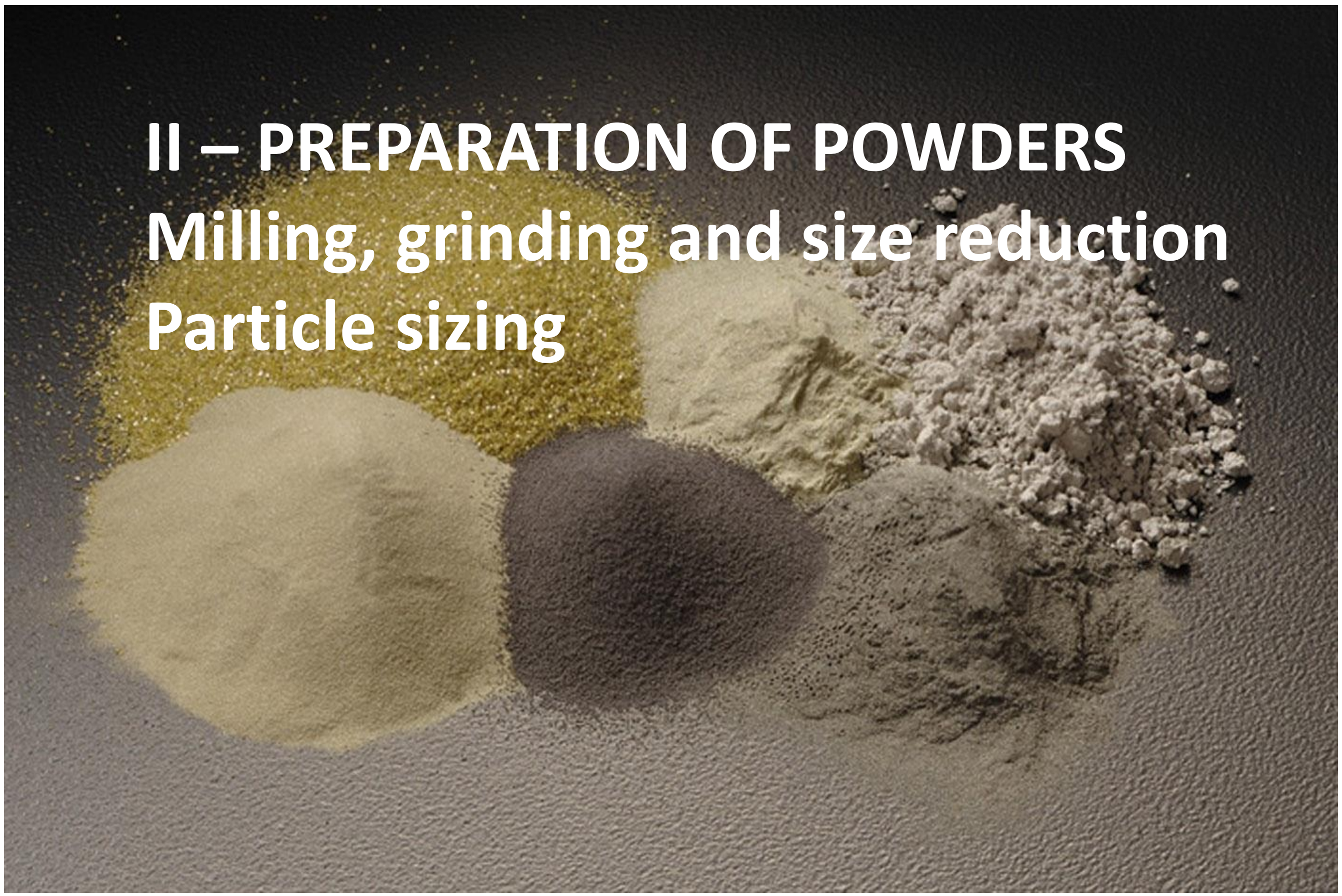
# TECNOLOGIA DOS MATERIAIS CERÂMICOS



## II – PREPARATION OF POWDERS

## Milling, grinding and size reduction

## Particle sizing

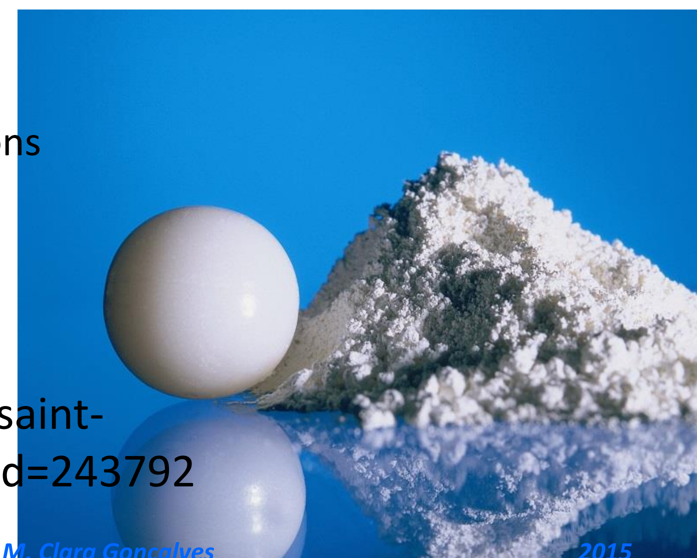
# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

→ In nature, raw materials are not found within a narrow spectrum of grain size and only on rare occasions occur as a pure mineral. Even synthetic raw materials may not fit the industrial size requirements.

# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

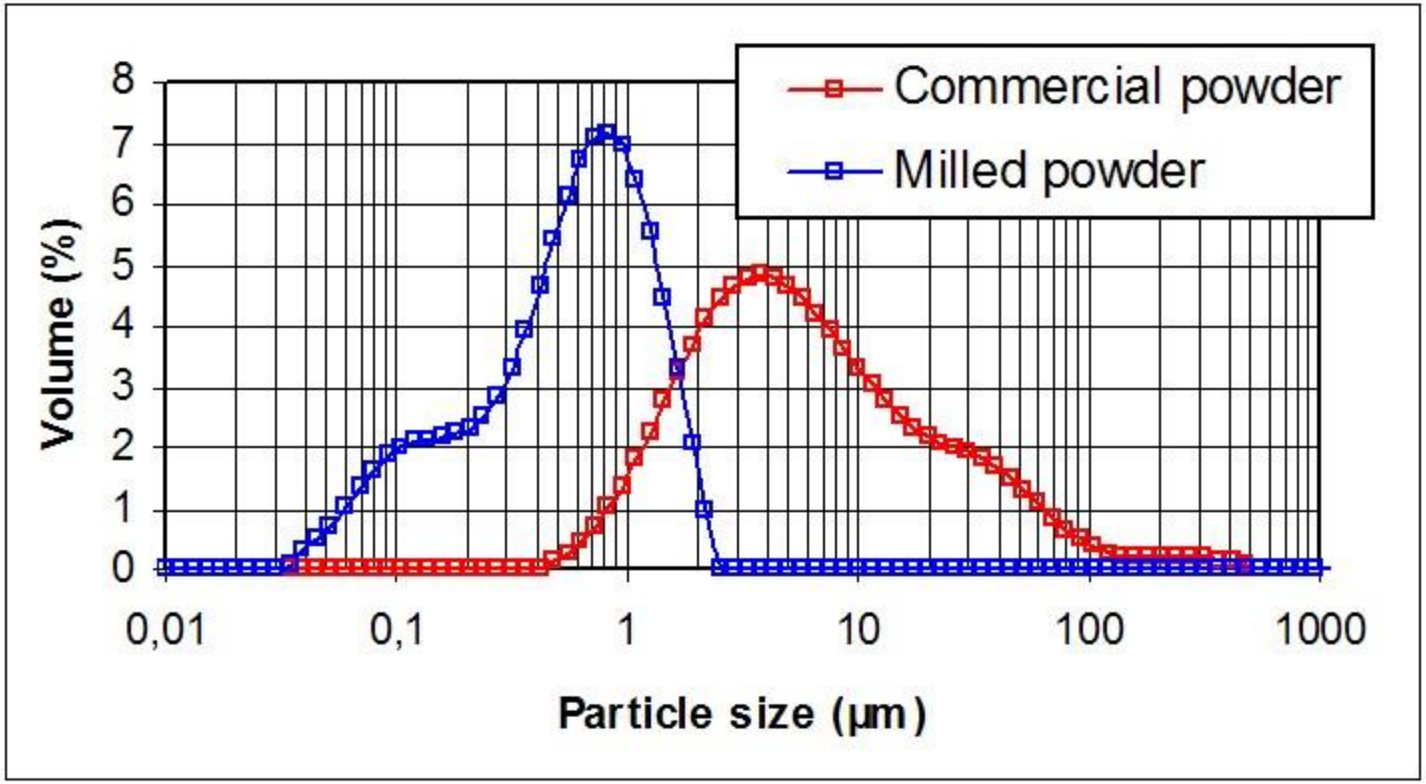
→ Current technology for processing ceramic powders requires that the particles in the powder meet certain criteria that depend on the specific material and its applications. Size reduction is an essentail step in almost all conventional powder preparation processes, because it achives these importantobjectives:

- → Desaglomerates by separating particles from clusters
- → Decreases the size of powder to eliminate unwanted coarse paricles above a certain size
- → Increases specific surface area by producing a large quantity of very fine size particles
- → Provides surface activation without causing large-scale size reduction
- → Homogenizes powder-solvent mixtures
- → Carries out surface chemical and bulk chemical reactions



http://www.ceramicmaterials.saint-gobain.com/landingimg.aspx?id=243792

# Raw Material Preparation: Comminution (Milling, grinding and size reduction)



https://www.youtube.com/watch?v=MikiTYpg2aQ


https://www.youtube.com/watch?v=L6sgGXXYdEU

# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

## *Mechanical Comminution to Obtain Fine Particles*

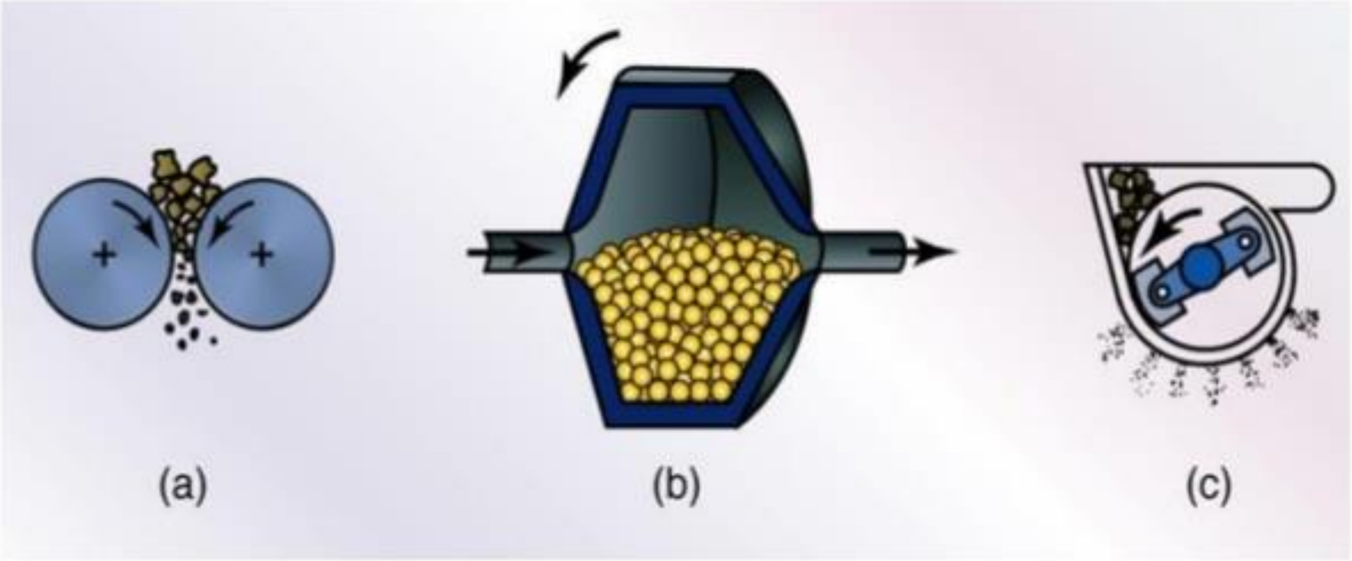



**Figure: Methods of mechanical comminution to obtain fine particles:**

**(a) roll crushing, (b) ball mill, and (c) hammer milling.**

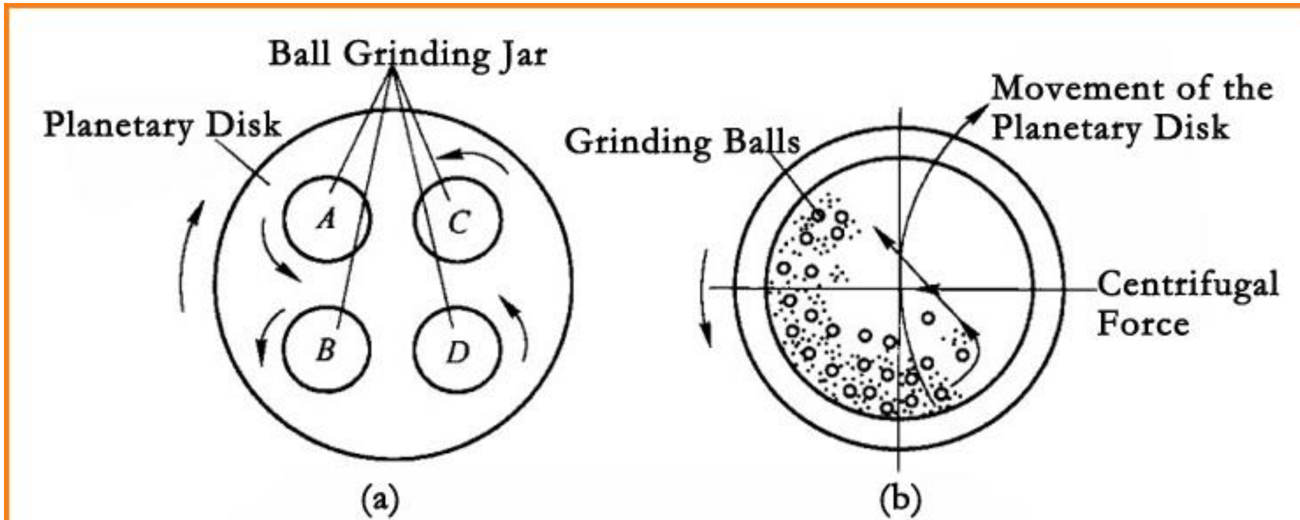
71

# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

Ball milling
Industrial scale

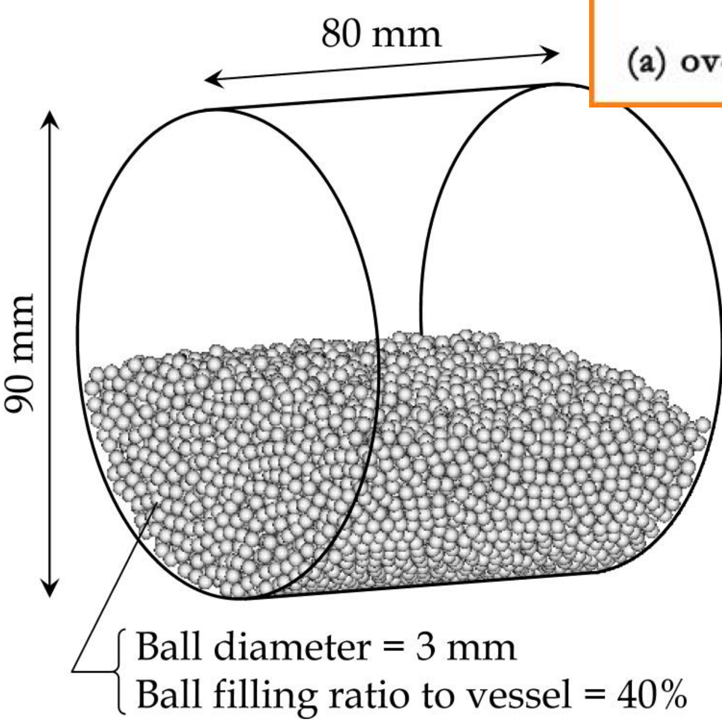
Ball milling
lab scale

# Raw Material Preparation: Comminution (Milling, grinding and size reduction)



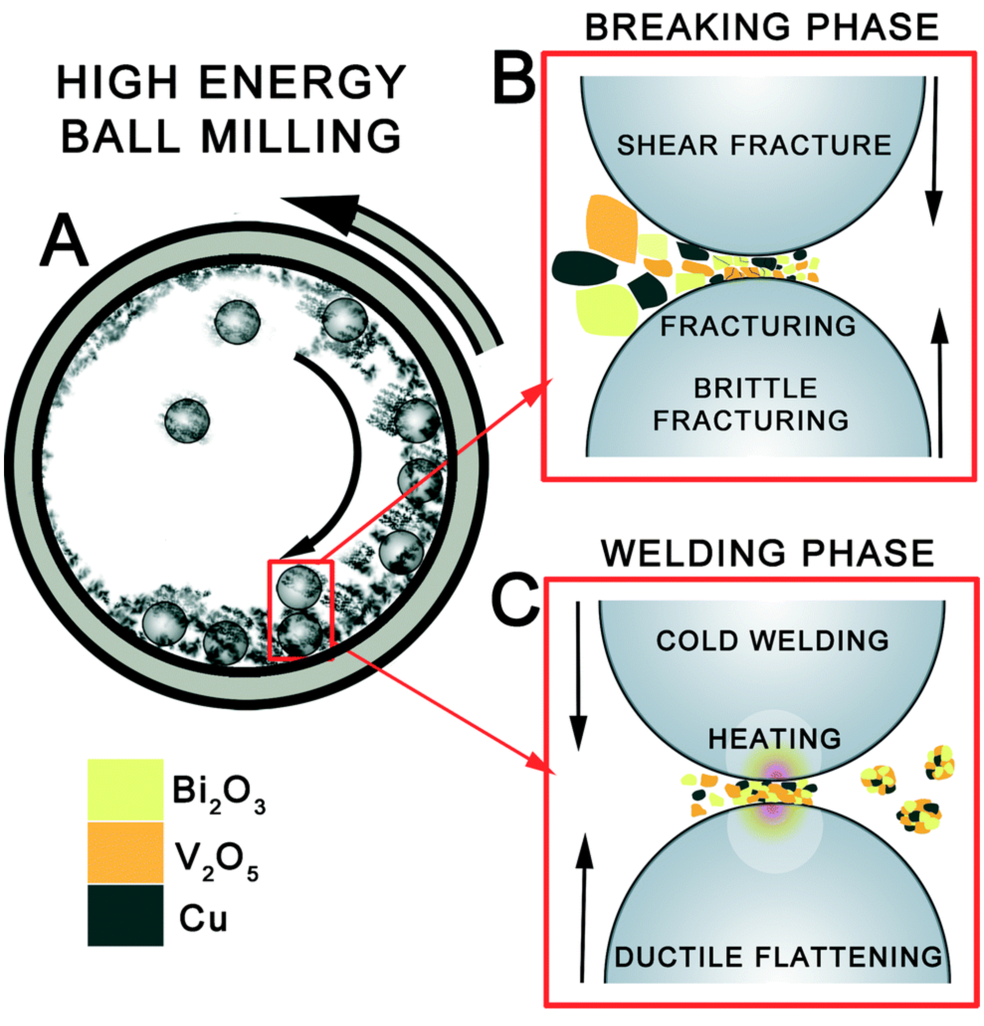

Working Principle of Lab Planetary Ball Mill

(a) overall layout of planetary disk (b) horizontal section of grinding jar




http://www.advancedmaterials.us/zirconia.htm

# Raw Material Preparation: Comminution (Milling, grinding and size reduction)



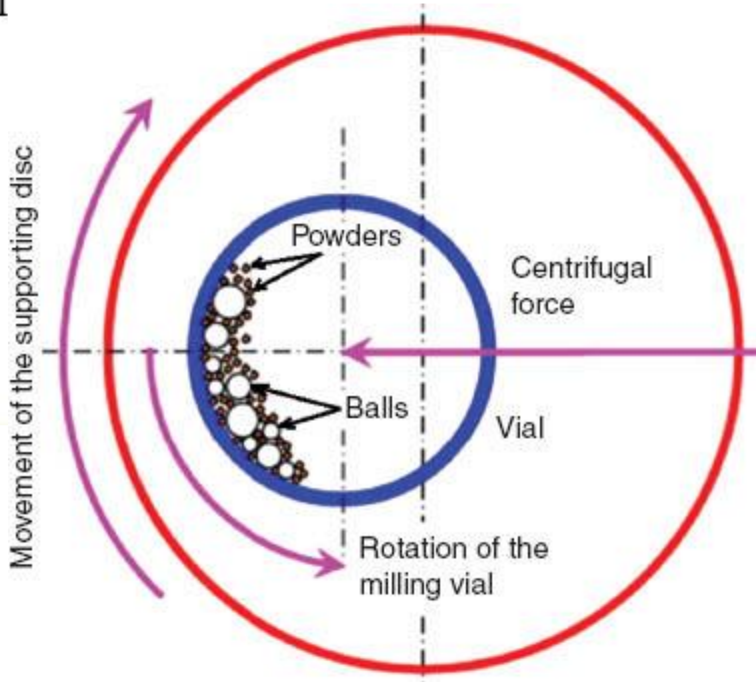

**DOI:** 10.1039/C5CE00173K

# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

## Ball milling

- Principle:A ball mill works on the principle of impact: size reduction is done by impact as the balls drop from near the top of the shell.
- Ball mills rotate around a horizontal axis, partially filled with the material to be refined plus the grinding medium (zirconium balls). An internal cascading effect reduces the material to a fine powder.

DOI: 10.1515/secm-2013-0148

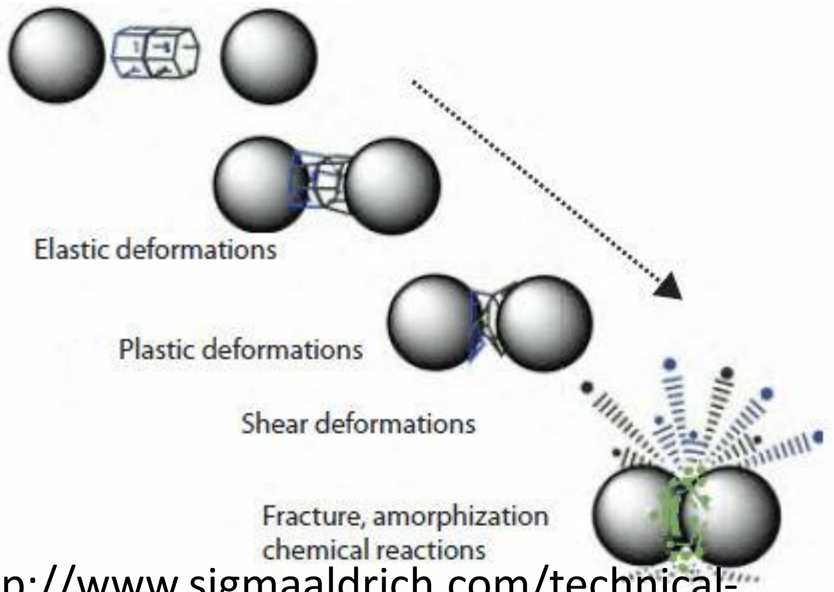


# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

→ Comminution is na inefficient and energy-intensive process.

→ Typically only 7 to 13% of the input energy is utilized for size reduction during ball milling, while the remainning energy dissipates mostly as heat.

→ The energy provided to the milling process is distributed among different subprocesses within a mill, which involve:




increased surface energy

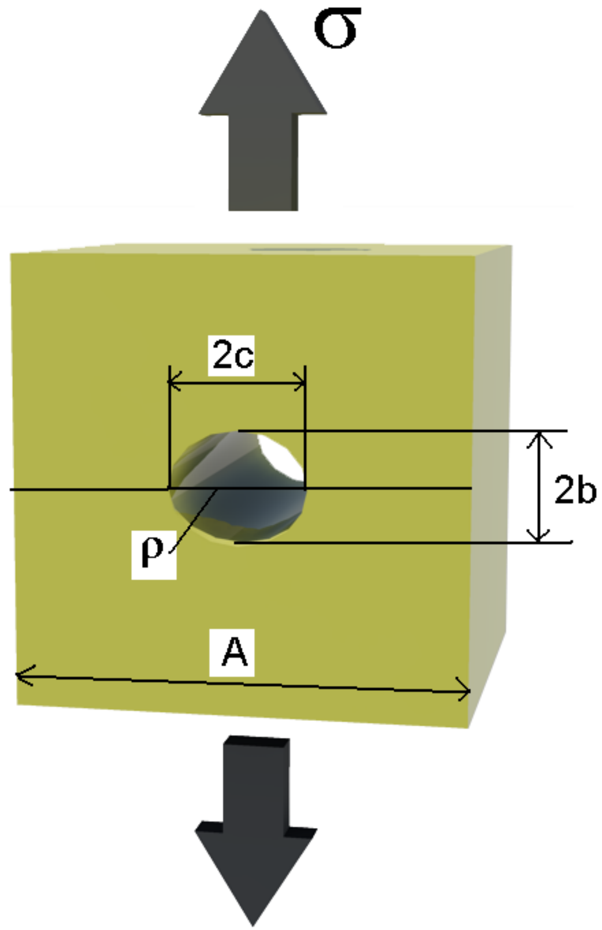
plastic deformation of particles

elastic deformation of particles

lattice rearrangements (gliding, slipping, twinning) within a particle

http://www.sigmaaldrich.com/technical-documents/articles/material-matters/mechanochemical-effect.html

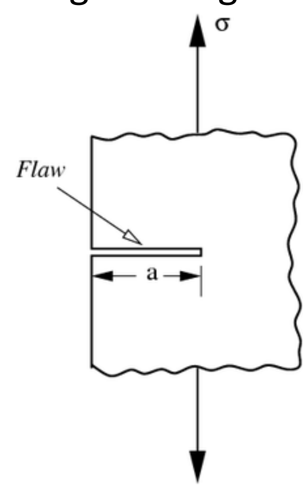
# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

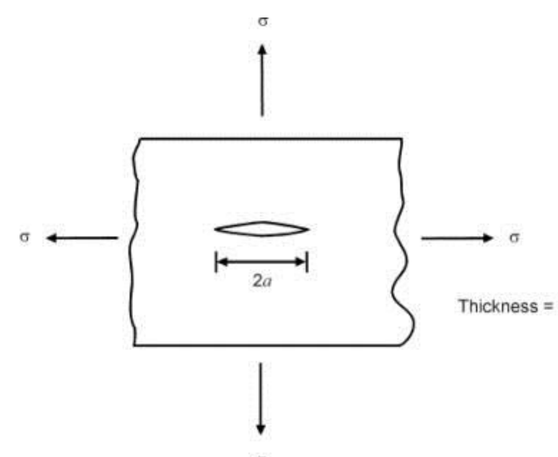



DOI: 10.5772/18127

→ **Particle breakage** is considered to be the elementary process of **Comminution** (Milling, grinding and size reduction process).

→ Particles are stressed by contact froces that deform and cause stress fields that produce cracks when the stress is large enough. The number of cracks and their directions determine the size and shape of daughter fragments.



# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

→ Crystalline materials tend to exhibit characteristic mechanical properties that arise, in part, from their crystal structure – crystallite size and the arranjement of thew crystallites within the macro crystal or powder particle.

→ In the size reduction of crystalline materials theoretically, the applied stress will be uniform throughout the particle if the crystal lattice were to be perfect. Therefore, when the stress reaches a level equal to that required for failure, the crystal structure breaks down to produce particles of the same order of size as the primary crystallites.

# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

→ The fracture of a particle involves the propagation of cracks that are either already present or initiated in the particle.

→ The stres required for fracture is given by the Griffith relationship:

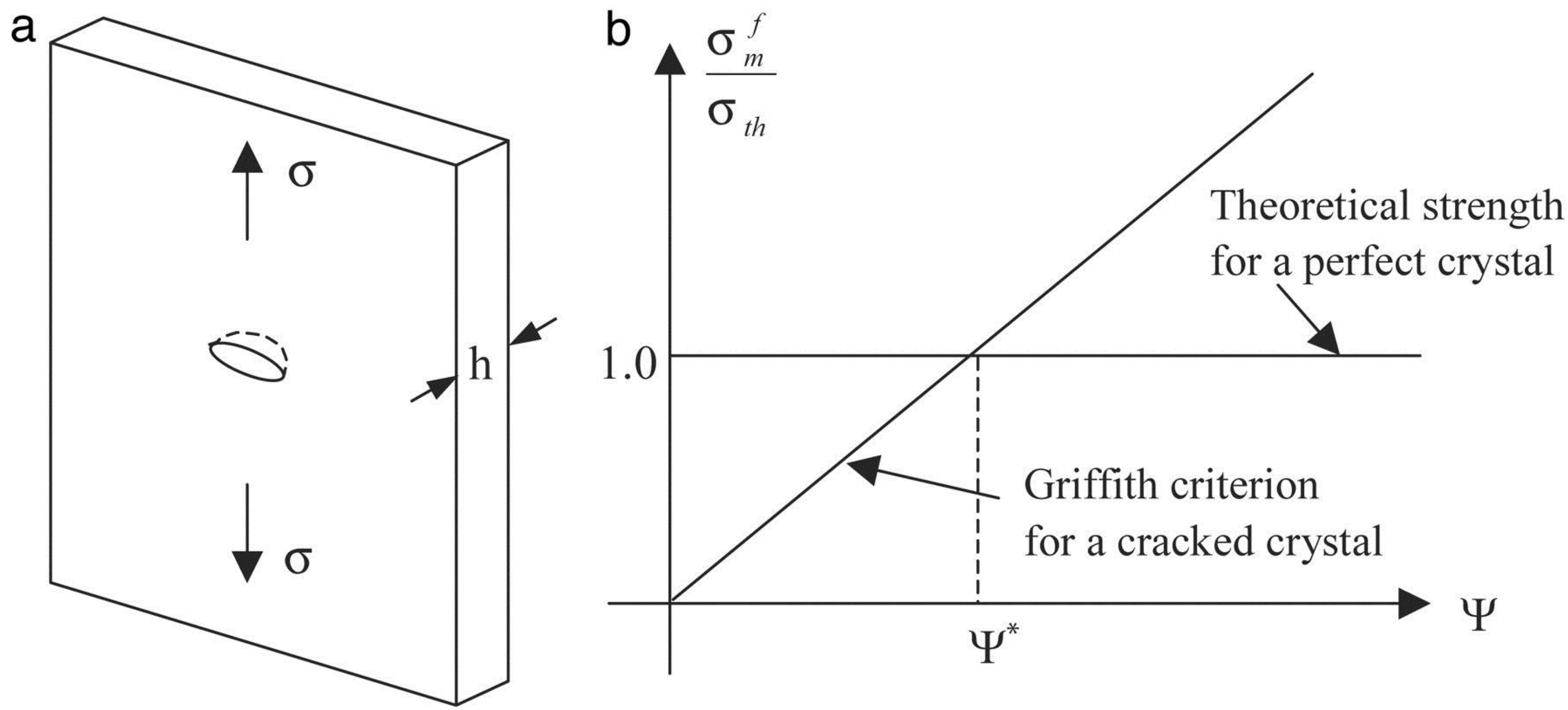
$$\sigma = \sqrt{\frac{2E.\gamma}{L}}$$

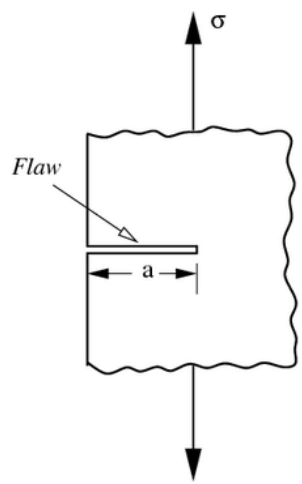
→ Where E is Young's modulus, $\gamma$ is the fracture energy, and L is crack length. For brtitle materials, to which most powders belong, the fracture energy is 1 to 10 μJ/m2 (103 to 104 ergs/cm2).

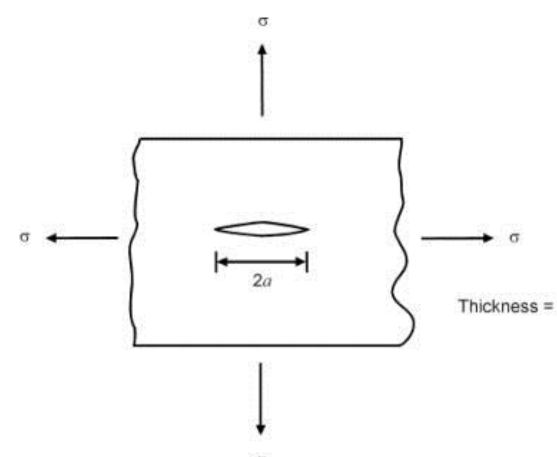
→ In na ideal size reduction process, the particles from a homogeneous material would be of the same strength, regardless of size. Therefore, a plot of fineness atained versus work required to obtain that fineness would be a straight line.

→ Since no crystal is perfect in a real material (becaus eof defects such as flaws, cracks, etc) its behavior is expected to be nonideal.

# Raw Material Preparation: Comminution (Milling, grinding and size reduction)



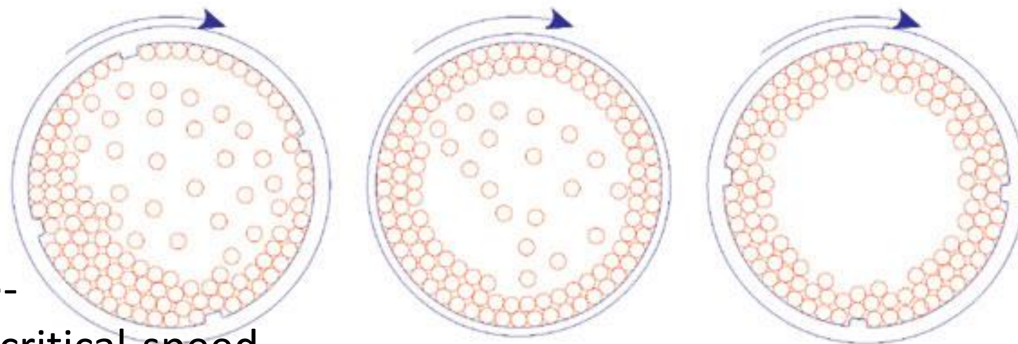



# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

***Mill Speed***

No matter how large or small a mill, ball mill, ceramic lined mill, pebble mill, jar mill or laboratory jar rolling mill, its rotational speed is important to proper and efficient mill operation. Too low a speed and little energy is imparted on the product. Too fast and inefficient media movement (known as cataracting) will generate high impact but also greatly increase mill wear. Even faster speed will result in the media centrifuging inside the mill and virtually no milling or movement of media or product will occur. In most cases, the ideal mill speed will have the media tumbling from the top of the pile (the shoulder) to the bottom (the toe) with many impacts along the way. The ideal mill speed is usually somewhere between 55% to 75% of critical speed.



First Critical Speed | Second Critical Speed | $N^{th}$ Critical Speed

http://www.pauloabbe.com/size-reduction/resources/mill-speed-critical-speed

The formula for Critical Speed $= \frac{1}{2\pi}\sqrt{(g/(R-r)}$

This equation simplifies to (units are inches) C.S. = $(265.45)/\sqrt{(\textit{mill I.D.} - \textit{media diameter})}$

***Critical Mill Speed***

**Critical Speed** (left) is the speed at which the outer layer of media centrifuges against the wall.

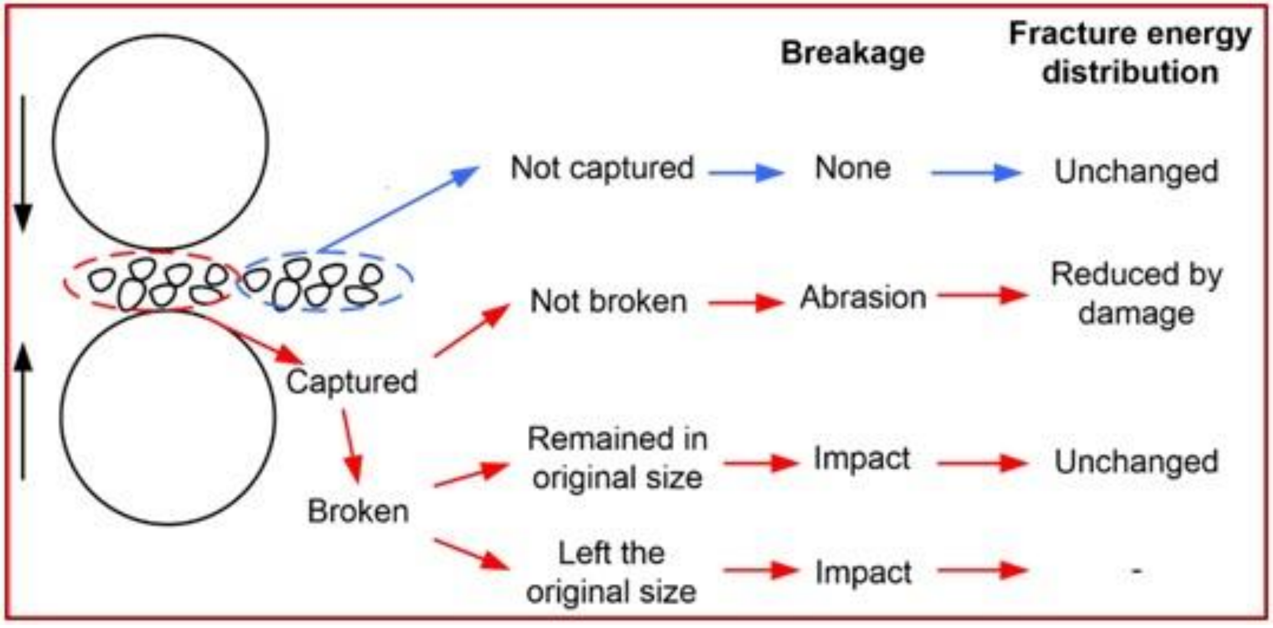
**Second Critical Speed** (middle) is the speed at which the second layer of media centrifuges inside the first layer.

**nth Critical speed** (right) is the speed at which the nth layer of media centrifuges inside the n-1 layer

# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

→ The size reduction that occurs in a mill is based on a combination of the following mechanisms:

- → Impact with the media
- → Abrasion with the media
- → Attrition with particles and media

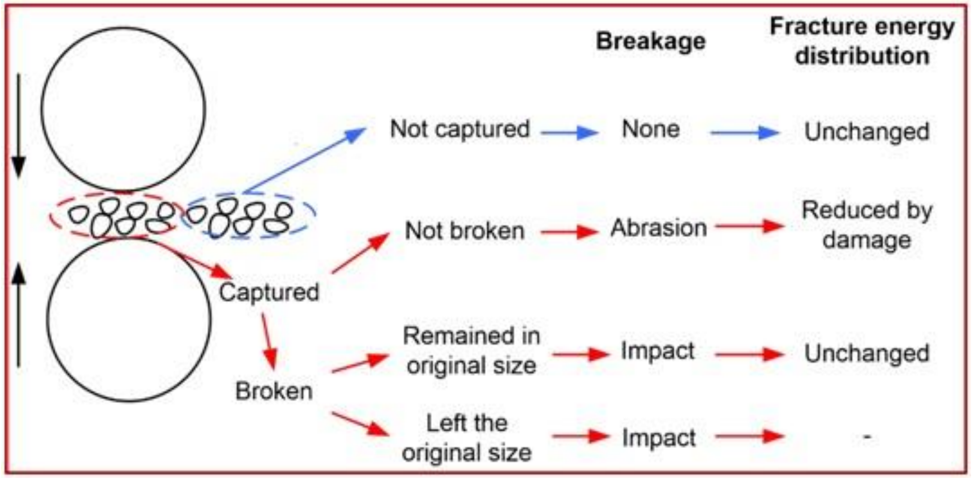


# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

→ In practice two phenomena are observed:

→ 1. When a aprticle is repeatedly fractured, each new particle tends to be stronger

→ 2. As fine particles are produced, na increasing degree of particle aggregation takes place

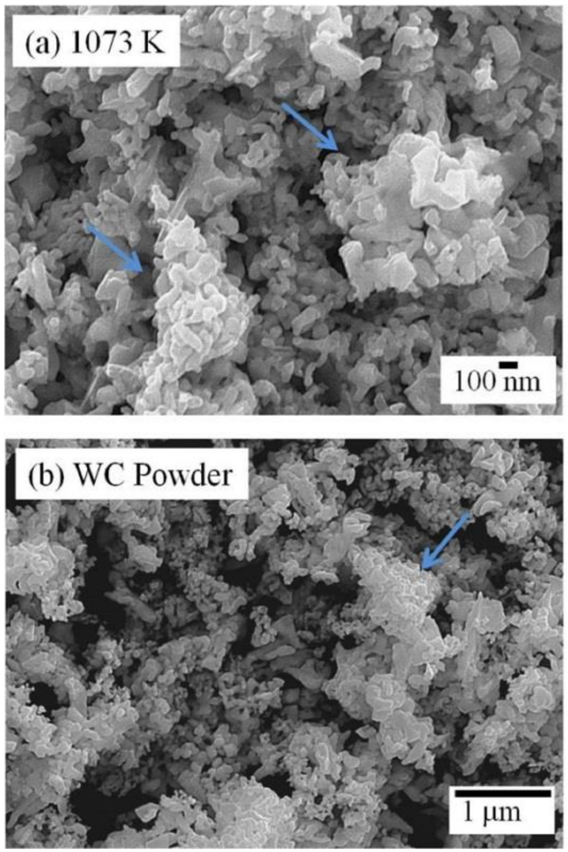


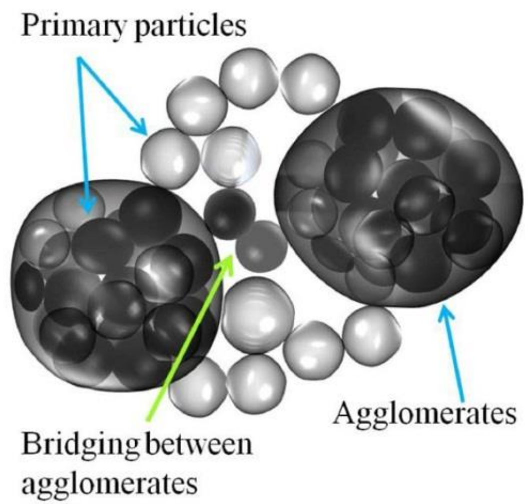

→ During fracture of particles, the larger cracks propagate first, leaving behind smaller cracks.As fragmentation proceeds, the required fracture stress may increase so much that some plastic deformation occurs. Subsequently the particle cannot be further reduced in size. A limit of fineness in milling may exist, depening on the actual process being used.

→ As milling proceeds, there is na increasing degree of particle aggregation, which makes it extremelly difficult to separate the primary particles from the aggregates.

# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

→ In dry comminution, air or na inert gas is used to keep the particles in suspension. The tendency of fine particles to agglomerate in response to van der Waals attractive forces limits the capabilities of dry processes.




DOI: 10.5772/55291

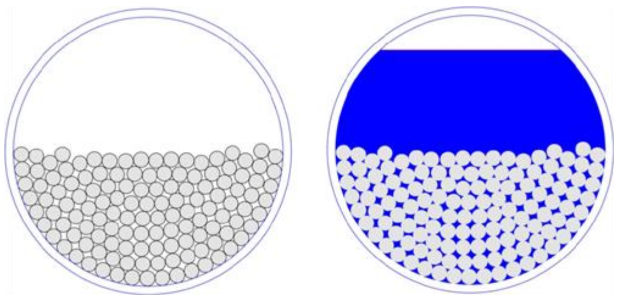
# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

Dry mills

→ An important requiremnt  of dry mills is the continuous removal of fines that have reached the desired product size distributions. Other wise process efficiency decreases drastically.

→ Becaus eof technonoly limitations and the interaction of surface forces (reagglomeration of dry particles begins to dominate) the classification porcess becomes extremelly inefficient as the particle size distribution approaches approximately 10 μm

# Raw Material Preparation: Comminution (Milling, grinding and size reduction)



Wet mills

http://www.metsoendr
struction/mct_service.n
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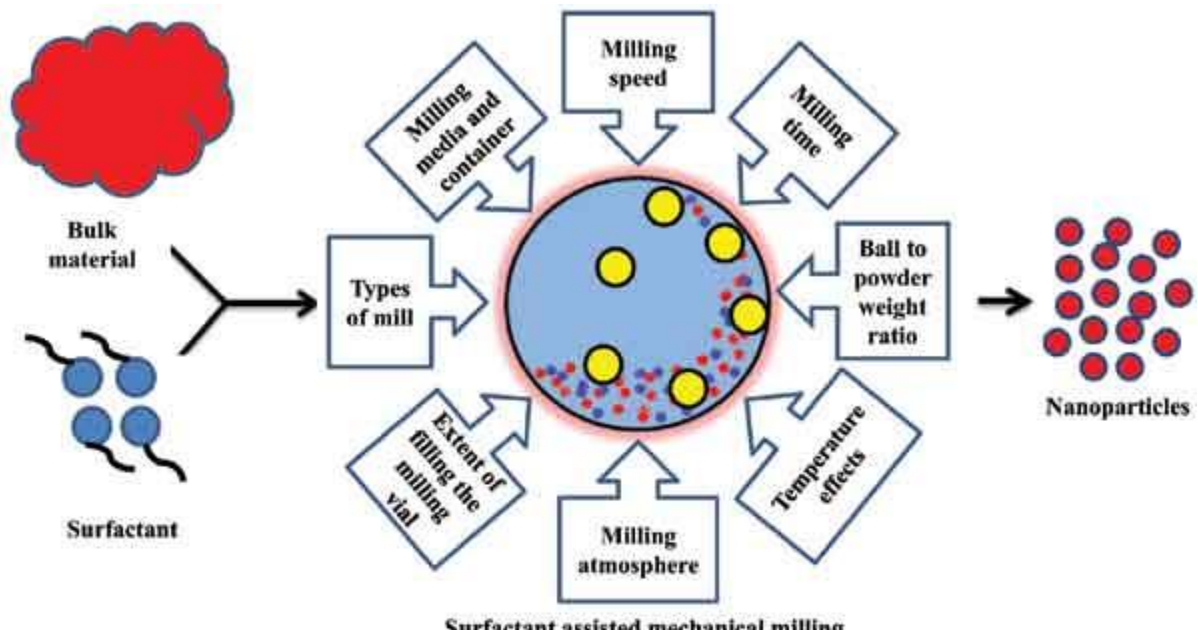
# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

→ Because wet milling can control the reagglomeration tendency of fine particles, it is used for comminution to submicrometer-sized particles. Water is the most commonly used liquid, although alcohols or other organics are used where oxidation by water is undesirable.

→ Further, the power to drive a wet ball mill is much as 30% less than that required by a dry mill.

→ Wet milling allows the introduction of surfactants, sintering aids, binders, and other additives, and results in a better mixing than in dry milling.

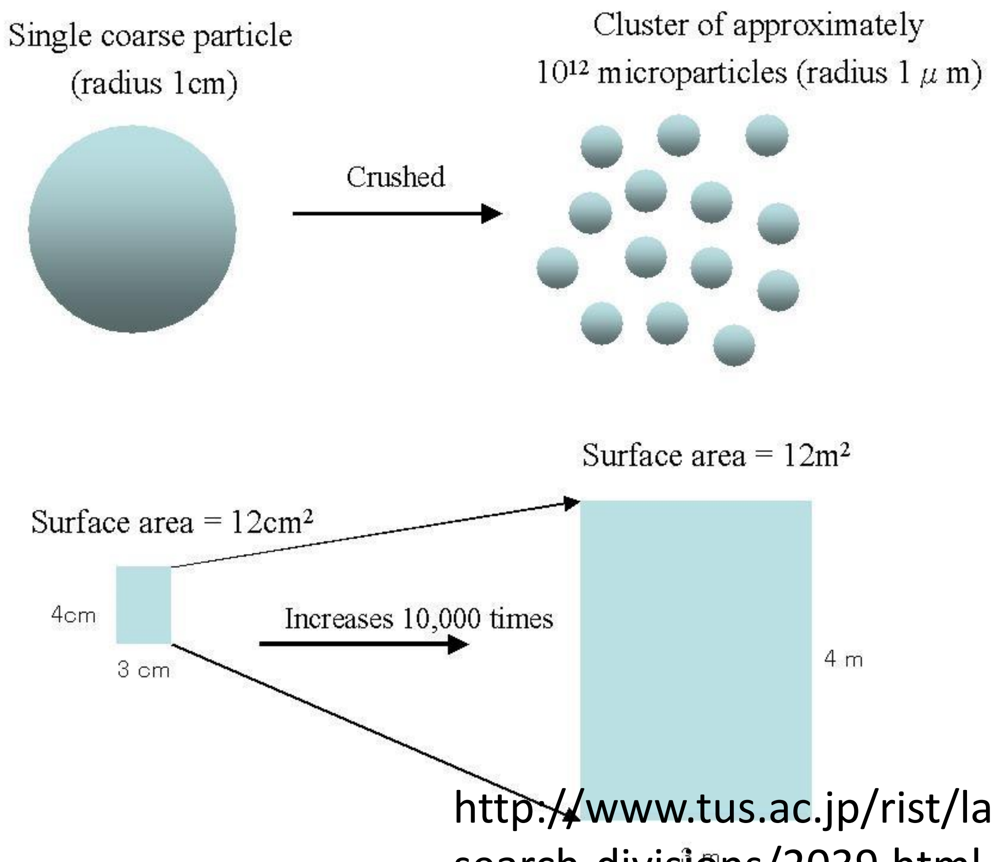
http://www.pauloabbe.com/size-reduction/resources/ball-mill-loading-wet-milling




DOI: 10.2174/1573413711309660114

# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

→ Although the primary objective of milling is to produce fine particles for further processing, the physical and chemical characteristics of the powders frequently undergo significant changes.




http://www.tus.ac.jp/rist/lab/introduction/1research-divisions/2039.html

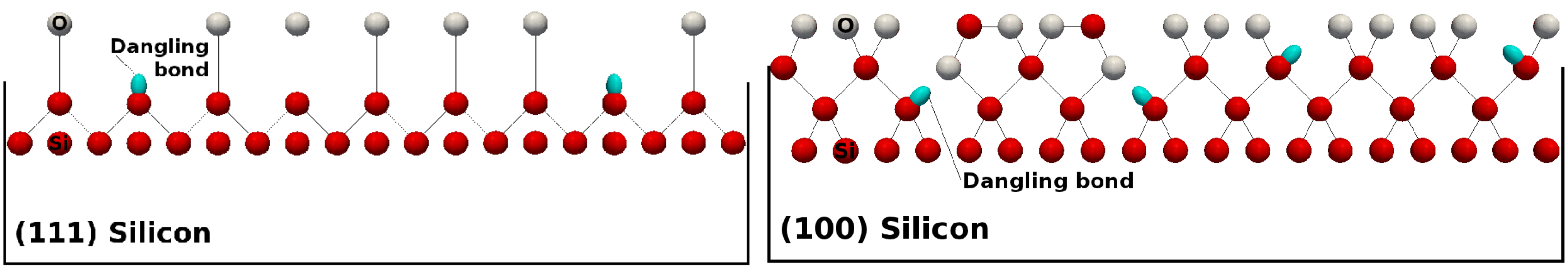
# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

→ Fine particles possess high surface energy, which favors physico-chemical reactions between the solid and surrounding medium.

→ After milling the fesh surface acquired hydrophilic properties and adsorbed relatively large quantities of water vapor.

→ Zeta potential and isoelectric points may change after milling process! Dry and wet milling processes may porduce different final products!

→ Oxygen is one of the major impurities picked up by silicon nitrid epowder during milling, but othe rimpuirites include C, Fe, Al, and othe relemnts from the milling fluid and mill hardware!




http://www.iue.tuwien.ac.at/phd/filipovic/node27.html

# Raw Material Preparation: Comminution (Milling, grinding and size reduction)

→ Case study

→ SiN were submitted to wet and dry milling. exhibited the formation of amorphous surface layers of oxynitrides up to 1.0 nm thick, whereas

Wet ball milling

→ formation of amorphous surface layers of oxynitrides up to 1.0 nm thick.

→ The isoelectric point of aqueous milled powders depend on the milling conditions. The increased abrasion of powder surface shift pHiso to a lower value, explained by the increased exposure of freshly created surfaces and their oxidation.

Dry ball milling

→ formation of amorphous surface layers of oxynitrides up to 10.0 nm thick

→ Zeta potential and isoelectric point are like that of amorphous silica.

http://phl.sika.com/en/solutions_products/02/cement-technology.html

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http://phl.sika.com/en/solutions_products/02/cement-technology.html

# Further reading

- **High Energy Ball Milling. Mechanochemical Processing of Nanopowders.** Małgorzata Sopicka-Lizer (Ed.)Elsevier (2010)

- **Ball Milling Towards Green Synthesis: Applications, Projects, Challenges.** Achim Stolle, Brindaban Ranu (Eds) Green Chemistry Series Royal Society of Chemistry (2018)

- **Fabrication of Nanostructured Materials by Mechanical Milling.** D. Chaira, S. K. Karak. In Handbook of Mechanical Nanostructuring M. Aliofkhazraei (Ed.) Wiley On Line Library (2015)