

Theory and Practice of Ceramic Processes



Lecture 4 Preparation of Ceramic Powders

Waldemar Pyda

Scope:
Building-up processes
Breaking-down processes

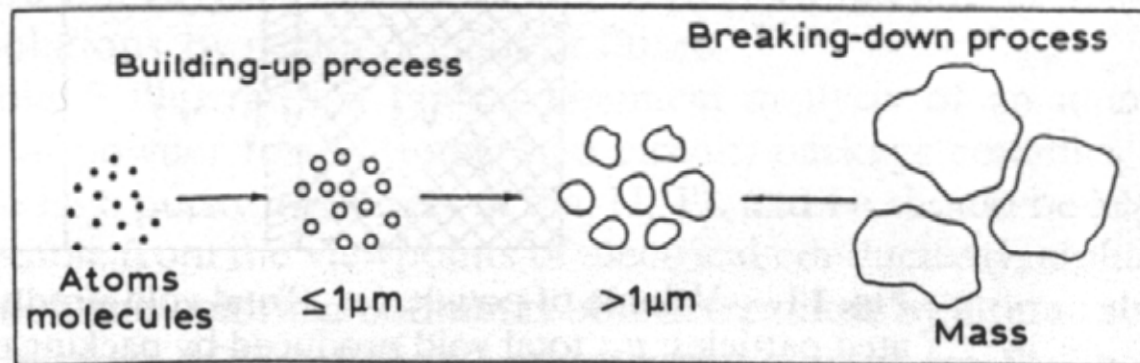
Requirements for sinterable powders

Properties of ceramic products are determined largely by the properties of the raw material powders, on which several requirements are imposed:

- (1) fine particles ($< 1 \mu\text{m}$);
- (2) narrow size range;
- (3) no aggregation;
- (4) controlled particle shape;
- (5) uniformity in chemical and phase compositions;
- (6) high purity.



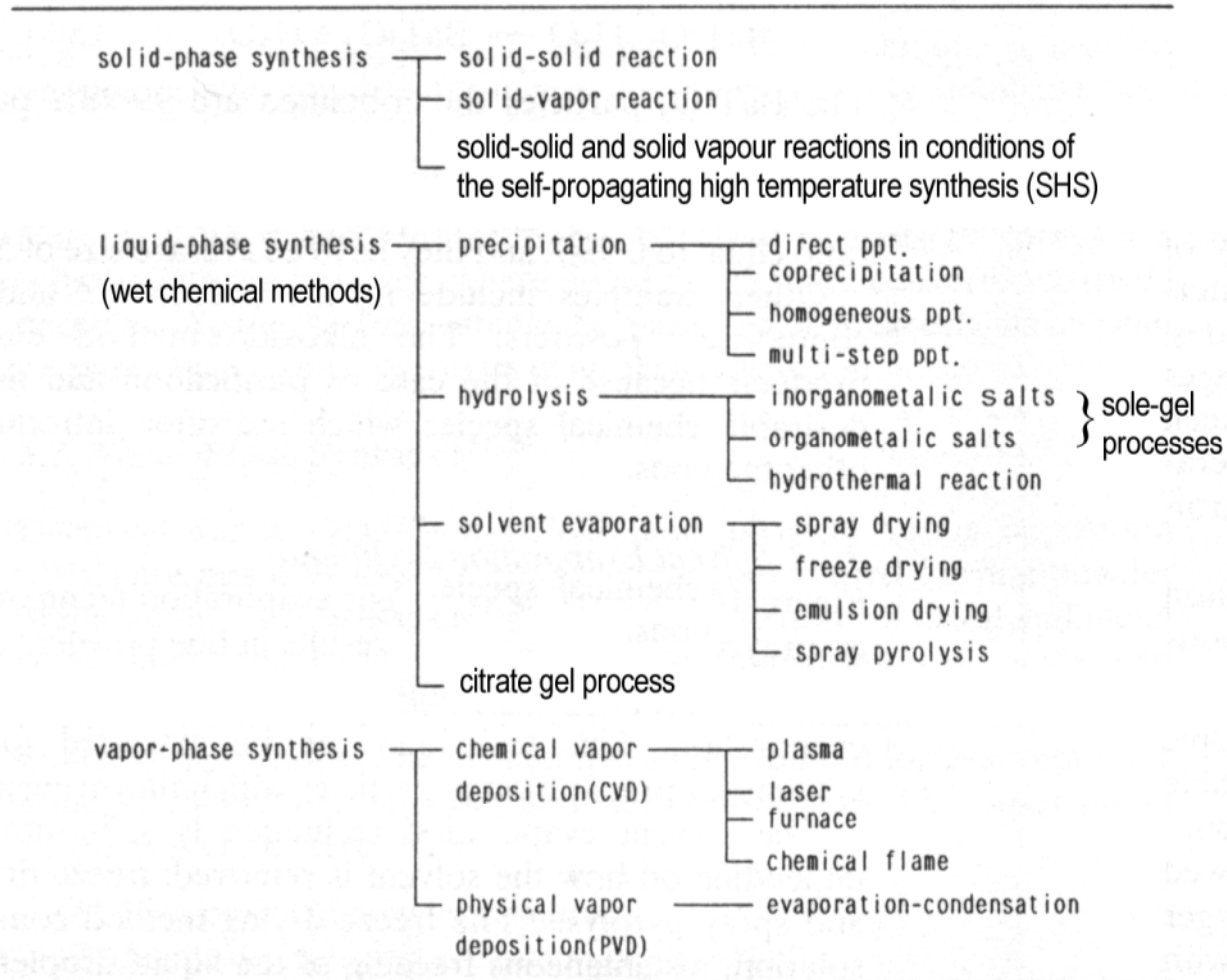
Ancient ceramic powder synthesis.



Fine Ceramic Powders for Sintering Mainly

'Building-up' processes

Synthesis Methods for Fine Ceramic Powders



Fine Ceramic Powders for Sintering Mainly

'Breaking-down' processes

Comminution and classification - powders by grinding and milling of raw materials that are either natural in origin or a natural mineral after thermal decomposition or materials synthesised in 'building-up' processes

Ceramic Powders for Other Applications

Sol-gel processing of colloids – nuclear industry, liquid chromatography, abrasives

Melt solidification – abrasives

Ceramic Fibers for Other Applications

Blow-spin process

Extrusion or draw process

Crystallization method

Vapour-phase routes (CVD)

Chemical transformation of precursor fibre

Unusual methods – ceramic cutting, directional freezing of gels

I Solid-Phase Synthesis

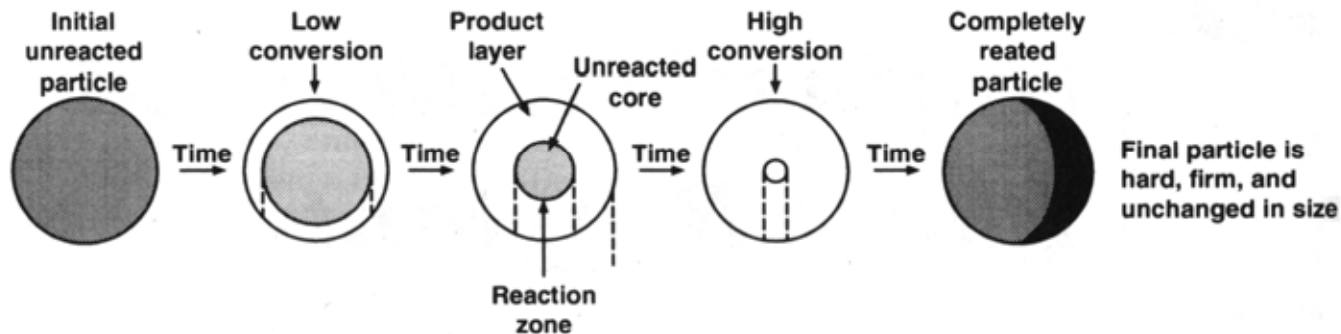
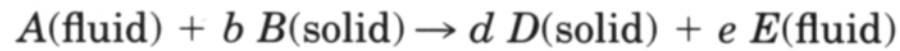


FIGURE 5.1 Shrinking core model.

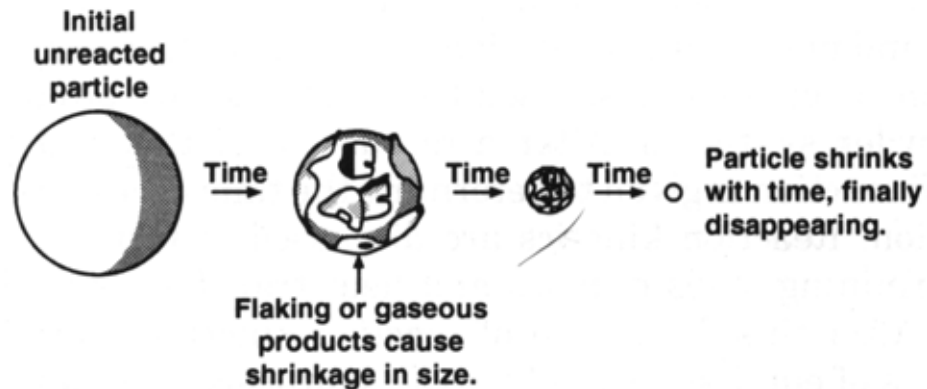


FIGURE 5.2 Shrinking sphere model. From Levenspiel [1], copyright © 1972 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

I Solid-Phase Synthesis

Fluid–solid reactions include thermal decomposition of minerals, roasting (oxidation) of sulfide ores, reduction of metal oxides with hydrogen, nitridation of metals, and carburization of metals.

Solid–solid synthesis reactions operate by different mechanisms, which include solid state diffusion and chemical reaction. Diffusion in ceramic solids is always ionic in nature and depends on defect or hole diffusivity, as well as, electron conductivity. Once the ionic reactants are in close association, chemical reactions can take place.

SPONTANEOUS
REACTION



EQUILIBRIUM
REACTION

THERMODYNAMIC ANALYSIS

Gibbs free energy (ΔG) !

Calculations from the free energy of formation for each of the species in the balanced reaction equation at given temperature and pressure

$\Delta G < 0$ *spontaneous reaction*

$\Delta G > 0$ *nonspontaneous reaction*

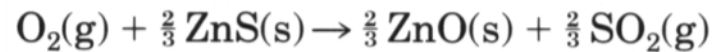
$\Delta G = 0$ *reaction in equilibrium*



Oxidation Reactions

Oxidation of sulphides

Roasting of zinc sulphide



$$\Delta H_{\text{RXN}}^{0-298} = -166.9 \frac{\text{kcal}}{\text{mole}}$$

Roasting of iron pyrite



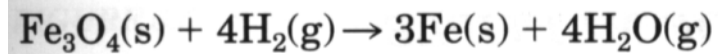
$$\Delta H_{\text{RXN}}^{0-298} = -592 \frac{\text{kcal}}{\text{mole}}$$

Oxidation of metals

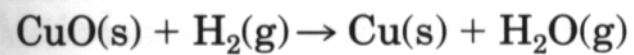


Reduction reactions

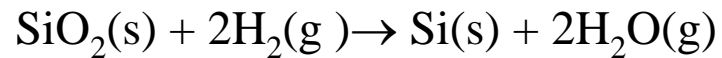
Used for to produce metal powders,
e.g. for production of carbide and nitride powders



$$\Delta H_{\text{RXN}}^{0-298} = +36.6 \frac{\text{kcal}}{\text{mole}}$$



$$\Delta H_{\text{RXN}}^{0-298} = -20.2 \frac{\text{kcal}}{\text{mole}}$$



Nitridation Reactions

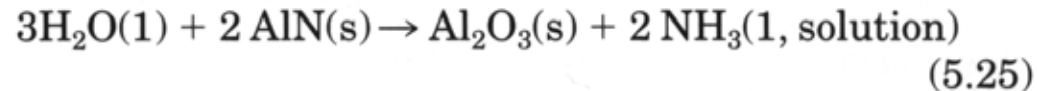
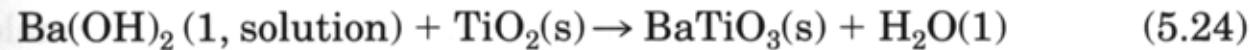
The direct nitridation of metal powders is commonly used to produce Si_3N_4 , BN, AlN, and other nitrides:



These and other nitrogen reactions are strongly endothermic, requiring energy to continue.

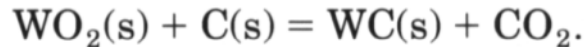
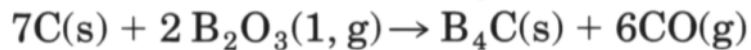
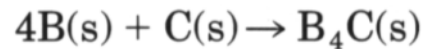
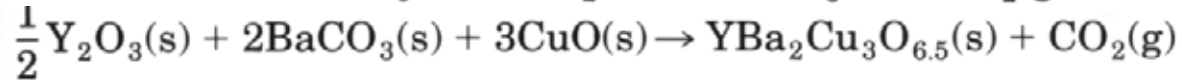
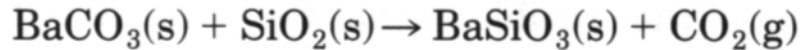
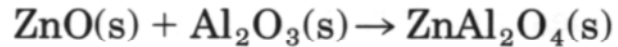
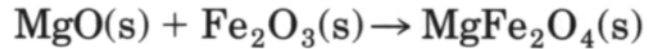
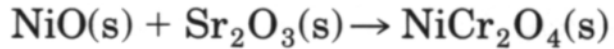
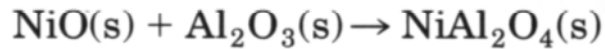
Liquid-Solid Reactions

Several reactions between solids and liquids produce ceramic powders:

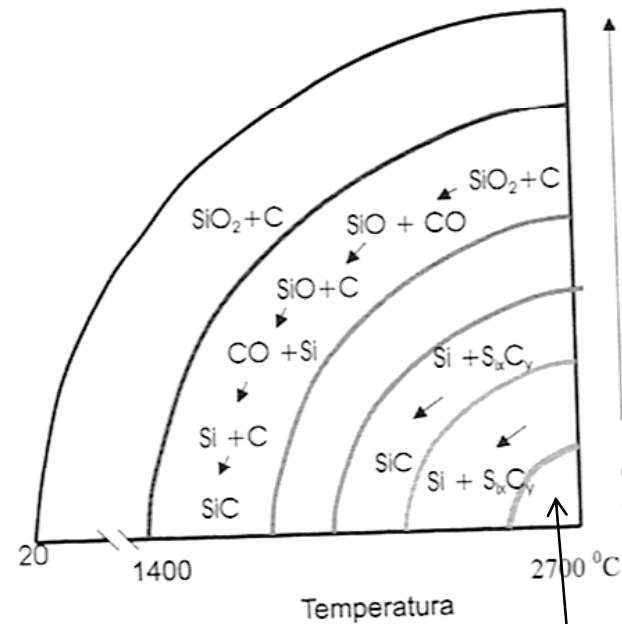
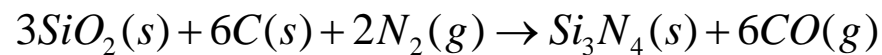
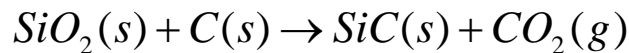


These reactions take place at ambient temperature and follow shrinking core kinetics similar to the solid–gas reactions discussed earlier. These reactions have reasonably fast reaction kinetics at low temperatures because the liquid has a very high concentration of reactant compared to the gas phase.

Solid-Solid Reactions



Acheson method for SiC production



Distance from the electrode

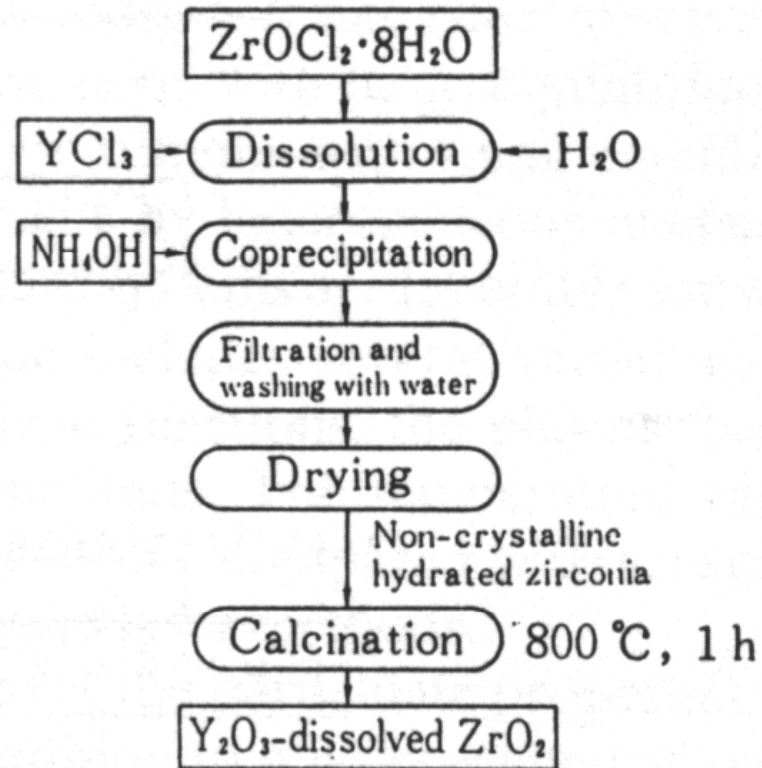
Scheme of reactions during the Acheson process

Graphite resistant electrode

II Liquid-Phase Synthesis

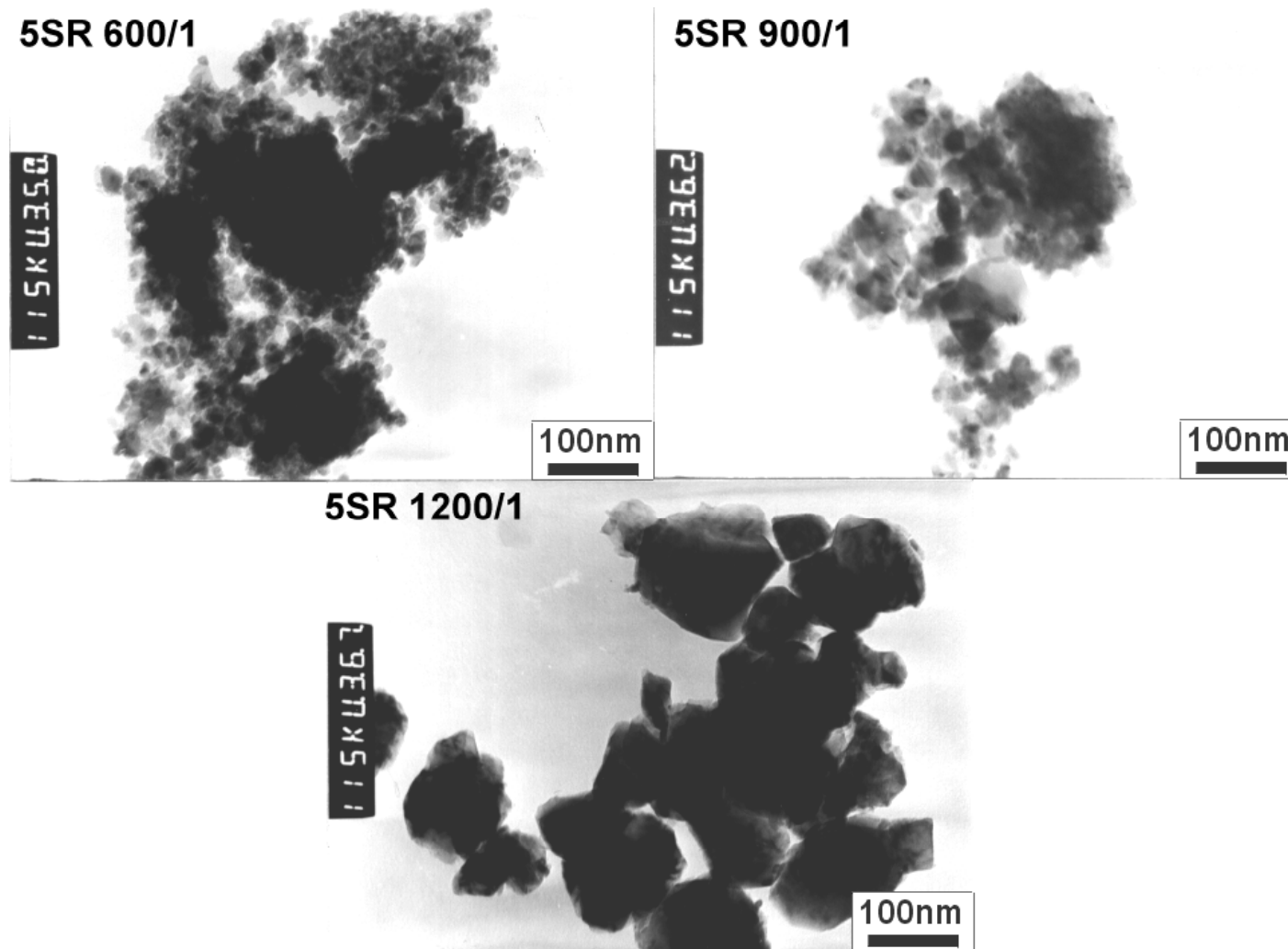
A variety of fine oxide powders have been made by the liquid-phase method. Recent progress in this technique has been remarkable, and new processes have been developed for purification, precise control of chemical composition, uniformity on an atomic scale and particle size. Preparation of fine particles from a liquid phase depends on their nucleation from supersaturated solutions and subsequent growth. The supersaturated solution results from solubility change, chemical reaction and solvent evaporation. Nucleation and growth are important processes responsible for the size of crystallites and particles. Liquid-phase synthesis is grouped into three categories: precipitation of insoluble salts, hydrolysis and solvent evaporation.

Precipitation Technique



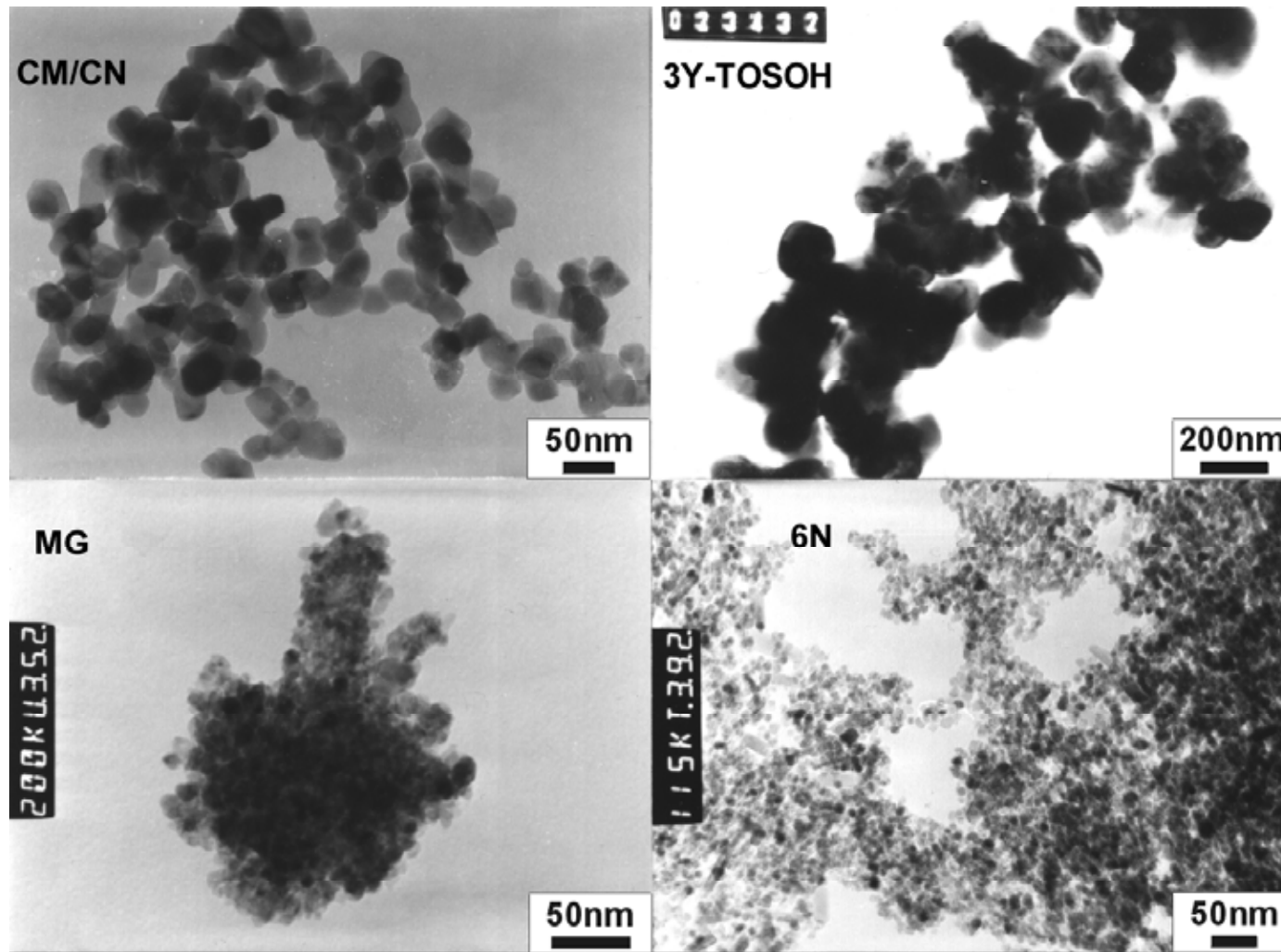
Preparation of zirconia by co-precipitation.

Morphology of calcined powders



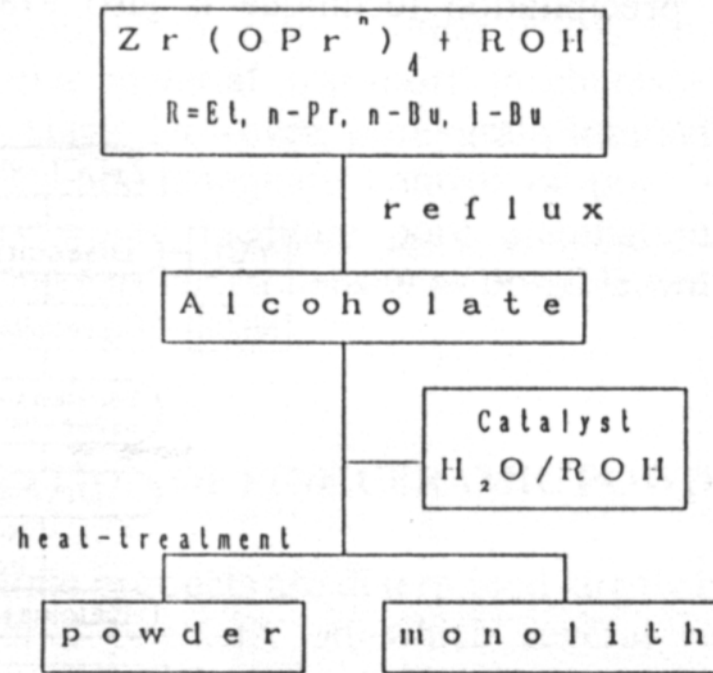
5 mol.% CaO-ZrO₂ powders calcined at indicated temperatures.

Morphology of calcined powders vs. hydrothermally treated

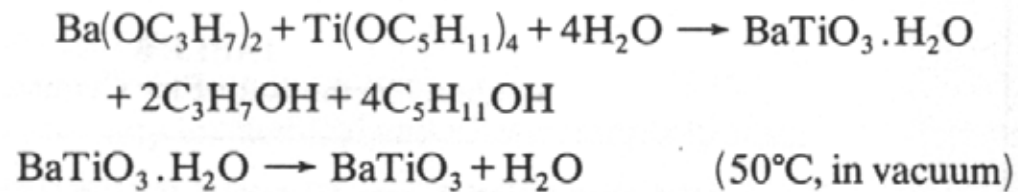


CM/CN– 3 mol % Y_2O_3 - ZrO_2 powder calcined at $950^\circ C$, 3Y-TOSOH – commercial calcined zirconia powder, MG - 5 mol.% CaO - ZrO_2 powders calcined at $600^\circ C$, 6N – 6 mol % CaO - ZrO_2 powder hydrothermally crystallized at $240^\circ C$.

Hydrolysis Technique



Preparation of ZrO_2 powders and monolithic gels by controlled hydrolysis of alkoxide.



Hydrolysis Technique

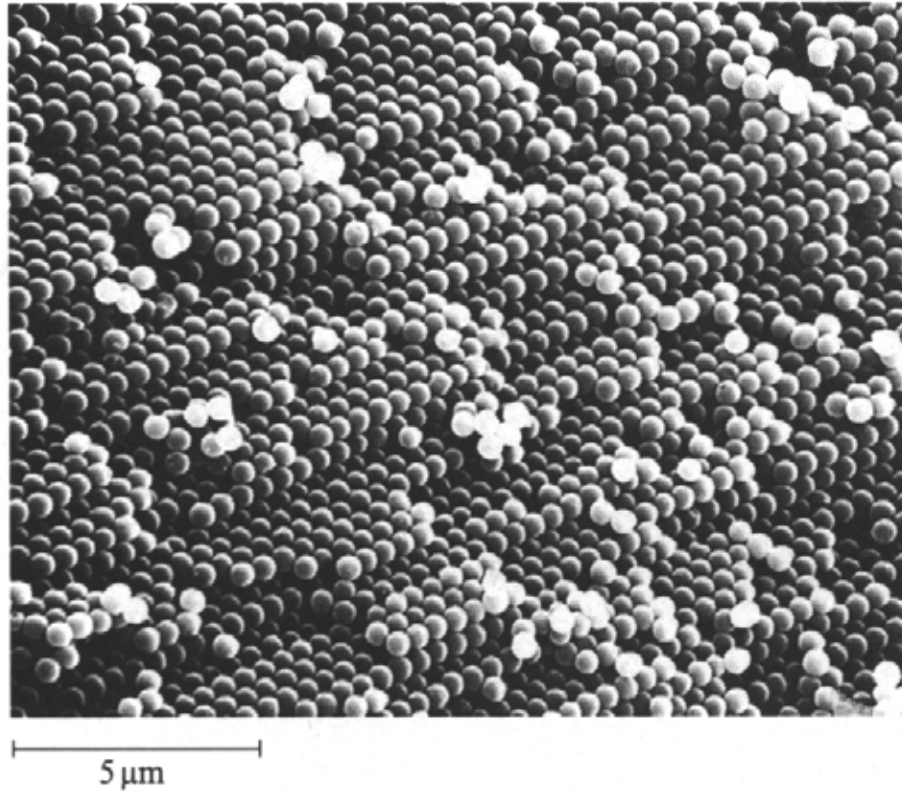
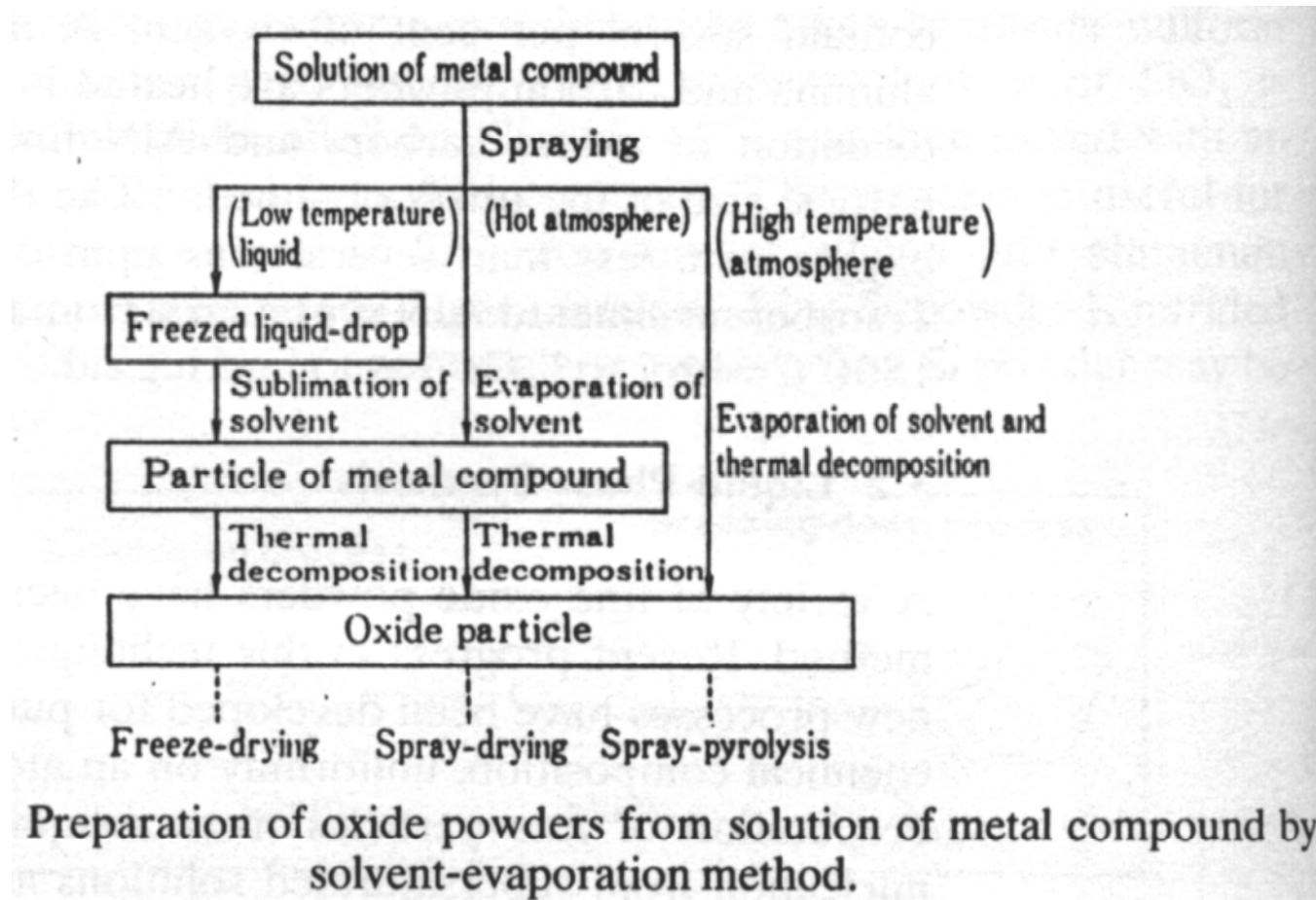


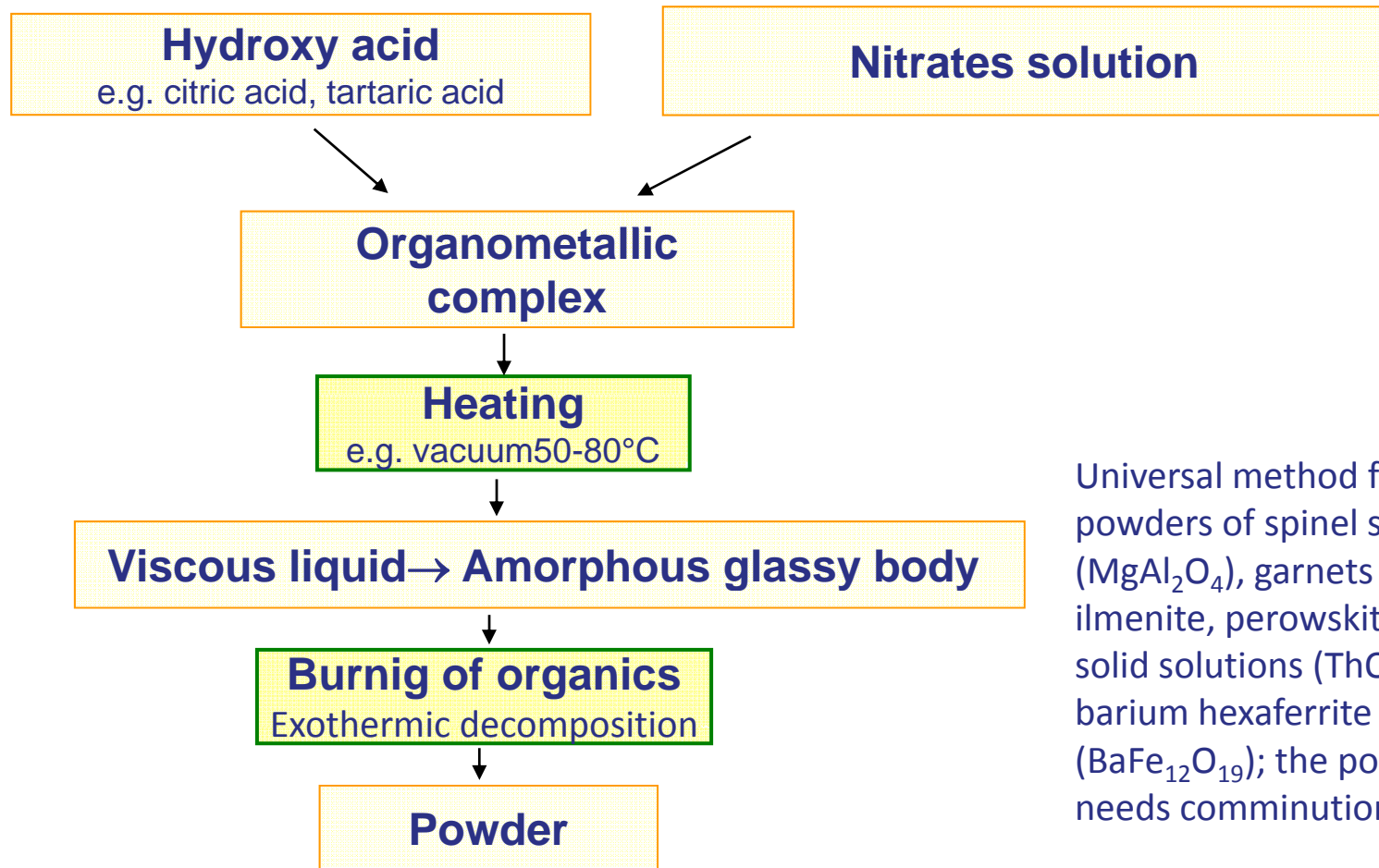
Figure 4.66 Monodisperse spherical ultra-fine particles of titania. (From T. Ikemoto, K. Uematsu, N. Mizutani and M. Kato, *J. Ceram. Soc. Jpn.*, **93**, 261 (1985).)

Solvent Evaporation Technique



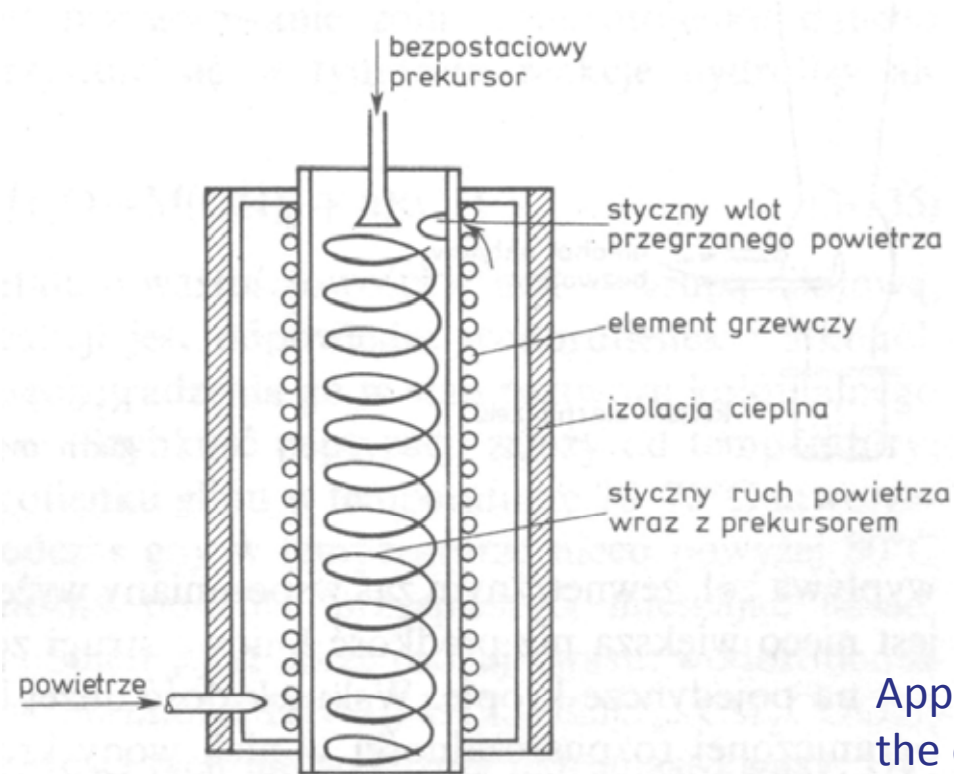
Citrate Gel Process

Elaborated by Marcilly & co-workers (1970)



Universal method for powders of spinel structures (MgAl_2O_4), garnets ($\text{Y}_3\text{Al}_5\text{O}_{12}$), ilmenite, perovskite, LaCrO_3 , solid solutions (ThO_2 , ZrO_2), barium hexaferrite baru ($\text{BaFe}_{12}\text{O}_{19}$); the powder needs comminution

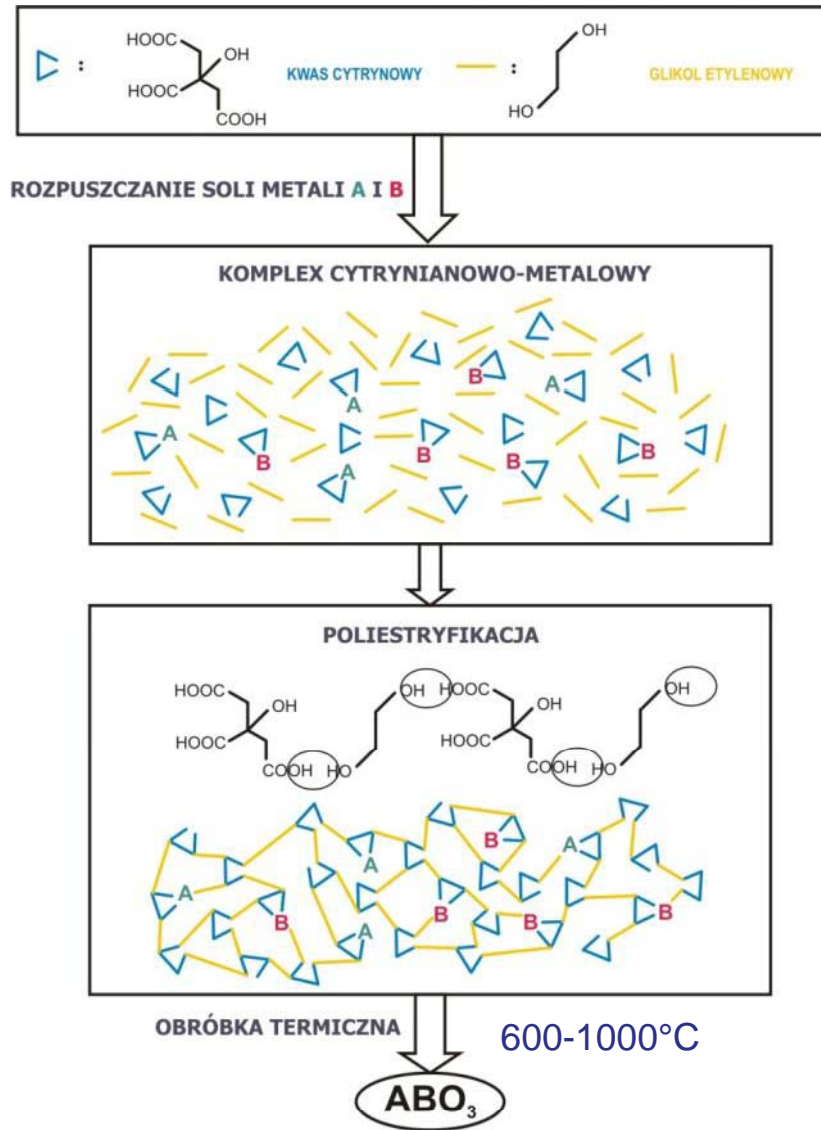
Citrate Gel Process



Apparatus for pyrolysis in the citric method

Powders of tissue-like morphologies are manufactured

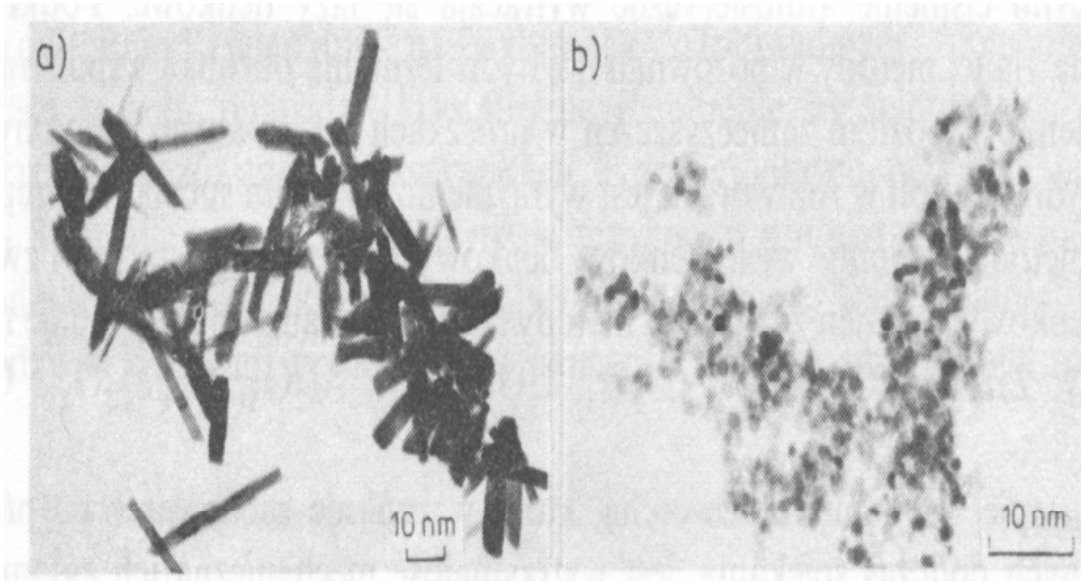
Metoda Pechinniego



Hydrothermal crystallization

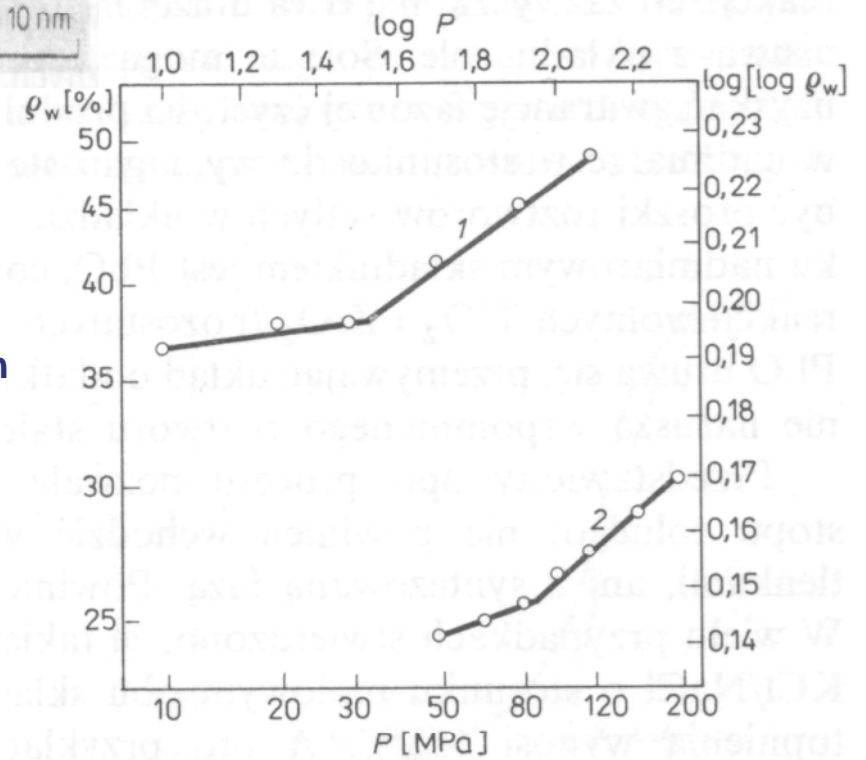
Factors affecting a size and shape of particles :

- ✓ Chemical composition of crystallisation environment
 - mineralizers,
 - pH,
- ✓ temperature,
- ✓ pressure
- ✓ time.



SEM images of ZrO_2 powders crystallised under hydrothermal conditions (8h, 250°C) from co-precipitated gels; crystallization environments: a) LiOH aqueous solution (2mol/l), b) H_2O .

Relative density of compacts as a function of compacting pressure (P). Powders of 13% mol. CaO - ZrO_2 solid solution
 1 – hydrothermal crystallisation
 2 – calcination treatment of the co-precipitated gel.



III Vapour-Phase Synthesis

Chemical vapor deposition (CVD) and physical vapor deposition (PVD) are major vapor-phase synthetic methods used for fine powder preparation. CVD uses chemical reactions of vapors of metal and metal compounds, and PVD uses evaporation–condensation of solids with similar compositions. The high temperature required for evaporation is achieved by arc, plasma, laser and electrical heating. The vapor-phase synthesis is characterized by

- (1) high purity of powder products;
- (2) highly discrete and non-aggregated particles;
- (3) preparation of ultrafine particles with narrow size distributions;
and
- (4) versatility in direct preparation of powders of metals and non-oxides in addition to oxides.

Principle of Powder formation by CVD Technique

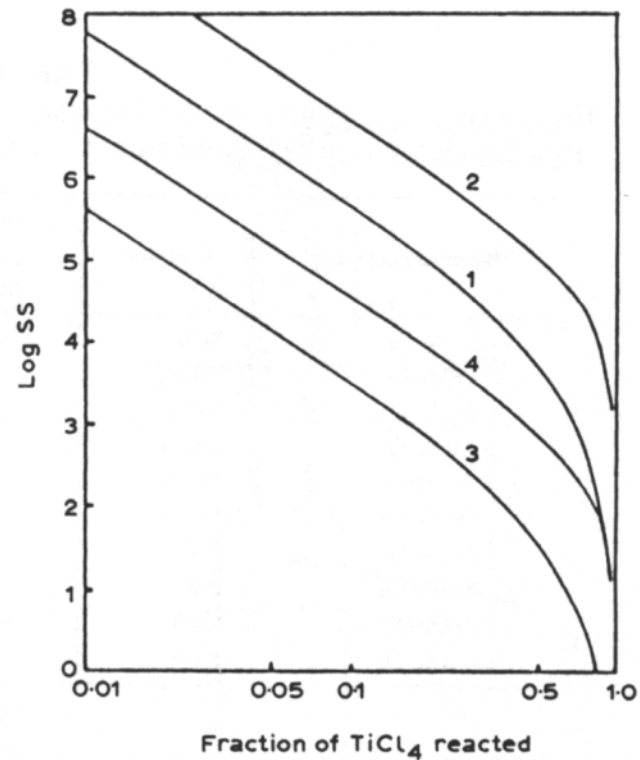


Fig. 17. Supersaturation ratios for formulation of TiO₂ (anatase) clusters by oxygenolysis of TiCl₄. (1) O₂/TiCl₄ = 1, 900°C; (2) O₂/TiCl₄ = 10, 900°C; (3) O₂/TiCl₄ = 1, 1400°C; (4) O₂/TiCl₄ = 10, 1400°C.

Effect of the equilibrium constant

Equilibrium Constants for the Deposition of Solid from Gaseous Systems and Powder Formation¹⁰ (Equilibrium Constant Based on 1 mole of Metal Source)

Reaction system	Product	Equilibrium constant (log k_p)		Formation of powder	
		1000°C	1400°C	1000°C	1500°C ≤ 1500°C Plasma
Oxides	SiCl ₄ -O ₂	10.7	7.0	○	
	TiCl ₄ -O ₂	4.6	2.5	○	
	TiCl ₄ -H ₂ O	5.5	5.2	○	
	AlCl ₃ -O ₂	7.8	4.2	○	
	FeCl ₃ -O ₂	2.5	0.3	○	
	FeCl ₂ -O ₂	5.0	1.3	○	
	ZrCl ₄ -O ₂	8.1	4.7	○	
	NiCl ₂ -O ₂	0.2		×	
	CoCl ₂ -O ₂	-0.7		×	
	SnCl ₄ -O ₂	1.0		×	
Nitrides and carbides	SiCl ₄ -H ₂ -N ₂	1.1	1.4	×	
	SiCl ₄ -NH ₃	6.3	7.5	○	
	SiH ₄ -NH ₃	15.7	13.5	○	
	SiCl ₄ -CH ₄	1.3	4.7	×	○
	CH ₃ SiCl ₃	4.5	(6.3)	×	○
	SiH ₄ -CH ₄	10.7	10.7	○	
	(CH ₃) ₄ Si	11.1	10.8	○	
	TiCl ₄ -H ₂ -N ₂	0.7	1.2	×	
	TiCl ₄ -NH ₃ -H ₂	4.5	5.8	○	
	TiCl ₄ -CH ₄	0.7	4.1	×	○
	TiI ₄ -CH ₄	0.8	4.2	○	
	TiI ₄ -C ₂ H ₂ -H ₂	1.6	3.8	○	
	ZrCl ₄ -H ₂ -N ₂	-2.7	-1.2	×	
	ZrCl ₄ -NH ₃ -H ₂	1.2	3.3	○	
	ZrCl ₄ -CH ₄	-3.3	1.2	×	
	NbCl ₄ -NH ₃ -H ₂	8.2	8.1	○	
	NbCl ₄ -H ₂ -N ₂	4.3	3.7	○	
	MoCl ₅ -CH ₄ -H ₂	19.7	18.1	○	
MoO ₃ -CH ₄ -H ₂	11.0	(8.0)	○		
WCl ₆ -CH ₄ -H ₂	22.5	22.0	○		
Metals	SiH ₄	6.0	5.9	○	
	WCl ₆ -H ₂	15.5	15.5	○	
	MoO ₃ -H ₂	10.0	5.7	○	
	NbCl ₅ -H ₂	-0.7	1.6	○	

○ : powders were formed, × : powders were not formed.

Electric Furnace Method

(1) *Synthesis of oxide powders.* The formation of oxide powders in the CVD technique is described by three types of reaction:

- (1) oxygenolysis or hydrolysis of metal chlorides;
- (2) oxidation of metal vapor;
- (3) thermal decomposition of metal compounds.

(2) *Synthesis of nitride and carbide powders*

TABLE 8
Particle Sizes of Nitrides and Carbides obtained by the CVD Method¹⁰

Reaction system	Reaction temperature (°C)	Product	Particle size (μm)
SiCl ₄ -NH ₃	1000-1500	SiN _a H _b ^a	0.01-0.15
SiH ₄ -NH ₃	500-900	SiN _a H _b ^a	<0.2
TiCl ₄ -NH ₃	600-1500	TiN	0.01-0.4
ZrCl ₄ -NH ₃	1000-1500	ZrN	<0.01
VCl ₄ -NH ₃	700-1200	VN	0.01-0.1
Si(CH ₃) ₄	900-1400	SiC	0.01-0.2
Si(CH ₃)Cl ₃	Plasma	SiC	<0.03
SiH ₄ -CH ₄	1300-1400	SiC	0.01-0.1
TiCl ₄ -CH ₄	Plasma	TiC	0.01-0.2
TiI ₄ -CH ₄	1200-1400	TiC	0.01-0.15
NbCl ₅ -CH ₄	Plasma	NbC	0.01-0.1
MoCl ₄ -CH ₄	1200-1400	Mo ₂ C	0.02-0.4
WCl ₆ -CH ₄	1300-1400	WC	0.02-0.3

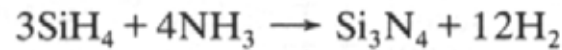
^aProduct is non-crystalline compound containing N and H in excess of stoichiometric Si₃N₄ and crystallizes into Si₃N₄ above 1300°C, forming a compound of Si₃N₄.



Plasma method

In the plasma method, a thermal plasma is used; this is a high-temperature gas characterized by relatively high electrical and thermal conductivity, high viscosity and high temperature gradient. Reactant gases introduced into a plasma will readily decompose into free atoms, ions and electrons. Quenching of these highly excited species results in ultrafine powders.

Si₃N₄ powders:



Characteristics of Typical Plasma Powders²²

Powder	SN-H	SN-Si	SN-Cl
Average particle size (nm)	260	Bimodal	230
Surface area (m ² /g)	65	53	92
Si ₃ N ₄ yield (%)	88	33	79
Oxygen (w/o)	2.1	3.9	10.2
Carbon (w/o)	0.11	0.30	0.03
Metallic impurities (ppm)	106	694	305
By-product	Si	Si	NH ₄ Cl

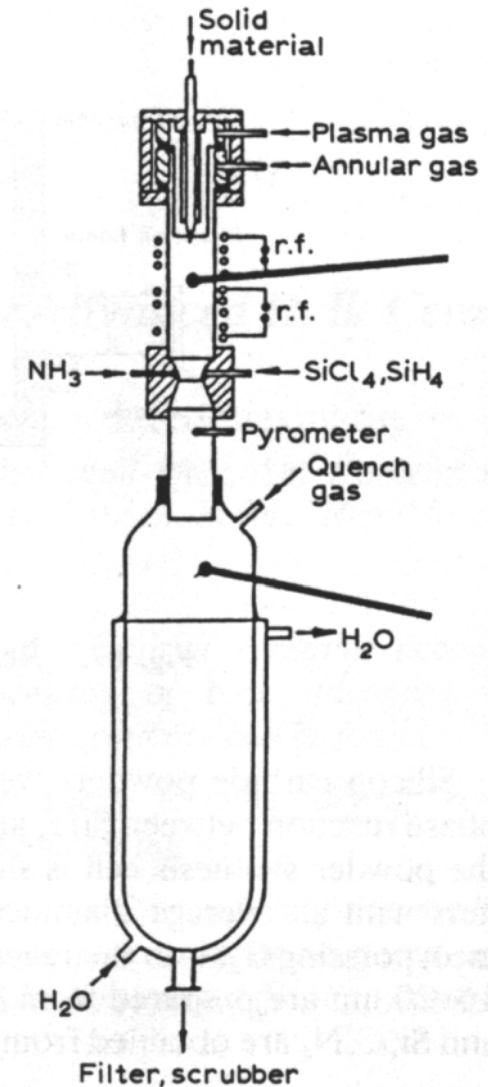


Fig. 18. Plasma reactor.



Laser Method

Laser radiation is used for vapor-phase synthesis of ultrafine powders. This laser-driven gas-phase reaction process offers many advantages over other gas-phase processes. It is a clean process. The laser radiation is absorbed directly by the gas molecules, resulting in a small, well-defined zone with high temperature and a very steep temperature gradient. These situations are favorable for controlling composition, size and particle distribution of product powders.

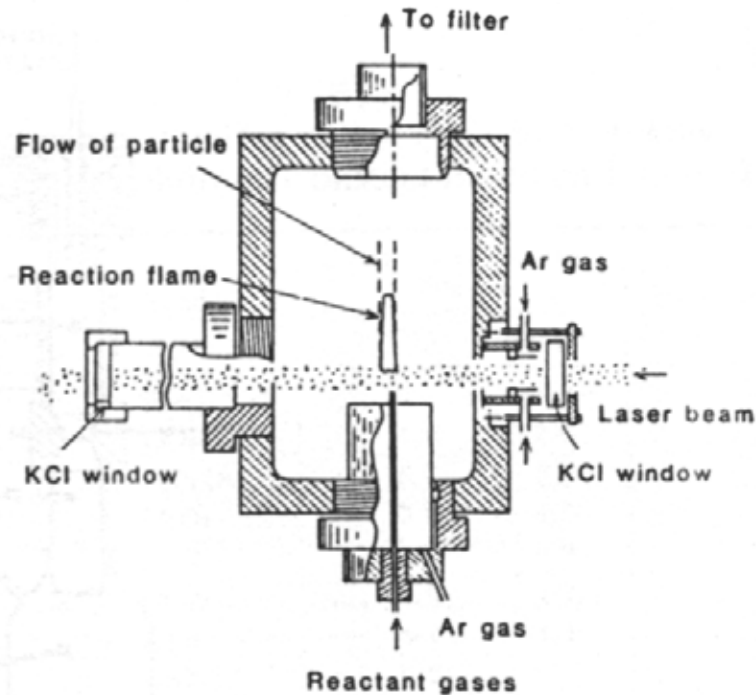


Fig. 19. Reactor for laser synthesis.

Spray Drying

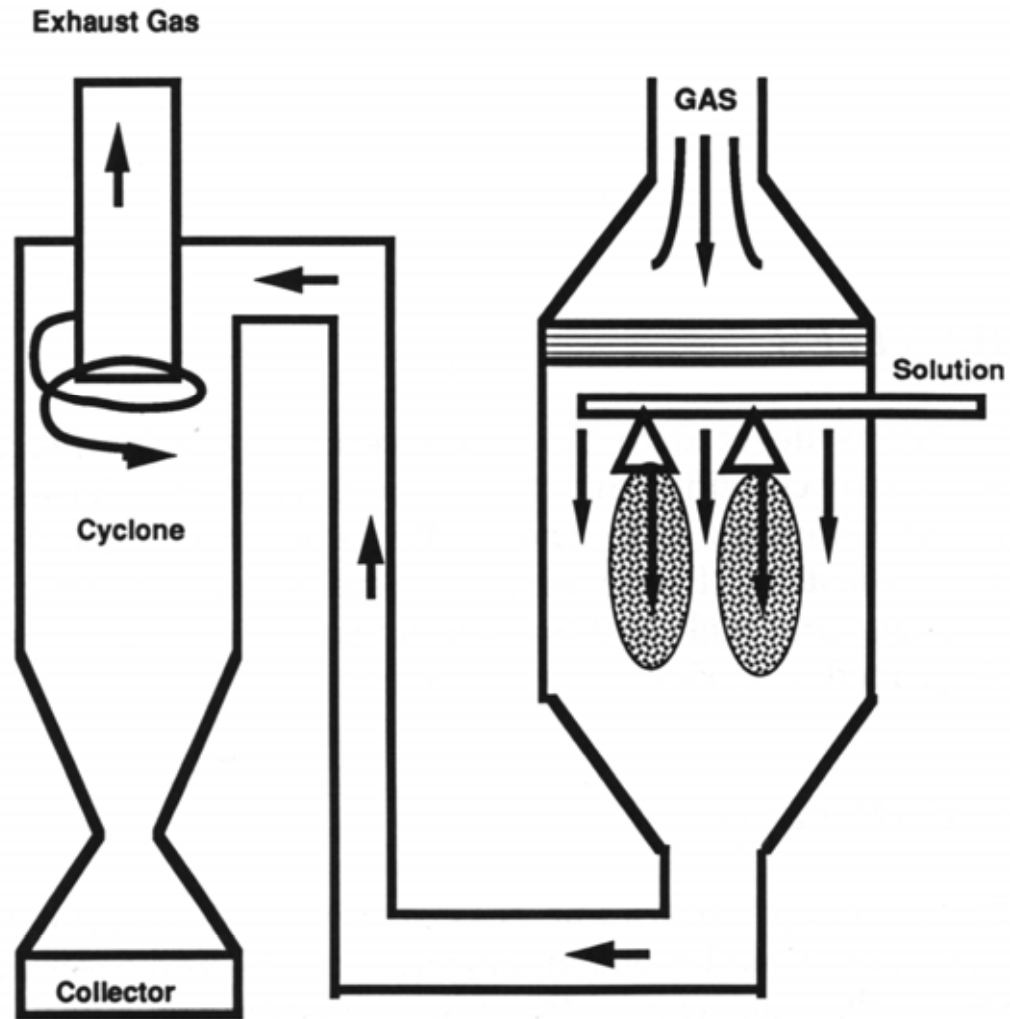


FIGURE 8.1 Schematic of spray drying process.

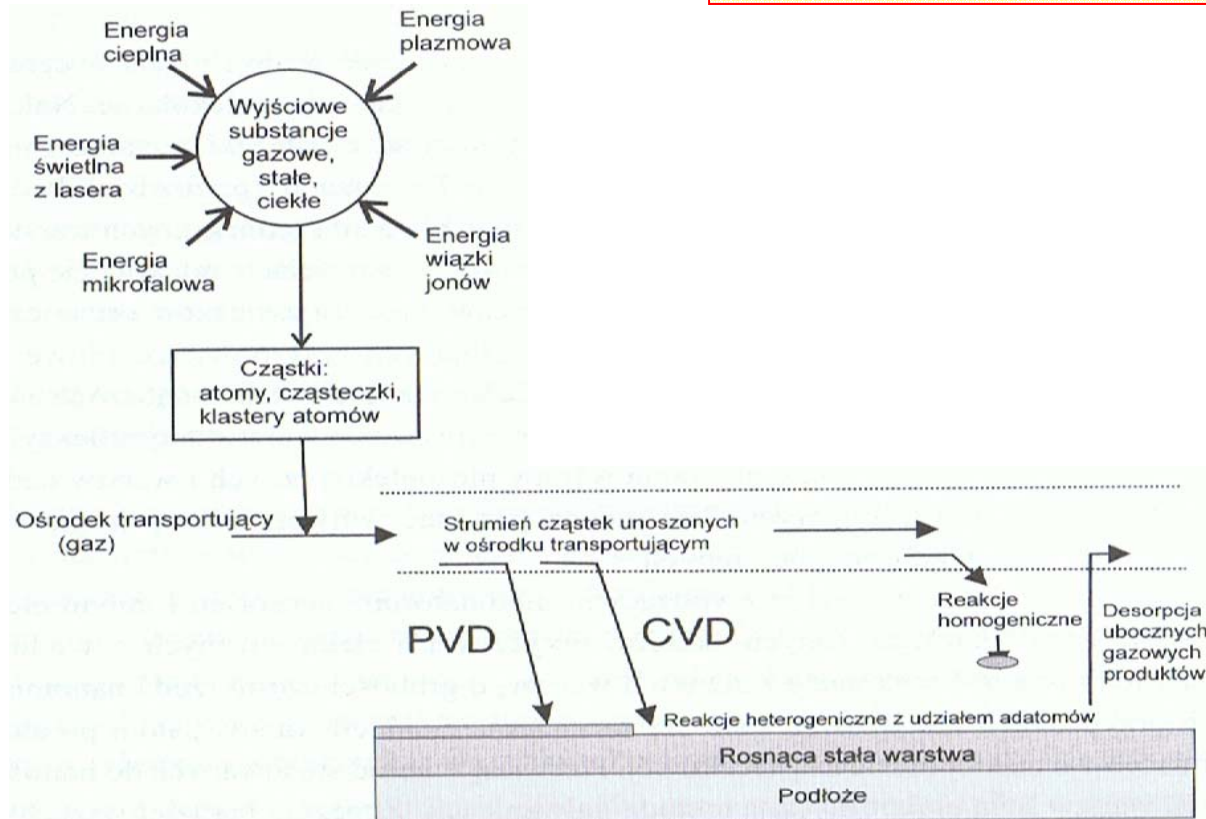
Otrzymywanie cienkich warstw ceramicznych z fazy gazowej

PVD

Physical Vapour Deposition
FIZYCZNE OSADZANIE Z FAZY GAZOWEJ

CVD

Chemical Vapour Deposition
CHEMICZNA KRYSZALIZACJA Z FAZY GAZOWEJ



COMMINUTION

The process of physically dividing solids into fine pieces by grinding in a mill is the best-known method for the manufacture of powders. However, there are problems associated with grinding, such as the contamination of the particle surface by atmospheric gases and by materials used in the construction of the mill. The smallest particle that can be produced by grinding is also limited by a tendency of the ground product to re-aggregate. The size, shape, size distribution and grinding limit of fine particles produced by mechanical reduction techniques are very dependent on the conditions of grinding and the type of mill used.

Mechanisms of Grinding

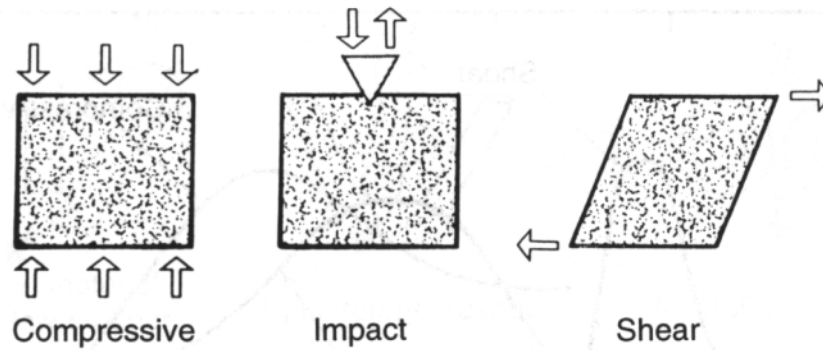


Figure 4.1 The most common forces in grinding.

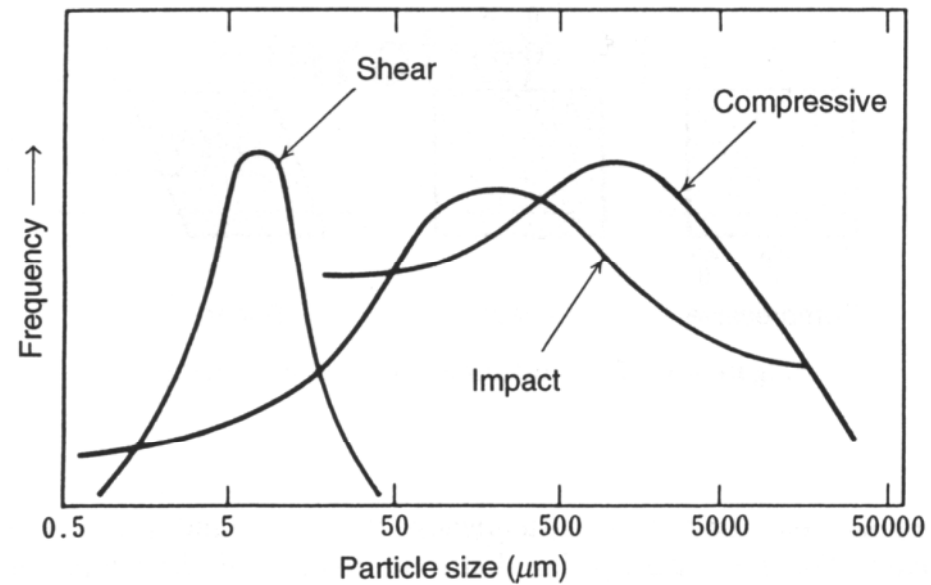
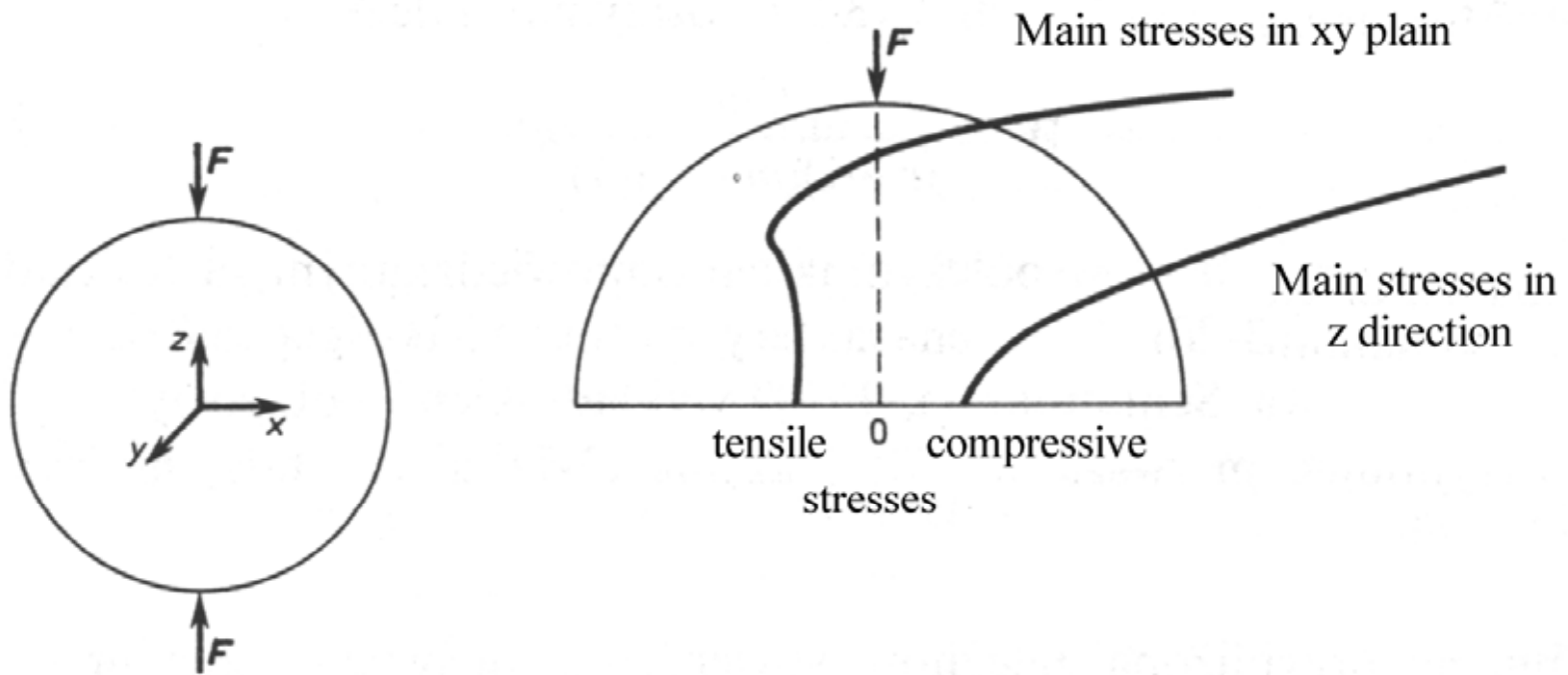
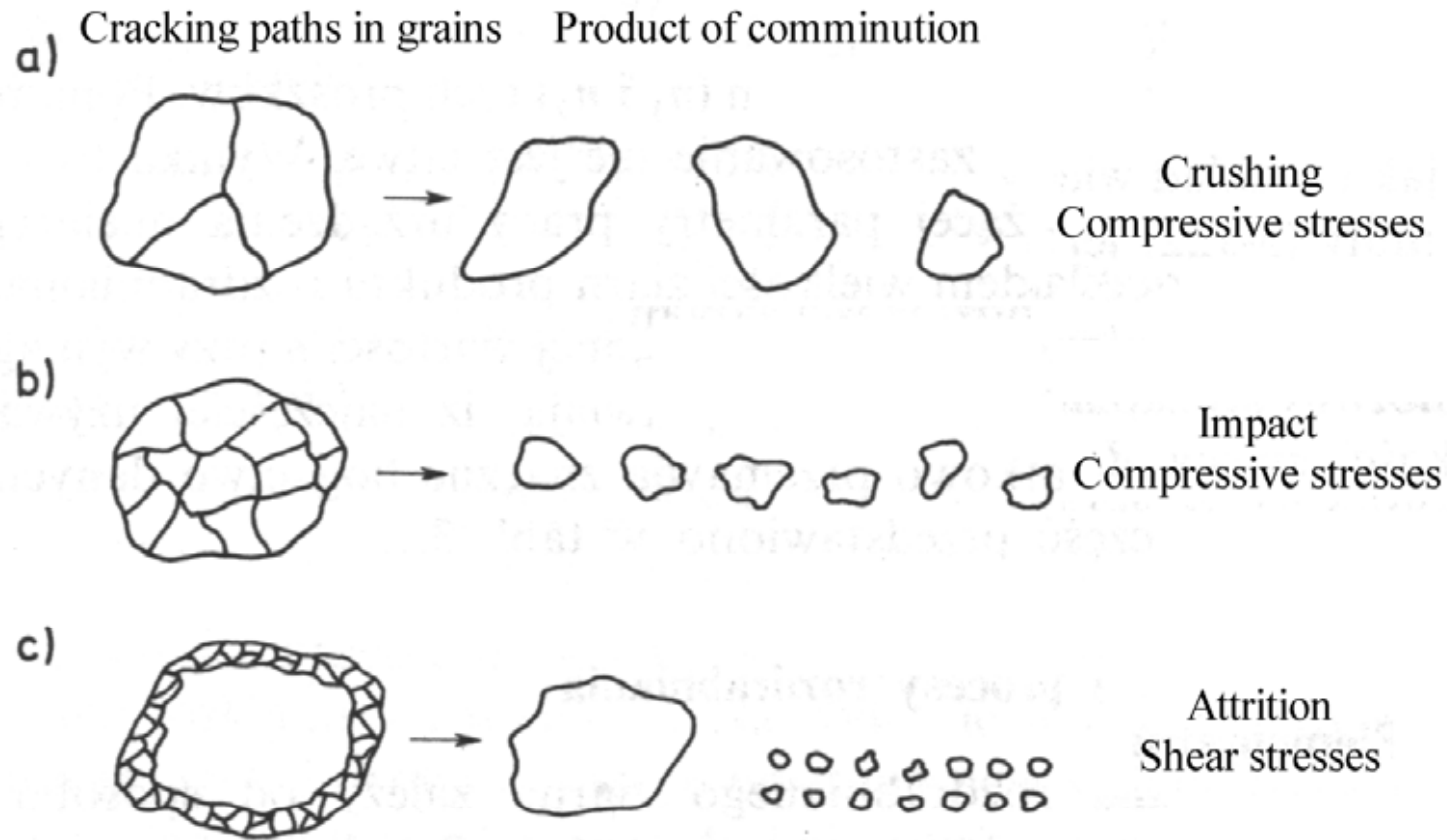


Figure 4.2 Size distribution of ground particles due to different grinding actions.

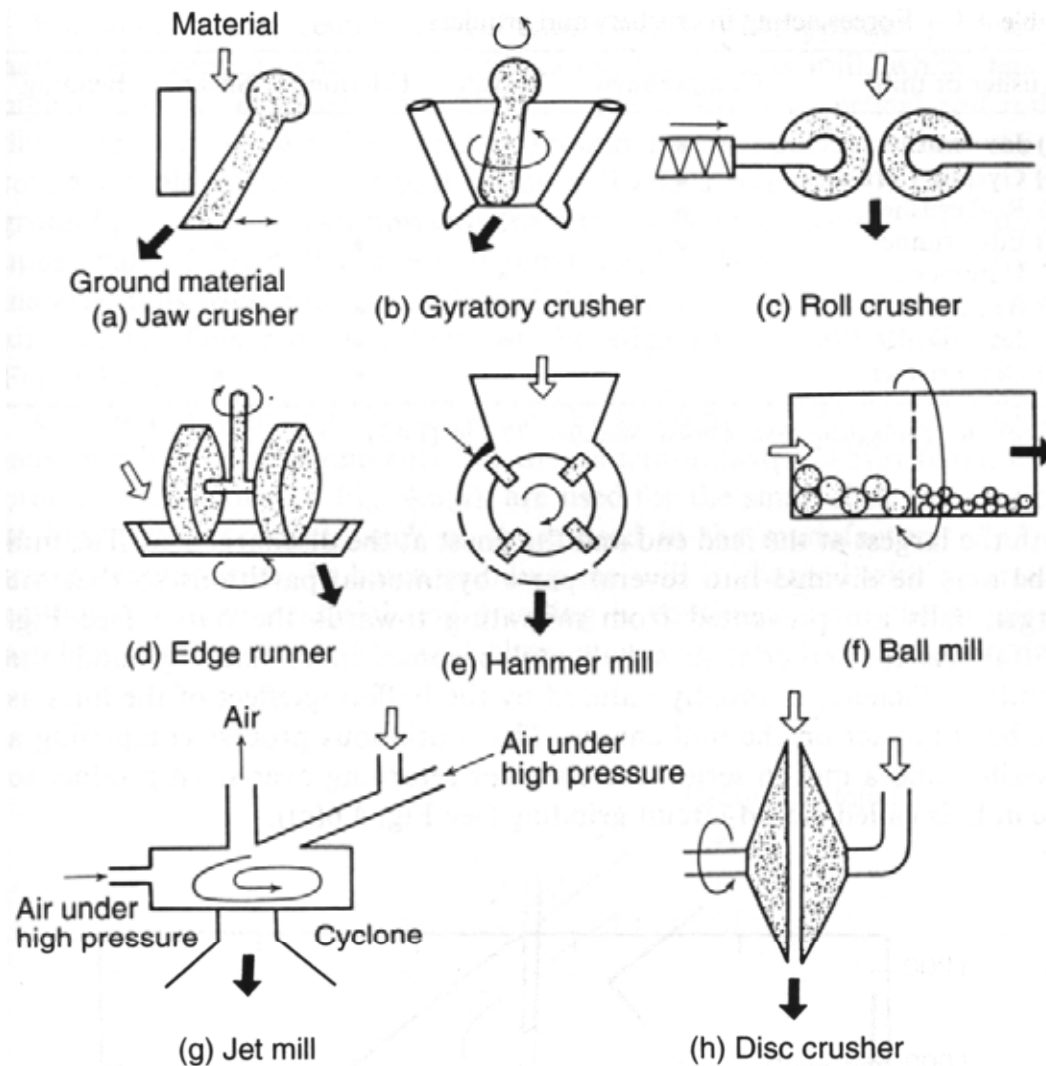
Main stresses distribution in the spherical grain subjected to a load F



Elementary processes of comminution



Comminution Equipment



Typical
crushers
and
grinders

Forces acting in crushers and grinders

Crusher or mill	Compressive	Impact	Friction	Shear	Bending
(a) Jaw crusher	•				
(b) Gyratory crusher	•				•
(c) Roll crusher	•			•	
(d) Edge runner	•		•	•	
(e) Hammer mill		•			
(f) Ball mill		•	•		
(g) Jet mill		•	•		
(h) Disc crusher			•	•	

Grinding systems

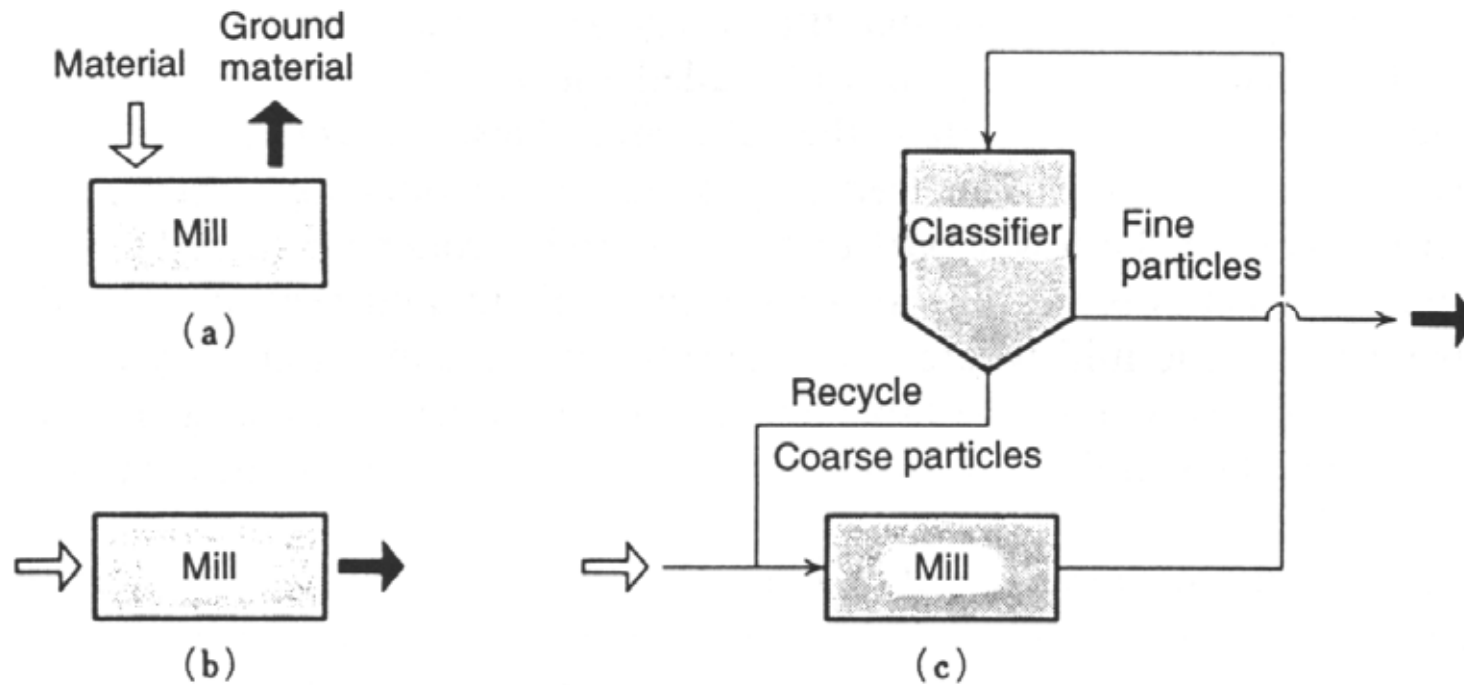


Figure 4.6 Grinding systems for a ball mill: (a) batch; (b) continuous; (c) continuous, closed circuit.

Types of Size-Reduction Equipment

Jaw crushers (continuous)

Gyratory crushers (continuous)

Heavy-duty impact mills (continuous)

 Rotor breakers

 Hammer mills

 Cage impactors

Roll crushers and shredders (continuous)

Tumbling media mills (batch and continuous)

 Ball mills

 Rod mills

 Autogeneous

Stirred media mills (batch and continuous)

 Stirred ball mills

 Stirred sand mills

Vibratory media mills (batch and continuous)

Fluid shear mills (batch and continuous)

 Colloid mills

 Microatomizer

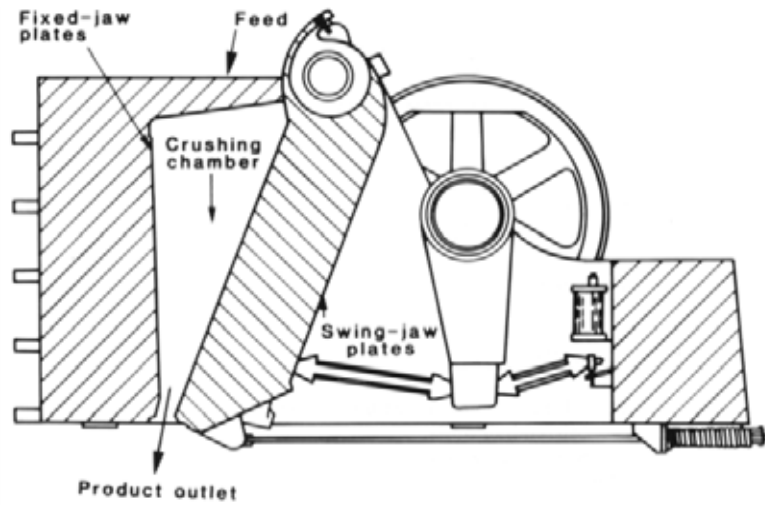
Fluid impact mills

 Opposed jet

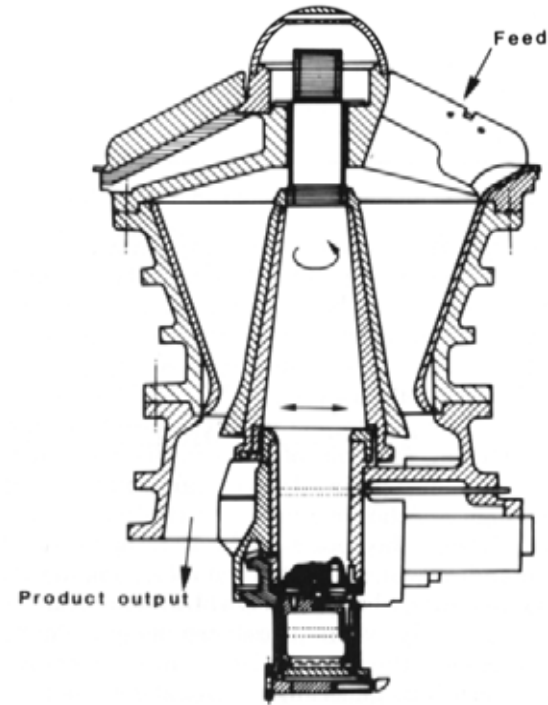
 Jet with anvil

 Centrifugal jet

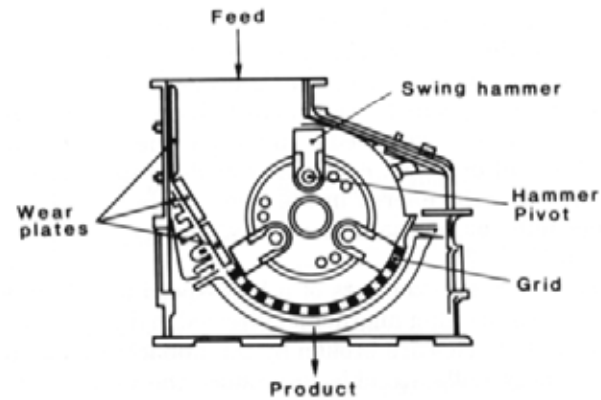
Crushing Equipment



Jaw crusher

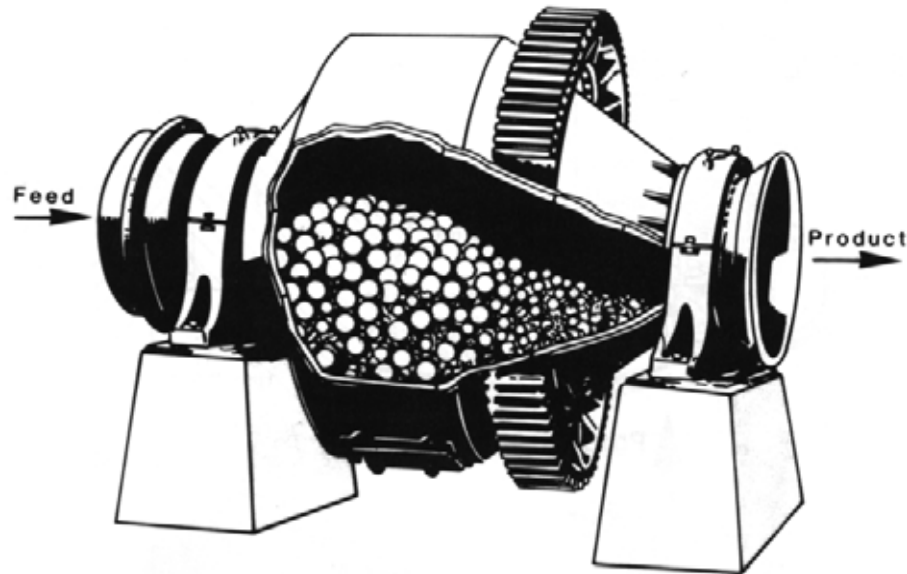


Gyratory crusher

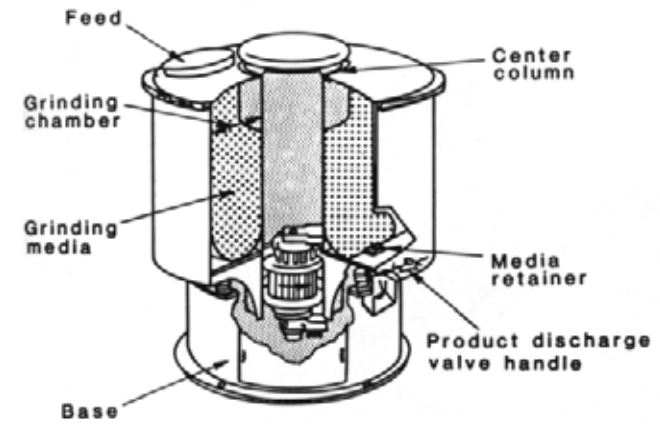


Hammer mill

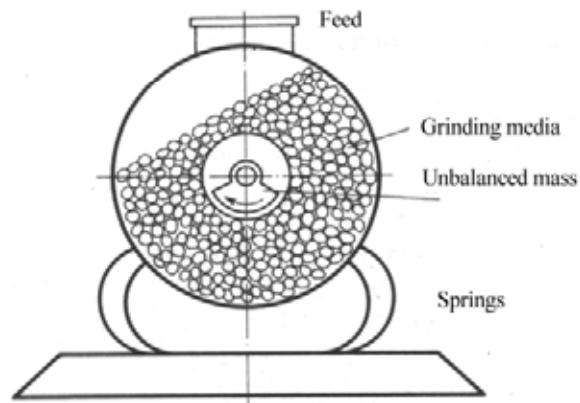
Grinding Equipment



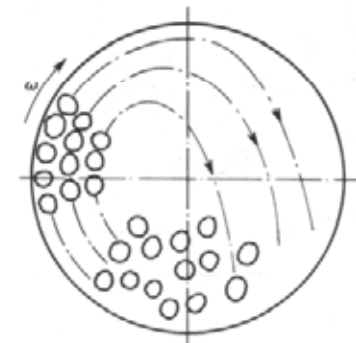
Ball mill



Vibratory mill

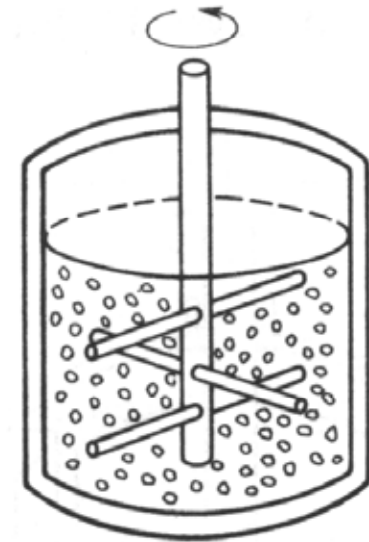
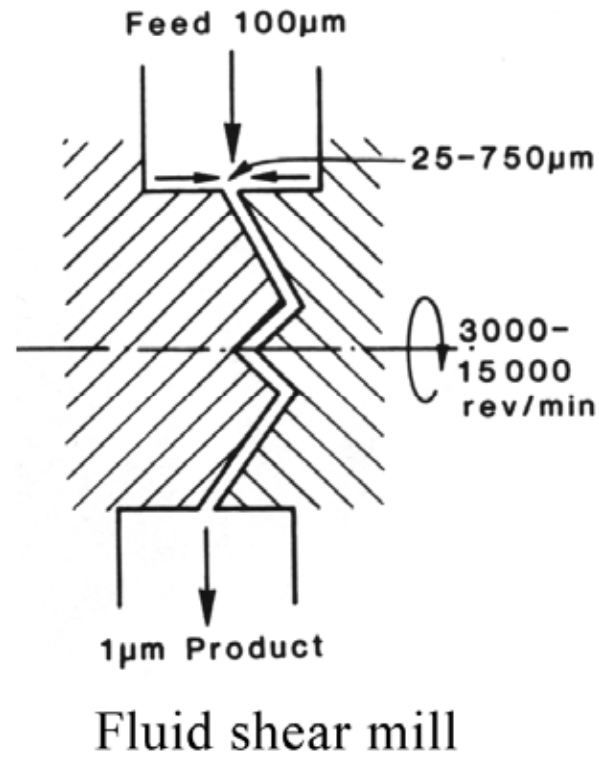
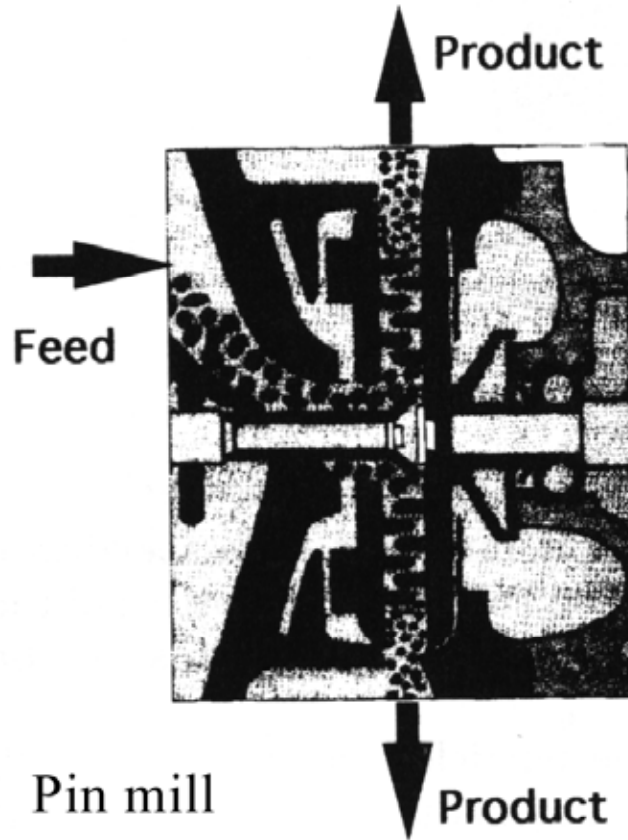


Vibratory tumbling mill



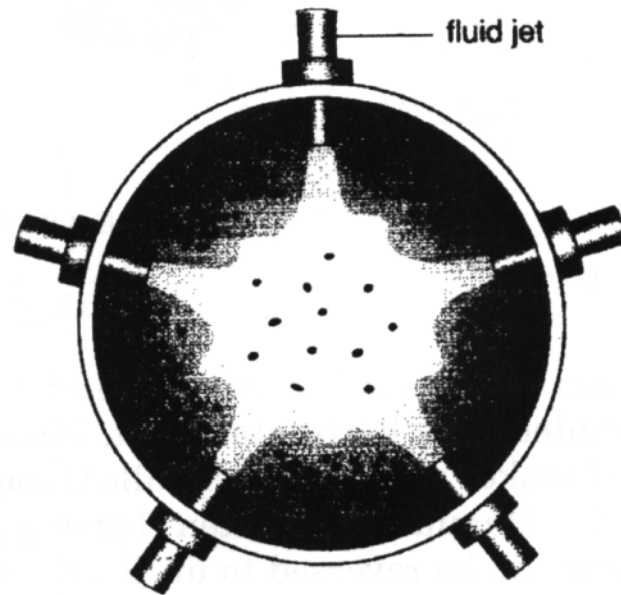
Movement of grinding media in a rotary-vibratory mill

Grinding Equipment

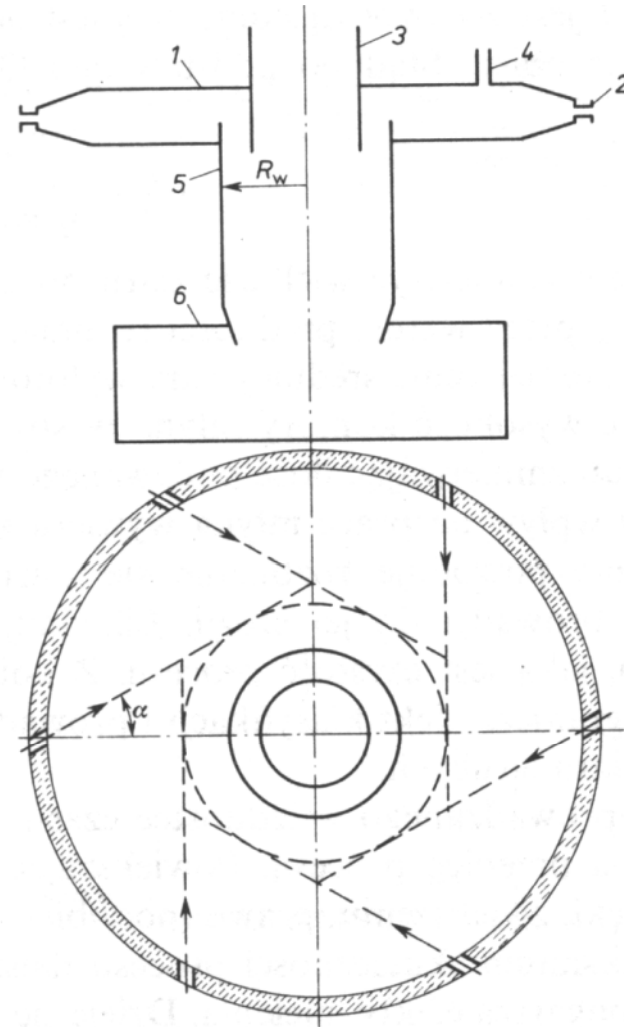


Stirred ball mill
Attrition mill

Grinding Equipment



Fluid jet mill



Energy Required for Size Reduction

If force is applied to the external surface of a particle, tensile and shear stresses are likely to be created within that particle. If the stresses exceed a critical value for an individual particle, that particle will suddenly fracture. The critical breaking stress σ is related to the Young's modulus of the solid by

$$\sigma = \sqrt{(E\gamma/r)} \quad (4.1)$$

The breaking stress σ is closely related to the surface energy γ , Young's modulus E and interatomic distance r between atoms in the crystal lattice.

Calculations show that σ is about $E/10$ for a perfect single crystal whilst $E/1000$ is typical of polycrystalline-like ceramics. The markedly lower values of σ in polycrystalline substances are attributed to the presence of intergrain boundaries and flaws. Even for single crystals, σ is markedly decreased by very fine cracks on the crystal surface. This effect of structure on strength is called 'structural sensitivity'. Equation (4.2), developed from equation (4.1), illustrates effects due to the presence of flaws and cracks:

$$\sigma = \sqrt{[E(\gamma + P)/L]} \quad (4.2)$$

where P is the work of surface plasticity and L is the depth of surface cracking. P is particularly significant in metals whilst L and γ are more important for ceramics.

Energy Required for Size Reduction

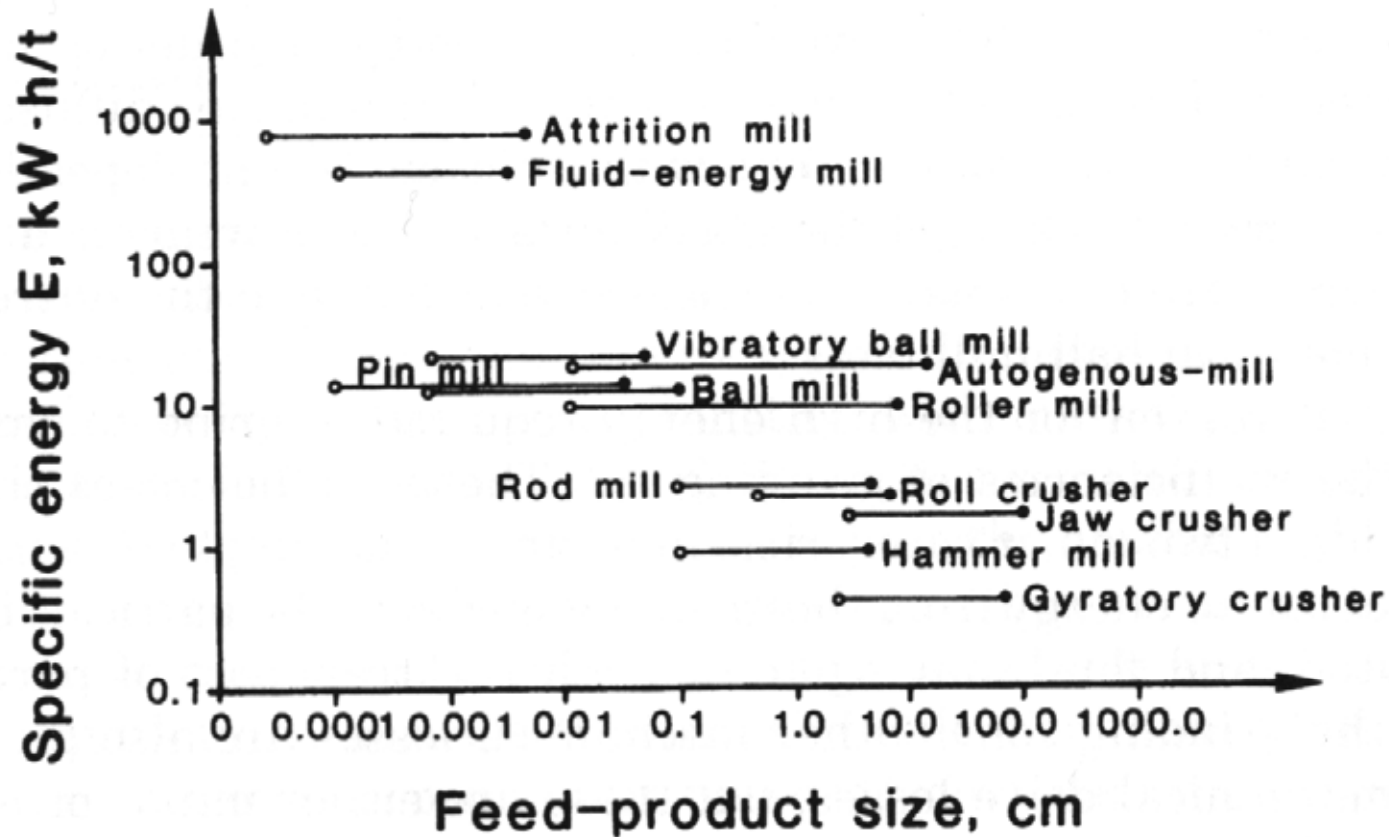


FIGURE 4.3 Average energy required for size-reduction equipment, ○ is typical product size, ● is typical feed size.

Energy distribution during milling

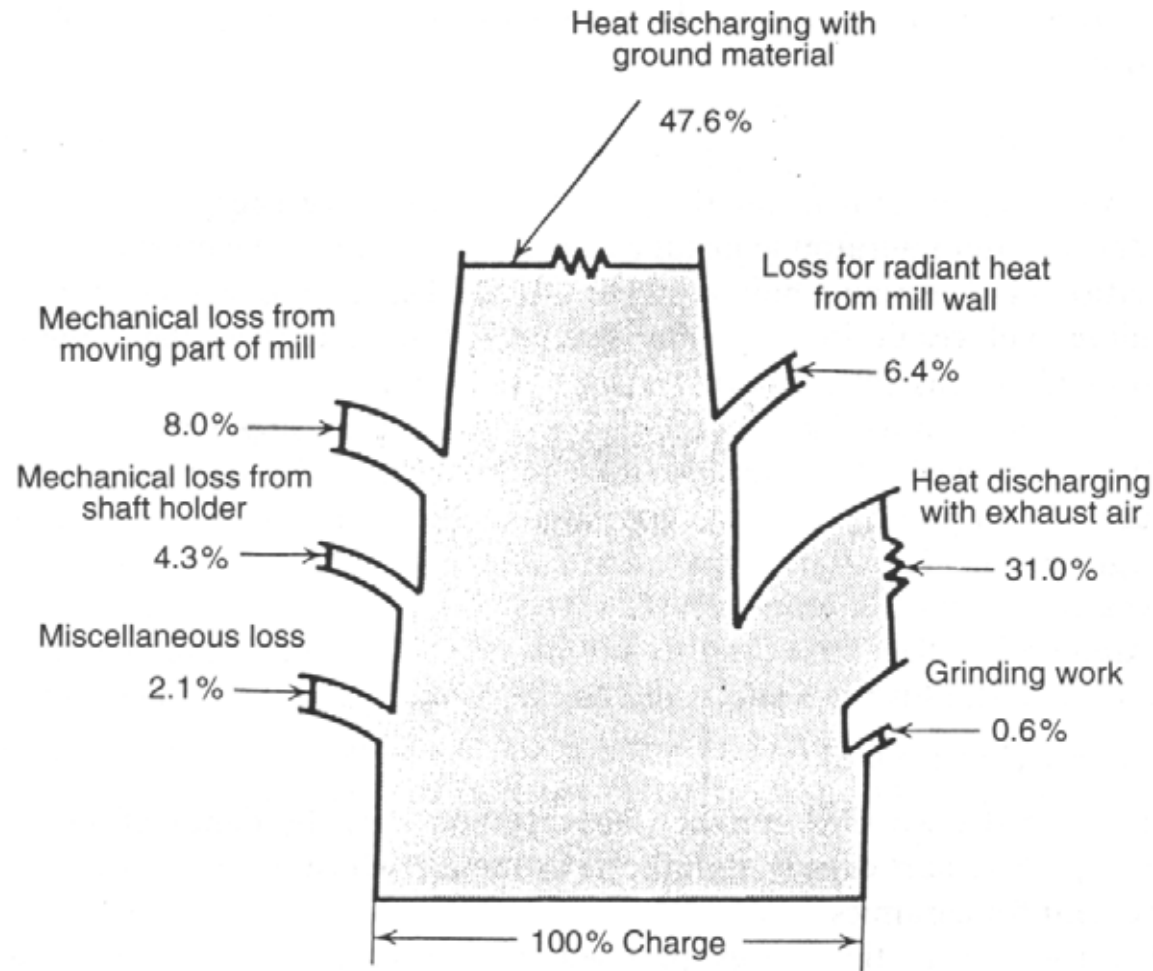


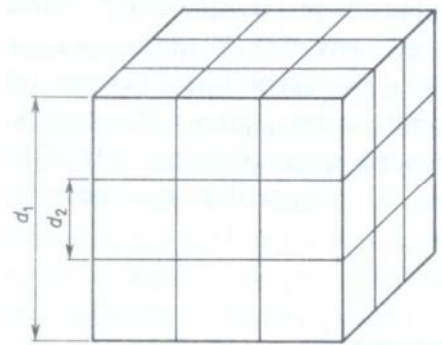
Figure 4.7 Heat balance of grinding by a vibratory ball mill. (From Y. Arai and T. Yasue, *Mater. Tech.*, 2, 43 (1984).)

Theoretical calculations of energy required for grinding

The energy, E , required to grind material into a smaller particle size, L , from size, L_0 , can be described by [6]:

$$E = - \int_{L_0}^L \frac{C}{L^n} dL \quad (4.1)$$

where C is a constant. This equation has an exponent, n , which is given by the following “laws” [7]:



Ritenger's model

n	“laws”
1	Kick's
2	Ritenger's
1.5	Bond's

$$W = c_2 \left(\frac{\sigma^2}{2E} \log v \right)$$

$$W = c_1 \left(\frac{1}{d_2} - \frac{1}{d_1} \right)$$

$$W = 10W_i \left(\frac{1}{\sqrt{d_2}} - \frac{1}{\sqrt{d_1}} \right)$$

Beke $\rightarrow W = C_4 \left(\frac{1}{d_2^{n_2}} - \frac{1}{d_1^{n_1}} \right)$

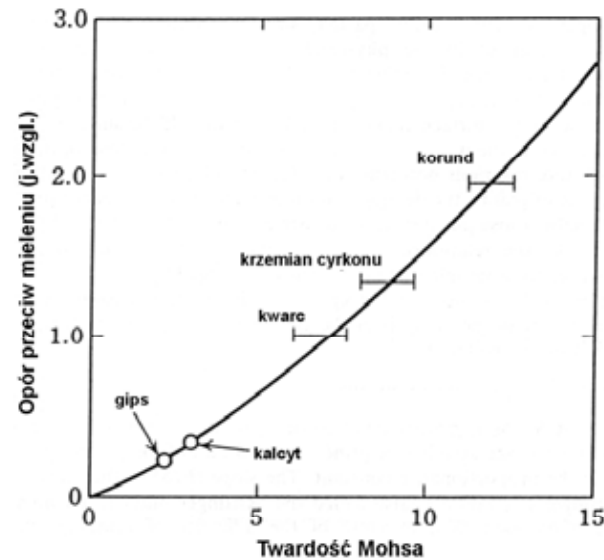
Grinding Energy from Bond

Consider

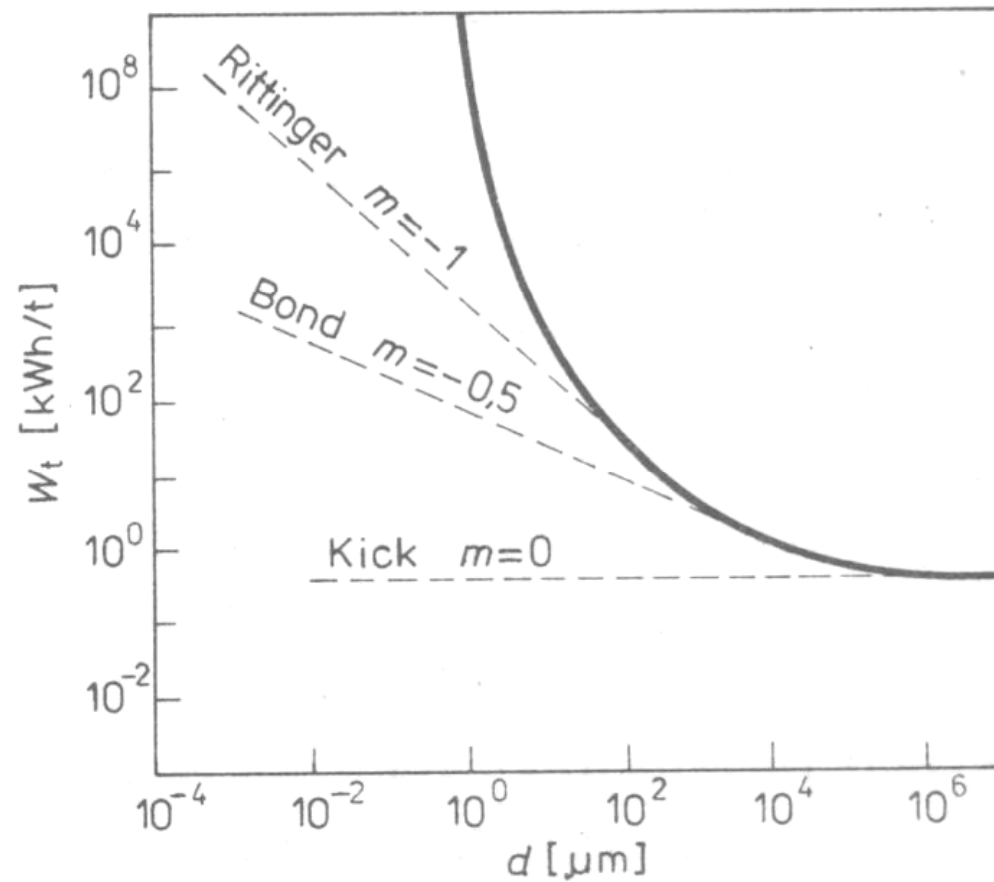
the particle size defined as d_{80} (μm), i.e. when 80% of the particles will pass through a sieve of aperture size d_{80} . The grinding energy E_g required for a grinding operation is

$$E_g = E_i(1 - 1/\sqrt{r})\sqrt{(100/d_{80})} \quad (\text{kWh t}^{-1}) \quad (4.3)$$

where r is the grinding ratio (the ratio of initial size to final size) and E_i is a characteristic coefficient called the 'work coefficient', which is the work (kWh t^{-1}) required for grinding from infinite size to $100\mu\text{m}$. E_i is also a measure of the difficulty of grinding and depends to some extent on both the mechanism of grinding and the design of the grinding machine. Some examples of E_i values that have been quoted are 56.70 for diamond, 43.56 for graphite, 13.57 for quartz, 12.74 for calcite, 9.92 for phosphate rock and 6.73 for gypsum. For all these materials, except graphite, the E_i values rank in the same order as the corresponding Mohs hardness values.



Grinding energy vs. product particle size



Comminution Efficiency

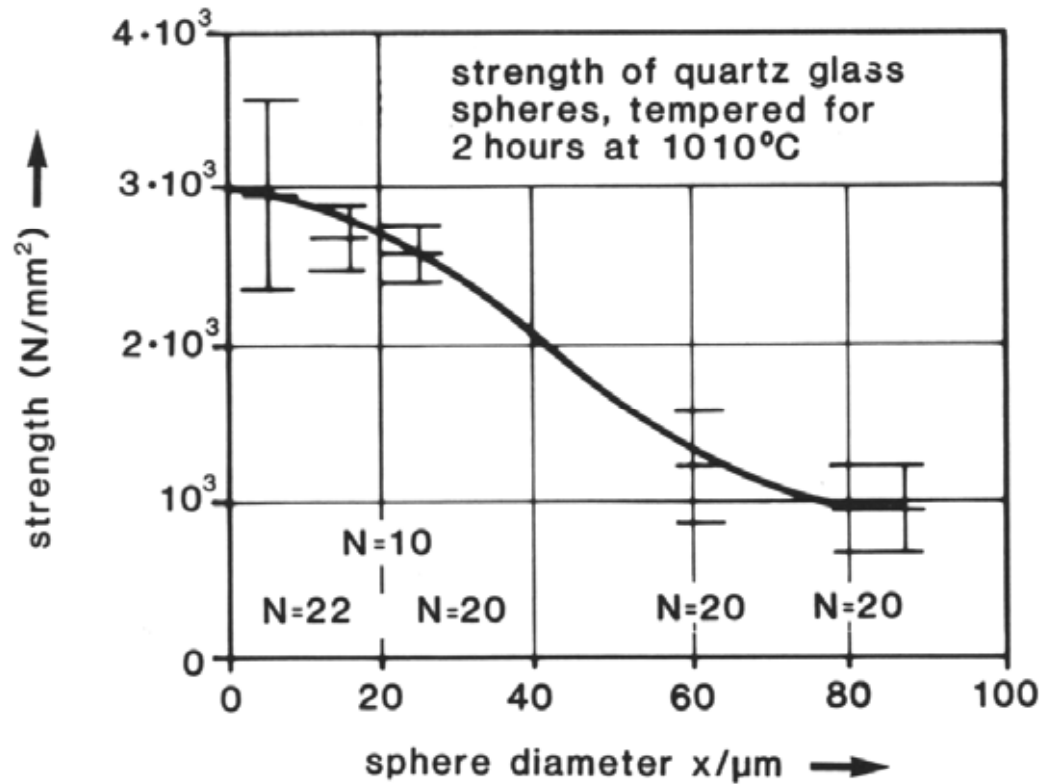


FIGURE 4.4 Strength of glass spheres. Taken from Leschonski [8].

$$K_I = \sigma \sqrt{\Pi a}$$

Stress intensity factor as a function of strength and flaw size

Agglomeration processes limit grinding.

Particle size distribution vs. grinding time

A reduction of grain sizes during grinding is accompanied by decreasing of a width of the grain size distribution with grinding time.

For ball mills, Beke has proposed:

$$n \approx f\left(\frac{t}{Dd^p}\right)$$

where n is an exponent in the Rossin-Rammler equation, D – mill chamber diameter, d - average diameter of grinding media, $p \sim 6$.

Tanaka's Equation

$$S = S_{\infty}(1 - e^{-KE})$$

This equation shows that the change in surface area during grinding is an exponential function of the energy E . Here, K is the grinding coefficient, which is dependent on the nature of the material being ground and on the conditions of grinding. As $S \rightarrow S_{\infty}$ the effect of continuing to add energy by grinding becomes less. The aggregation of particles due to van der Waals or electrostatic forces and the relaxation of stresses by lattice distortion of the surface are possible causes of the existence of S_{∞} .

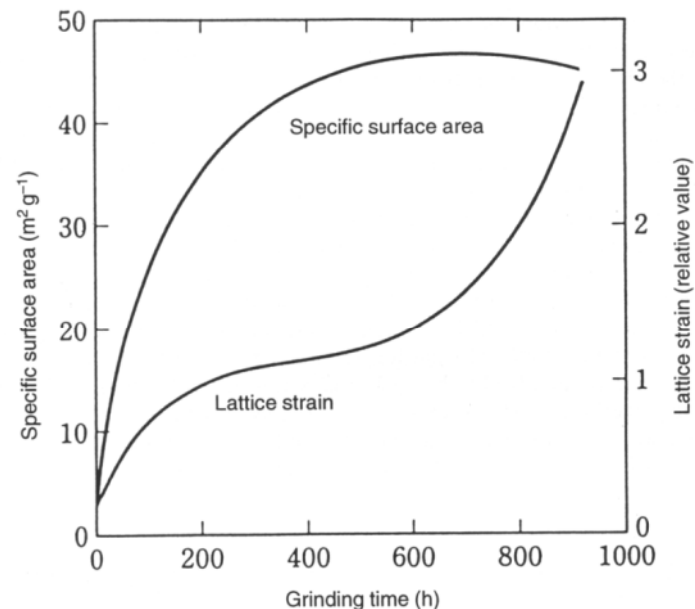


Figure 4.11 Changes in specific surface area S and lattice strain ϵ of ground dolomite with grinding time t . (From Y. Arai and T. Yasue, *J. Ind. Chem. Jpn.*, **72**, 1980 (1969).)

Effect of environment on grinding

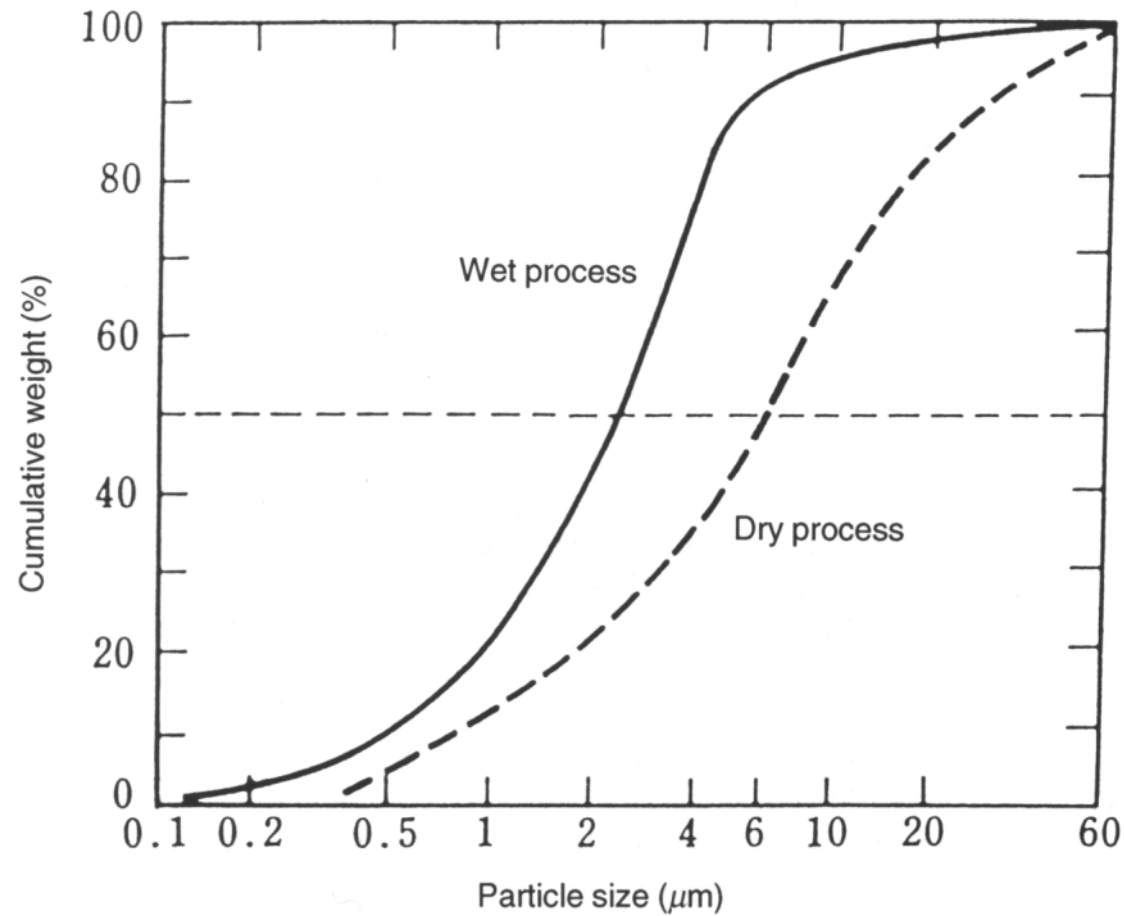


Figure 4.12 Size distribution of α -alumina powder. (From Y. Arai, *Materials Chemistry of Ceramics*, 2nd edn, Dainihon-Tosho, p. 192 (1980).)

Classification of Ceramic Powders

TABLE 4.2 Classification Equipment

Classification	Size range
Wet	
Screens	1 m–44 μm
Sedimentation Classifiers	1 mm–10 μm
Hydrocyclones	500 μm –0.1 μm
Elbow Classifier	100 μm –0.1 μm
Centrifuge	50 μm –0.1 μm
Dry	
Screens	1 m–44 μm
Expansion chamber	100 μm –10 μm
Air Classifier	1000 μm –0.1 μm
Gas Cyclone	500 μm –0.1 μm

Dry Classification Equipment

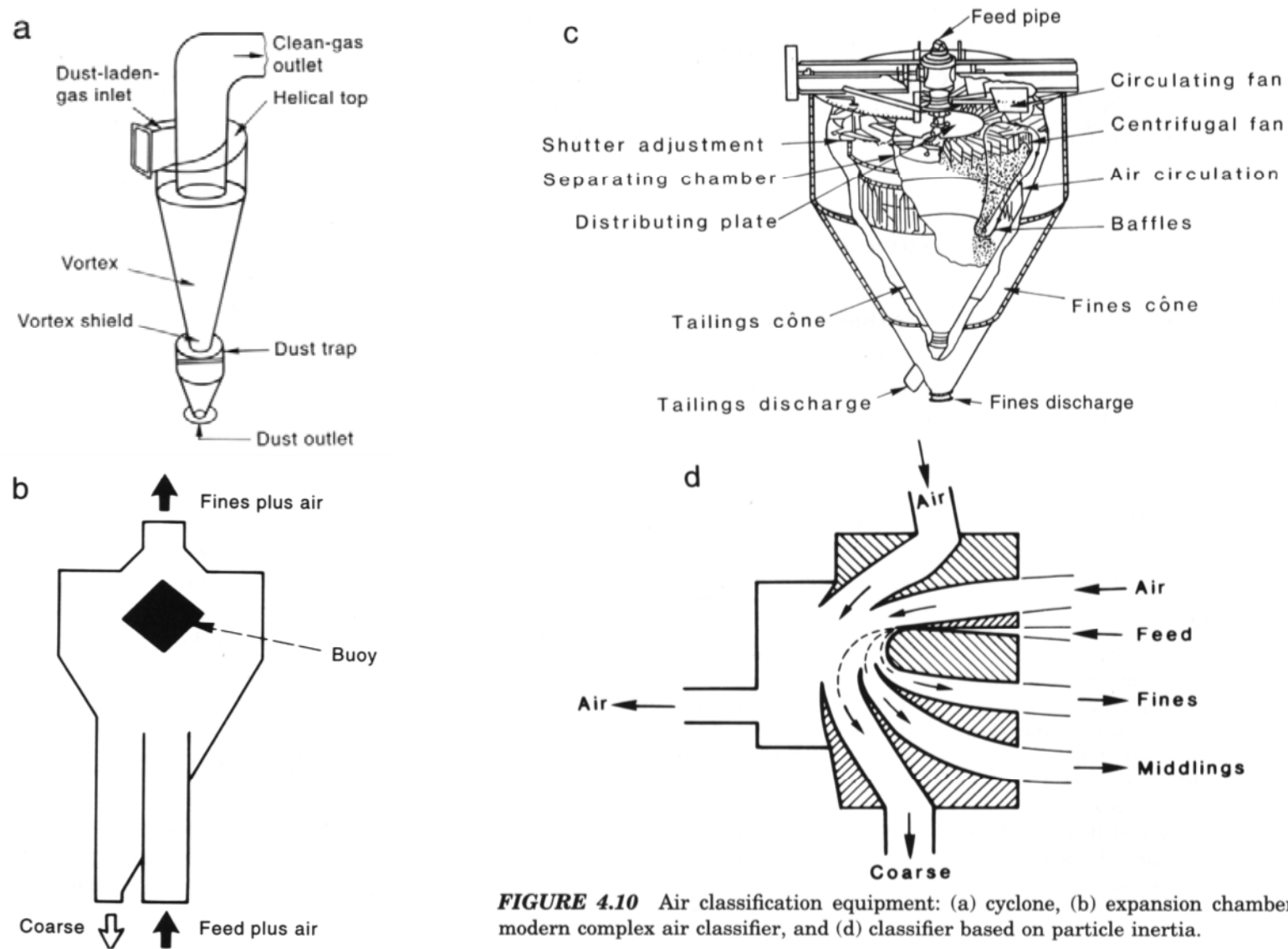


FIGURE 4.10 Air classification equipment: (a) cyclone, (b) expansion chamber, (c) modern complex air classifier, and (d) classifier based on particle inertia.

Wet Classification Equipment

Wet classification is performed by filtration, settling, centrifugation, and hydrocyclones. When operated in conjunction with grinding equipment, the wet classification equipment must operate continuously and give a pumpable fluid. This is often accomplished in practice with hydrocyclones because the other methods are unsuitable (e.g., settlers and centrifuges are used for dilute suspensions, filters and screens produce a nonpumpable cake.)

Thank you for your kind attention



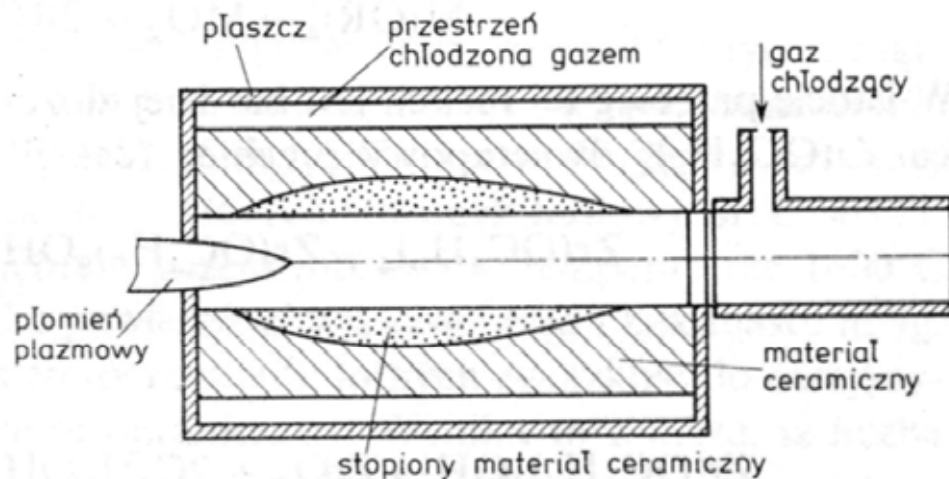
Wytrącanie z fazy gazowej – metoda PVD

Parowanie i kondensacja

Sposoby ogrzewania:

Piec z łukiem o dużej gęstości prądu (stałego) – ok. 7000°C

Odśrodkowy piec z ciekłymi ściankami



Proszki złożone z cząstek kulistych o rozmiarach 5-200 nm i powierzchni właściwej 10-150 m²/g

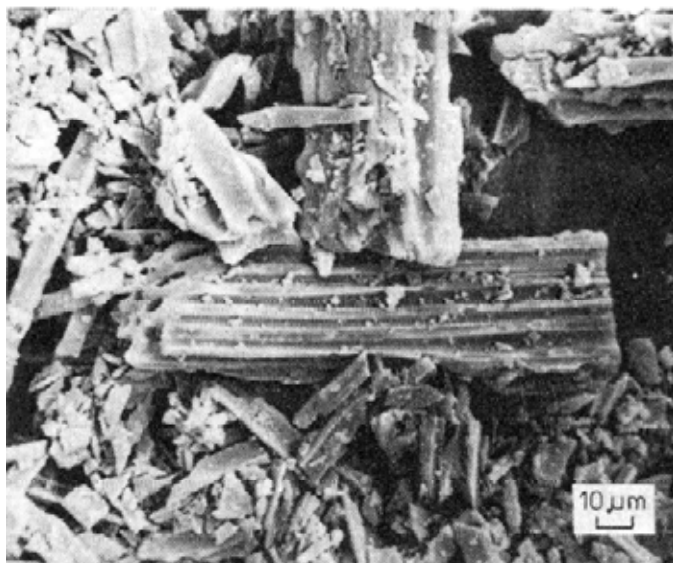
Proszki: tlenków (np.: SiO₂, Al₂O₃, Fe₂O₃, ThO₂, MoO₃, ZrO₂ i inne) oraz węglików (np.: ThC, TiC, B₄C, UC, TaC, SiC).

Plazmowy piec osrodkowy z cieklymi sciankami

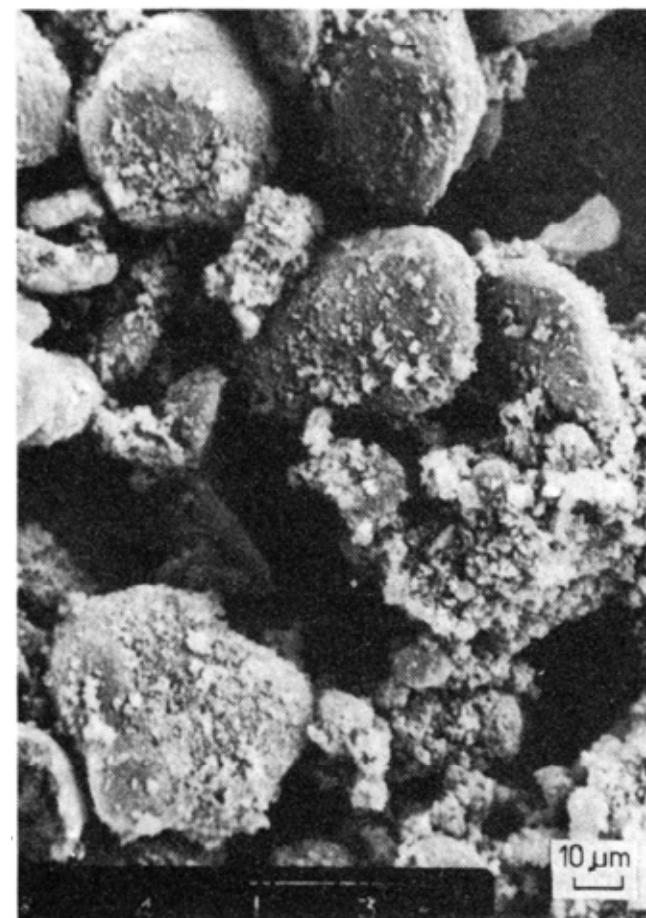
Samorozwijająca się synteza wysokotemperaturowa SHS

Związek	Reakcja	Ciśnienie podczas syntezy [MPa]
TiB ₂	Ti + B ₂ O ₃ + 3Mg = TiB ₂ + 3MgO*	0,1
	Ti + 2B = TiB ₂	1,0
	2TiO ₂ + B ₄ C + 3C = 2TiB ₂ + 4CO	0,1
B ₄ C	2B ₂ O ₃ + 6Mg + C = B ₄ C + 6MgO*	0,1-10
SiC	Si + C = SiC	0,1
TiC	Ti + C = TiC	0,1
AlN	2Al + N ₂ = 2AlN	10
BN	B ₂ O ₃ + 3Mg + N ₂ = 2BN + 3MgO*	12
Si ₃ N ₄	3Si + 2N ₂ = Si ₃ N ₄	10

* Produkty reakcji usuwane przez wmywanie chemiczne.



Morfologia proszku SiC otrzymanego w reakcji węgla drzewnego z krzemem



Morfologia proszku SiC otrzymanego w reakcji sadzy z krzemem

Krystalizacja hydrotermalna

- Wytwarzanie hydrotermalne proszków ceramicznych polega na ogrzewaniu substratów w wodzie w podwyższonych temperaturach (do 300°C) i przy podwyższonym ciśnieniu (do 100MPa).
- Substratami mogą być: sole metali, tlenki, wodorotlenki lub proszki metali w postaci roztworów lub zawiesin.
- Zarodkowanie i wzrost w warunkach hydrotermalnych daje submikronowe lub nanometryczne cząstki tlenków, związków nietlenkowych i metali o kontrolowanym kształcie i rozmiarze.

Czynniki wpływające na rozmiar i kształt cząstek proszków:

- ✓ skład środowiska krystalizacji
 - mineralizatory,
 - pH,
- ✓ temperatura,
- ✓ ciśnienie
- ✓ czas.

Proces hydrotermalny wykorzystywany jest również w przemyśle ceramicznym do wytwarzania monokryształów kwarcu, do poprawy właściwości kompozycji cementów hydraulicznych i do syntezy skaleni.