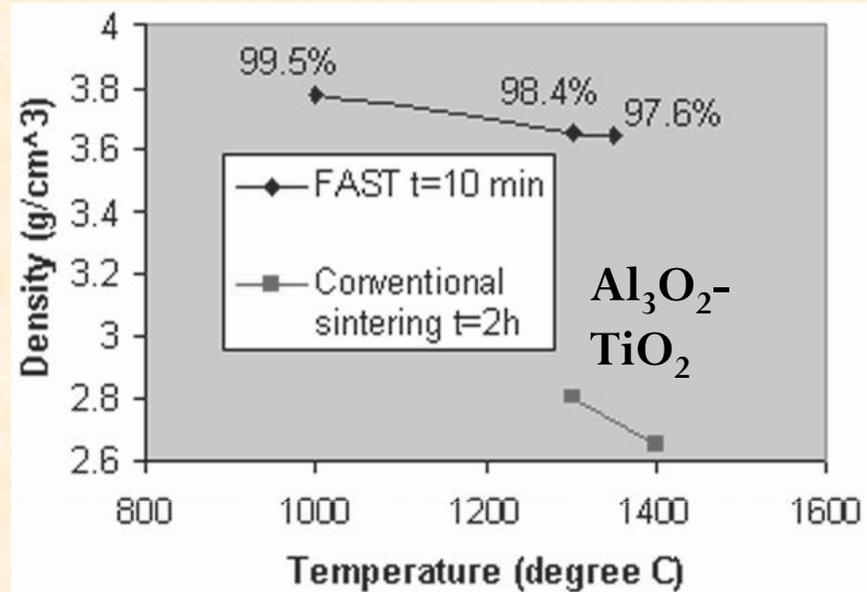
Field – assisted sintering



The FAST/ SPS device HPD 25/1 at the IKTS

Example:

FAS for **3 minutes** at 998°C of mechanically synthesized Fe-85%Fe₃C achieved **99% density** with a final grain size of **45 nm**. This is to be compared to high isostatically pressing (HIP) of the same powders at 1298 C for **60 minutes**, with the **97.6% density** value but final grain size of **87 nm**.



The consolidation process consists of **two stages**:

- (1) an initial activation through the application of a pulsed voltage, and
- (2) the subsequent heating and densification by using DC current.

The sintering cycles are very short. Typically less than 10 minutes for the full densification of both conductive and non-conductive materials.

Why field – assisted sintering?

All FAS results indicate *accelerated densification with minimum grain coarsening while achieving a good metallurgical grain-to-grain bonding.*

The latter may be partly explained by the ability to remove the oxides and impurities from the particle surfaces.

In general the remaining oxides on powder particles are known to cause consolidation difficulties and low mechanical properties (e.g. ductility and fracture toughness) of the sintered part.

These properties are critically dependent on the metallurgical bonding to take full advantage of the intrinsic strength of the material. Sintering at high temperatures in vacuum or reducing atmospheres usually provides good interparticle bonding due to oxide decomposition.

Another notable feature of FAS consolidation is the *enhancement of either phase transformations* in single phase ceramics (e.g., anatase to rutile in TiO_2) or in reactions of single components to form compounds (for example, the formation of Al_2TiO_2 from Al_2O_3 and TiO_2 components).

Spark plasma sintering

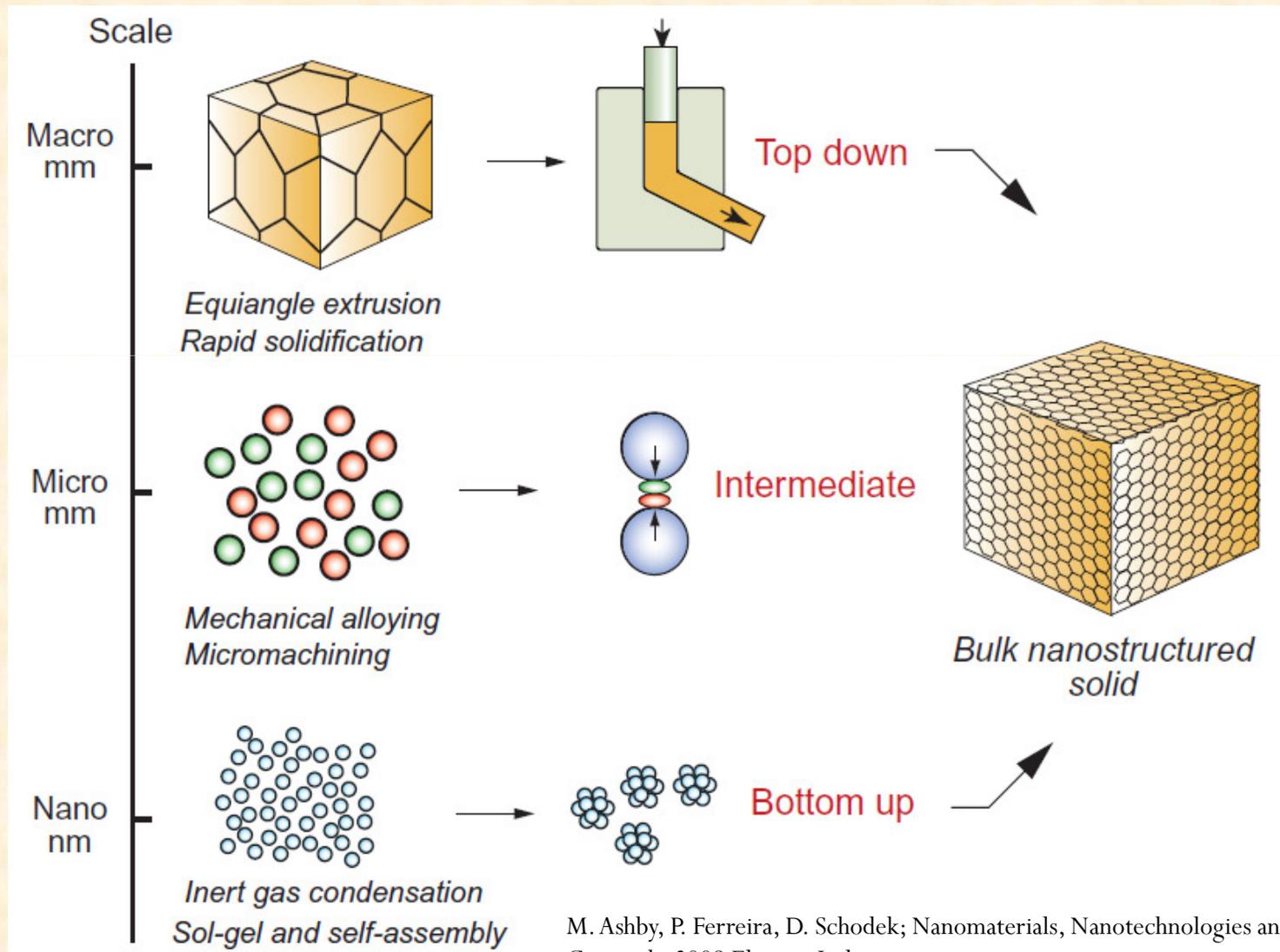
Plasma state is achieved by the effect of the pressure and pulsed current ON-OFF DC pulse energizing. The repeated application of an ON-OFF DC pulse voltage and current between powder materials results:

- (I) The electrons are withdrawn from one power (the cathode) and accelerate toward the anode.
- (II) The electrons collides the gas atoms in the powder gap, then the gas is ionized.
- (III) The accelerated electrons hit to the anode, the ions of the sintered materials are evaporated like a sputtering process.

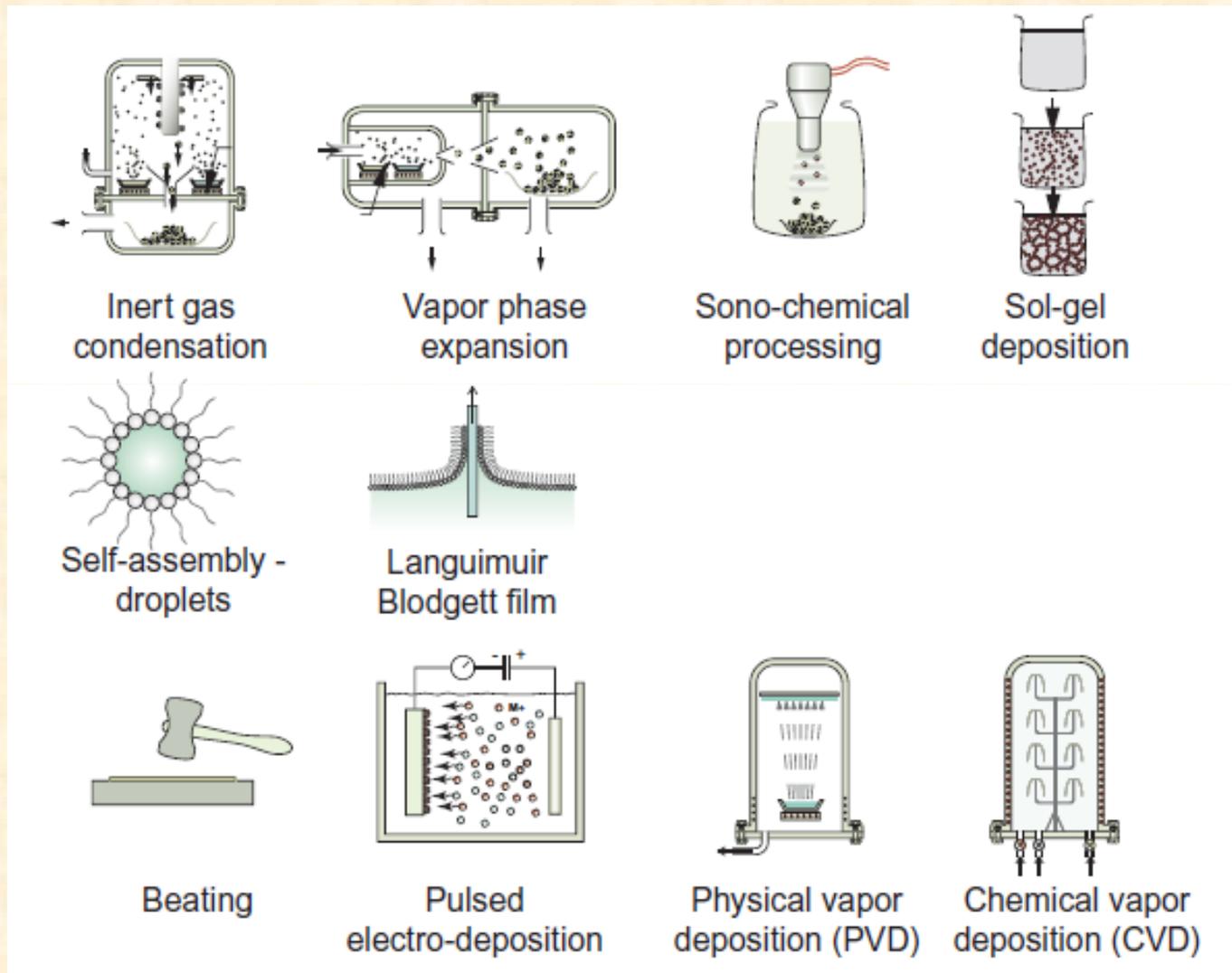
The spark plasma, generated by spark discharge appears in the gap between the particles of a material, increases a local high temperature state of several to ten thousand °C. This causes vaporization and the melting of the surfaces of the powder particles during the SPS process; constricted shapes or “necks” are formed around the contact area between the particles.

The necks gradually develop and plastic transformation progresses during sintering, resulting in a sintered compact of over 99% density. Since only the surface temperature of the particles rises rapidly by self-heating, particle growth of the starting powder materials is controlled. Therefore, a precision sintered compact is manufactured in a shorter time. At the same time, bulk fabrication of particles with amorphous structure and nano-crystallization formation are now possible without changing their characteristics

The top-down, intermediate, and bottom-up approaches to making bulk nanostructured solids



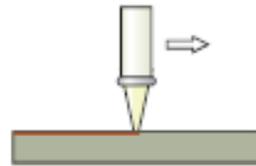
Summary - Methods for making nanoparticles, nanoclusters and nanolayers



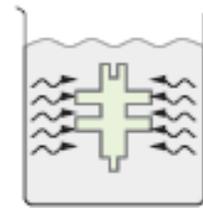
Summary - Methods for making bulk nanostructures



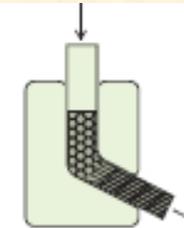
Melt spinning



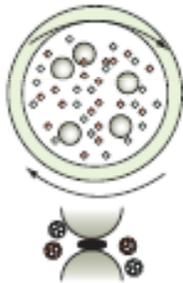
Laser surface hardening



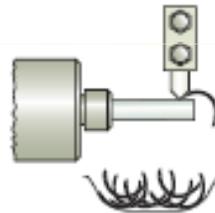
Electroless nickel process



Equal angle extrusion

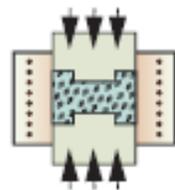


Powder milling

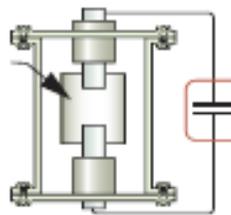


Micro-machining

*Clusters,
particles, chips*



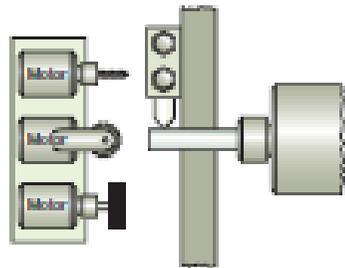
Pressure sintering



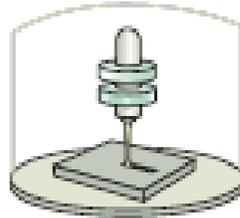
Electric discharge
("Flash" sintering)

*Consolidation
methods*

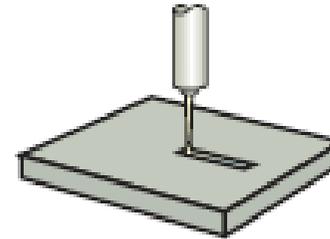
Summary - Methods for nanoprofilng



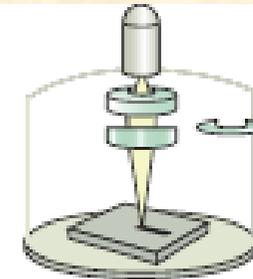
Micro-machining workstation



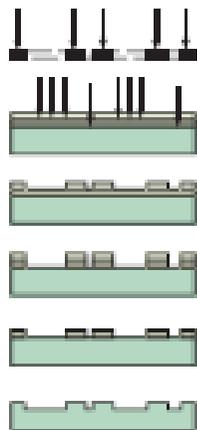
Electron beam machining



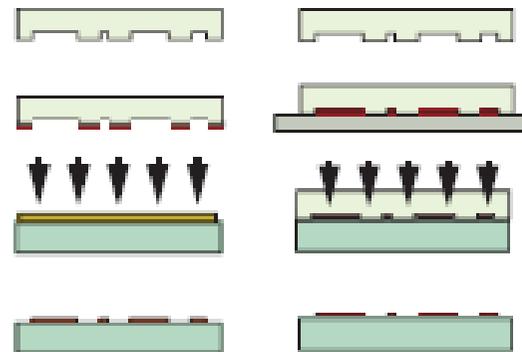
Femto-second laser machining



Focused ion beam machining



Photolithography



Two soft lithography processes

Summary of processes used to make nanomaterials

