



**UNIVERSITY OF ROME "LA SAPIENZA"**  
**NANOTECHNOLOGIES ENGINEERING**

# **PRODUCTION FROM SOLID PHASE**

## PRODUCTION FROM SOLID PHASE

The starting material is a solid.

Most approaches are top-down strategies.

Processes include:

- Grinding
- Synthesis in solid phase
- Mechanochemical grinding

## GRINDING

Mechanical energy is produced and transferred to the coarse material in order to produce nanoparticles.

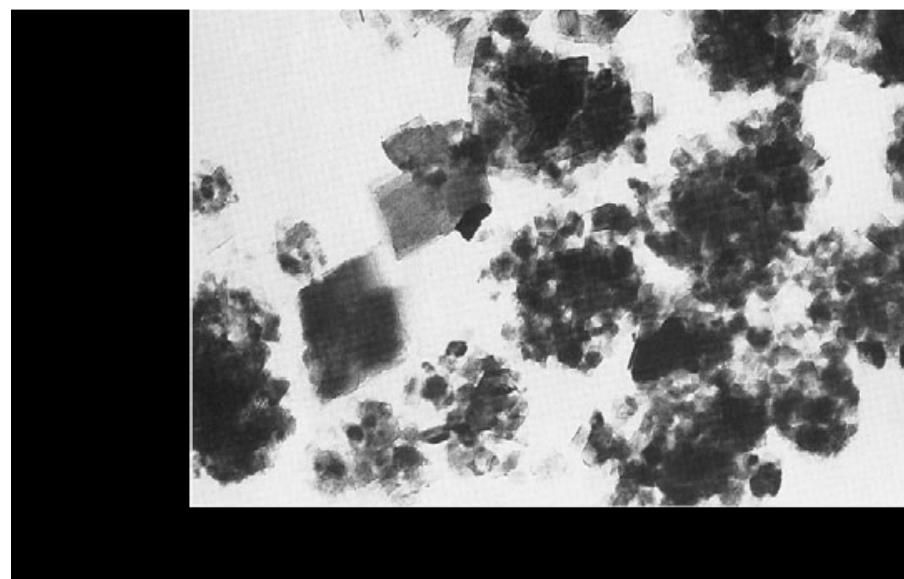
The breakage and aggregation mechanisms are not well known.

The size of the particles ranges from some micron down to hundreds of nano.

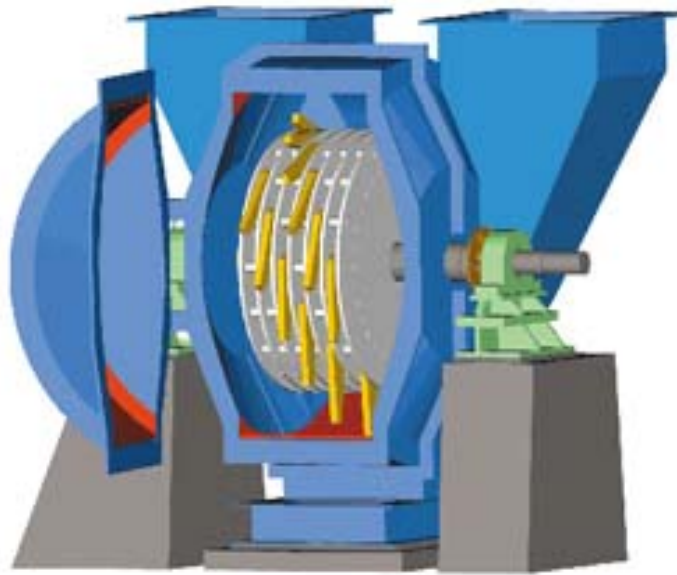
Grinding is performed by mills, such as:

- Impact
- Attrition
- Balls

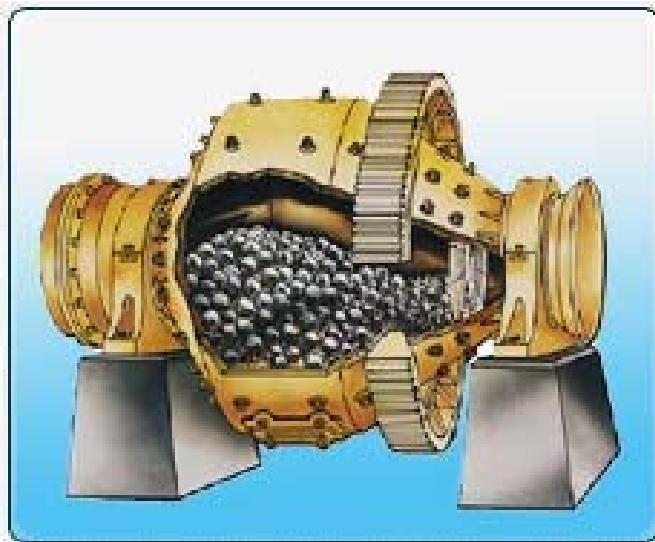
In the figure below, calcium carbonate by attrition mill is shown.



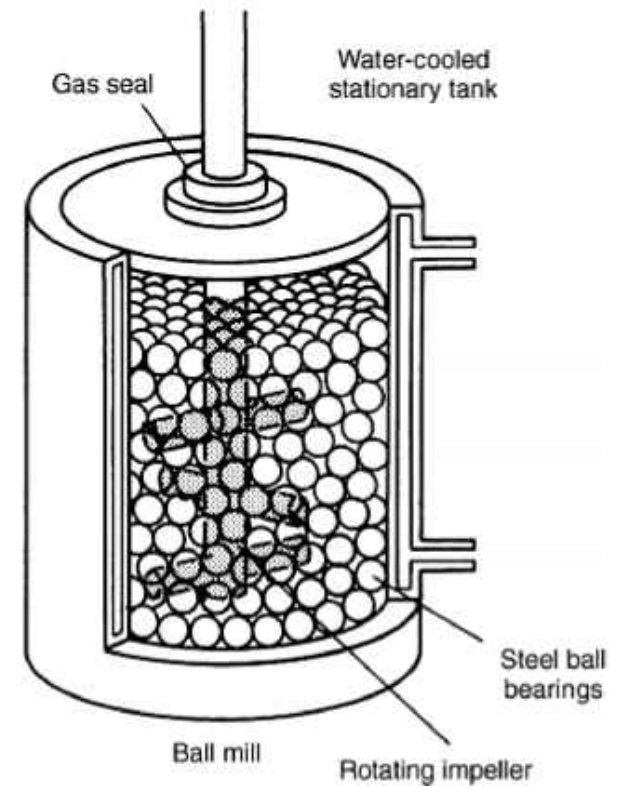
Impact



Balls

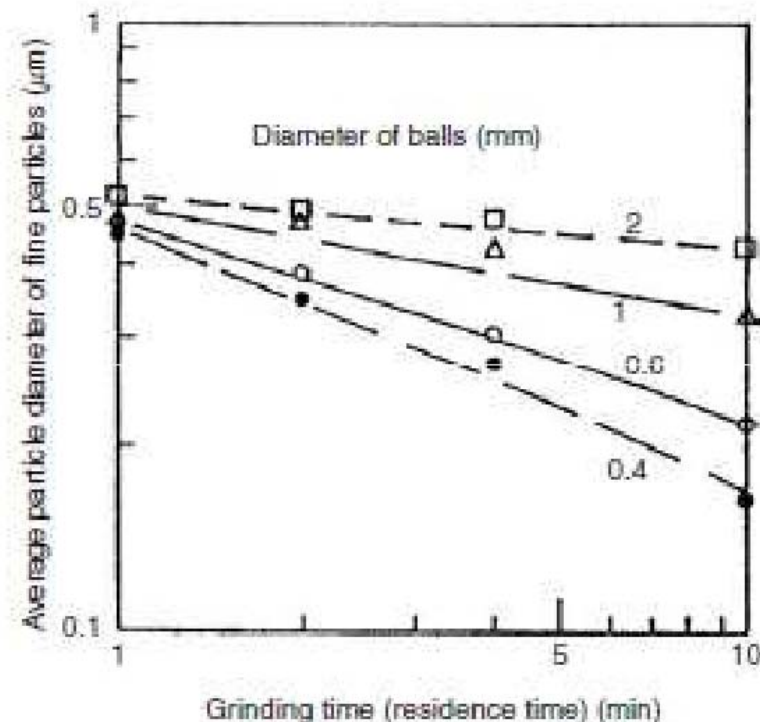


Attrition

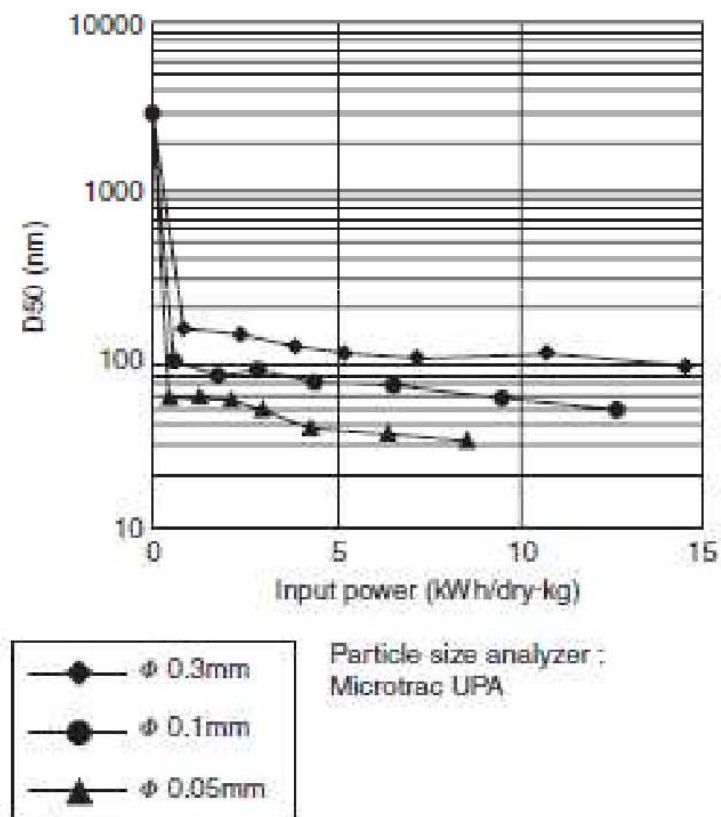


## WET GRINDING

In order to inhibit agglomeration, grinding is performed in presence of a liquid, sufficient to cover the new formed particles with a liquid film. Attrition mills appears to be the best device for wet grinding, since high mechanical energies and the mixing of the wetted solid is possible simultaneously. The final size is a function of the grinding times.

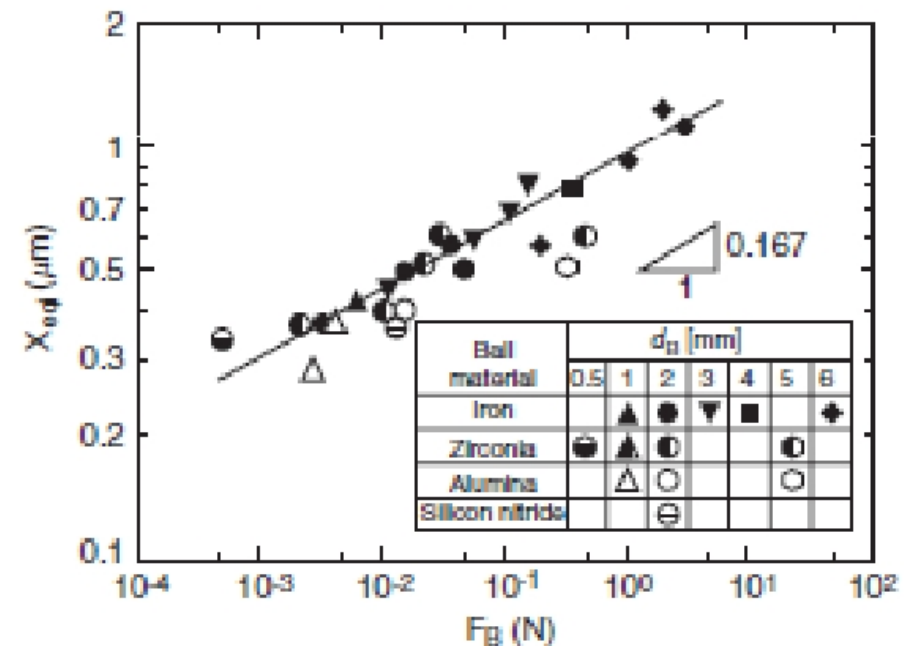


## EFFECT OF THE DISPERSED ENERGY vs PARTICLE SIZE (example: $\text{TiO}_2$ )



There is a limit of the dispersed energy (critical) value to use in mills: increasing this value, a minimum particle size at fixed grinding time is reached; after this, the size appears to increase again up to a point, where a reduction is again obtained (at higher energy costs).

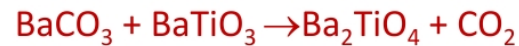
In the figure below, the critical dispersed energy values as a function of the applied forces are reported.



## SOLID STATE SYNTHESIS

Traditional process to obtain ceramics where a mild grinding and mixing of the solid reactants is followed by calcination.

For example: BaTiO<sub>3</sub> is produced by mixing BaCO<sub>3</sub> and TiO<sub>2</sub>, both solid powders, together. After this, heating at 900-1200°C give rise to following reactions:





## UNDERSTANDING SOLID STATE SYNTHESIS

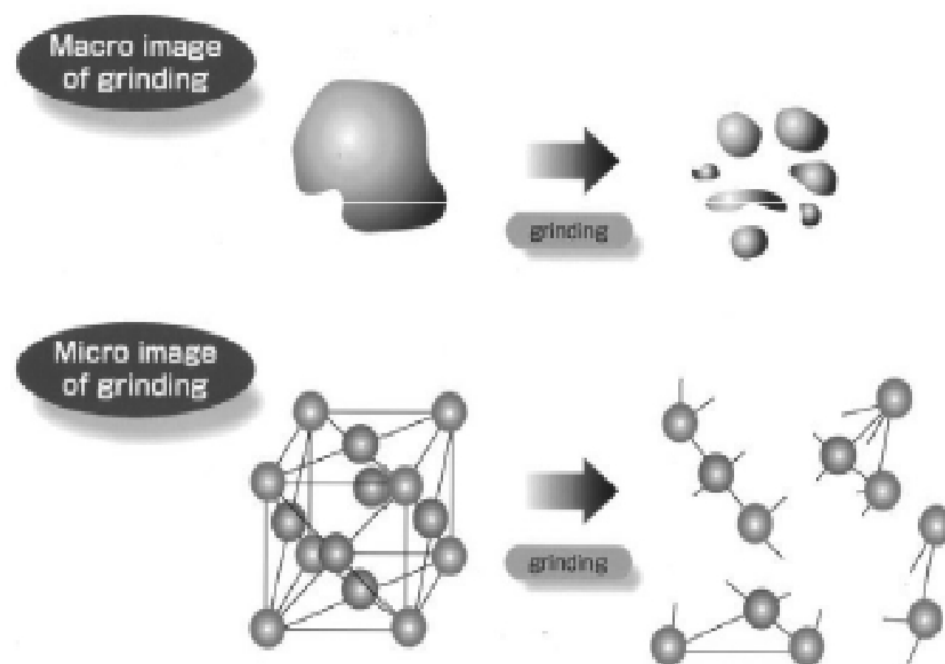
The high temperature promotes the diffusion of the solids, the grinding have the purpose to minimize the distance between the reactants (particles). A well performed grinding and mixing allows to lower the operating temperatures of about 150°C.

On the other side, the high temperatures promotes agglomeration and growth, resulting to obtain particles of 500nm or above.

By technological means, a minimum size of 300nm was reached in lab: far away from 100nm.



## MECHANOCHEMICAL GRINDING



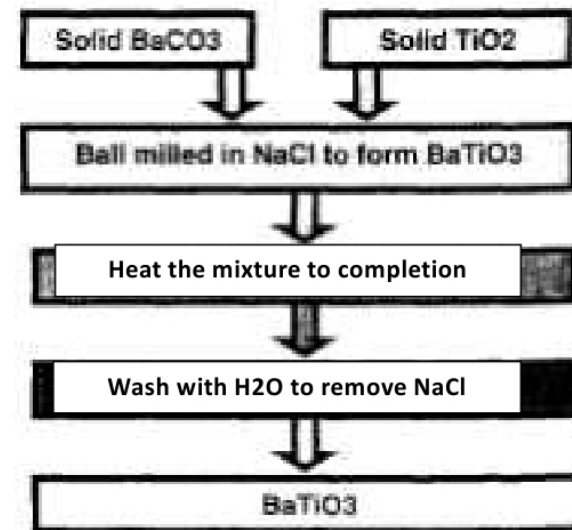
## MECHANOCHEMICAL GRINDING

The particles have amorphous habit, given by dislocation of the solid state used to perform the breakage. With post treatment processes, crystalline solid may be obtained.

The advantage is the ease of operation, but the control of the final product is difficult.

## MECHANOCHEMICAL GRINDING

Beside grinding and supplying energy to the reaction (heat), a third solid is used only to reduce agglomeration of the solid reactants (called sacrifice solid).



The temperatures required for mechanochemical grinding are not high, since energy is transferred to the system by direct heating and attrition.

The final size of the particles may range from few nano to 500nm.

A washing of the product is required for the removal of the sacrifice solid (huge water consumption). The drying process may lead to severe agglomeration.

## EXAMPLES

Reaction	Metal volume ratio (%)	Size (nm)
$\text{FeCl}_3 + 3\text{Na} \rightarrow \text{Fe} + 3\text{NaCl}$	8.1	10–20
$\text{CuCl}_2 + 2\text{Na} \rightarrow \text{Cu} + 2\text{NaCl}$	11.6	20–50
$\text{CoCl}_2 + 2\text{Na} + 1.5\text{NaCl} \rightarrow \text{Co} + 3.5\text{NaCl}$	6.6	10–20
$\text{NiCl}_2 + 2\text{Na} + 1.5\text{NaCl} \rightarrow \text{Ni} + 3.5\text{NaCl}$	6.6	5–10

Starting mixtures	Reaction products
$2\text{AlCl}_3 + \text{CaO}$	$\rightarrow \text{Al}_2\text{O}_3 + 3\text{CaCl}_2$
$\text{ZrCl}_4 + 2\text{CaO}$	$\rightarrow \text{ZrO}_2 + 2\text{CaCl}_2$
$\text{GdCl}_3 + 3\text{NaOH}$	$\rightarrow \text{Gd}_2\text{O}_3 + 3\text{NaCl} + 1.5\text{H}_2\text{O}$
$\text{CeCl}_3 + \text{NaOH}$	$\rightarrow \text{CeO}_2 + 3\text{NaCl} + \text{H}_2\text{O}$
$\text{Na}_2\text{Cr}_2\text{O}_7 + \text{S}$	$\rightarrow \text{Cr}_2\text{O}_3 + \text{Na}_2\text{SO}_4$
$2\text{NbCl}_5 + 5\text{Na}_2\text{CO}_3$	$\rightarrow \text{Nb}_2\text{O}_5 + 10\text{NaCl} + 5\text{CO}_2$
$\text{SnCl}_2 + \text{Na}_2\text{CO}_3 + \text{O}_2$	$\rightarrow \text{SnO}_2 + 2\text{NaCl} + \text{CO}_2$
$2\text{FeCl}_3 + 3\text{Ca(OH)}_2$	$\rightarrow \text{Fe}_2\text{O}_3 + 3\text{CaCl}_2 + 3\text{H}_2\text{O}$
$\text{ZnCl}_2 + \text{Na}_2\text{CO}_3$	$\rightarrow \text{ZnO} + 2\text{NaCl} + \text{CO}_2$