

Ceramic Processing

2 Powder Preparation



Introduction

□ Traditional ceramics

- Composition very rough – in a wide range and not precisely controlled
- Often a mixture of different raw materials
- Complex densification process that often involves reactions
- Raw material often mined without much processing

<https://en.wikipedia.org/wiki/Porcelain>
<http://mfg.regionaldirectory.us/pottery/>
<http://www.linea-aqua.com/shop/LineaAqua-Caraway-One-Piece-Siphonic-Toilet-28-x-15-x-30-Luxury-White-Porcelain-Toilet-with-S-Trap-and-Soft-Closing-Seat-pr-17486.html>



□ Advanced ceramics

- Precise **composition** control – much higher purity powder (>~98%)
- Precise **physical characteristics** control
 - Particle size and grain size
 - Degree of agglomeration
- Raw materials often highly refined chemical or ceramics

<http://www.sqp.co.jp/e/seihin/guide/4/>
<http://crashmax.com/tools-and-supplies/dent-fix-spitznagel/dent-fix-tungsten-carbide-drill-bit-for-boron-3-edge-special-coating.html>
http://skyknife.en.ec21.com/Bulletproof_Boron_Carbide_Plate_B4C-685040_6044908.html



Reed (1995), p. 35-49

Raw Materials for Ceramic Processing

❑ Ore/crude material

- Mined directly from natural deposits with minimal processing
- Purity: variable; Particle size: variable
- Example: crude bauxite: hydrous alumina mineral containing mostly $\text{Al}(\text{OH})_3$, $\text{AlO}(\text{OH})$, and clays

❑ Industrial minerals

- Minerals processed (beneficiated, i.e., often crushing/grinding then separation in some way) to have major impurities removed for improved purity and physical consistency
- Purity: ~80-95%; Particle size: ~1-100 μm
- Examples: Kaolin (primarily $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) for whitewares, talc ($\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$) for ceramic tile and porcelain; feldspar ($\text{KAlSi}_3\text{O}_8 - \text{NaAlSi}_3\text{O}_8 - \text{CaAl}_2\text{Si}_2\text{O}_8$) for fluxes in whitewares and glazes; quartz (SiO_2) for white ware, refractories, and glaze; zircon (ZrSiO_3) for refractories

❑ Industrial inorganic chemical/ceramics

- Chemicals/ceramics that have gone through significant chemical processing and/or refinement for significantly improved chemical purity and/or consistency
- Purity: ~98-99.5%; Particle size: ~0.2-10 μm
- Examples: Calcined Al_2O_3 , calcined MgO , TiO_2 , BaTiO_3 , SiC

❑ Special inorganic chemicals/ceramics

- Specially processed chemical for high purity and/or physical characteristics
- Purity: $\geq 99.9\%$; Particle size: $< 0.1 \mu\text{m}$
- Examples: Nano Y_2O_3 -stabilized ZrO_2

❑ Other non-powder form special chemicals (liquids and gas)

- Examples: SiH_4 , TiCl_4 , etc.

Reed (1995), p. 35-49 

Methods of Powder Preparation

□ Common methods

- Comminution - mechanical size reduction
- Mechanochemical synthesis or mechanical alloying
- Chemical synthesis
 - Solid state synthesis
 - Liquid state synthesis
 - Precipitation
 - Solvent removal (drying)
 - Gel routes
 - Vapor-state synthesis
- Other (e.g., granulation)

□ Considerations

- Industrial selection of powder synthesis depend primarily on cost, local situation, and requirements from specific applications
- Most ceramics (except for situations such as abrasive powders, battery electrodes, catalysts, fillers) are used in bulk form, meaning powder is only an intermediate

Reed (1995), p. 35-49

Rahaman (2003), p. 49-118



Powder Preparation by Mechanical Methods

❑ Comminution

Using mechanical force, which involves crushing, grinding, and milling to produce powders with small particle size from larger particles and even gravels.

❑ Coarse size reduction

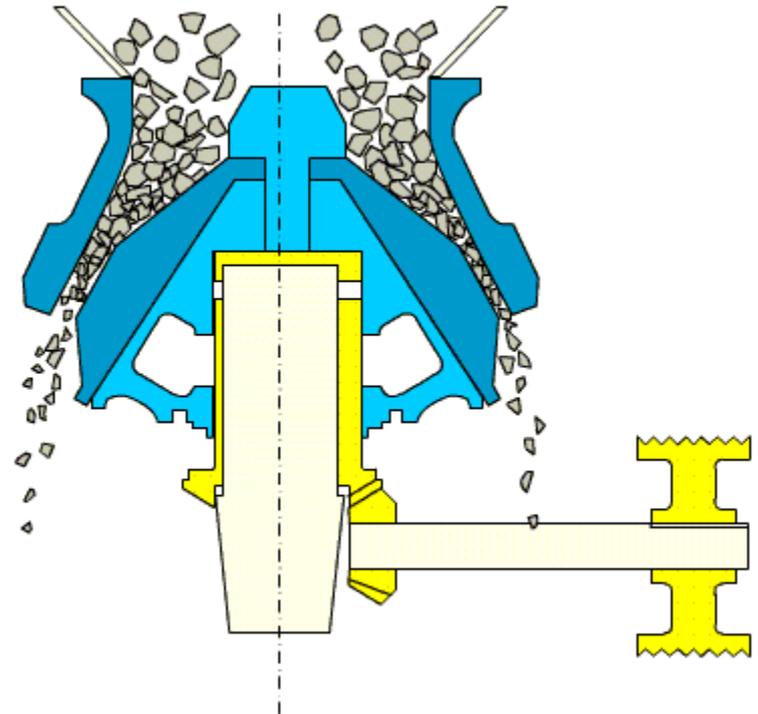
- Reducing particle size to **~10 - 0.1 mm** range
- Using equipment such as jaw, or gyratory, or cone crushers

❑ Fine size reduction

- Milling to **~10 - 0.5 μm** range
- Using various milling techniques

Reed (1995), p. 35-49

Rahaman (2003), p. 49-118



<http://www.aggdesigns.com/Cone-Crusher-info.htm>

High Compression Roller Mill & Jet Mill

❑ High compression roller mill Rahaman (2003), p. 54-55

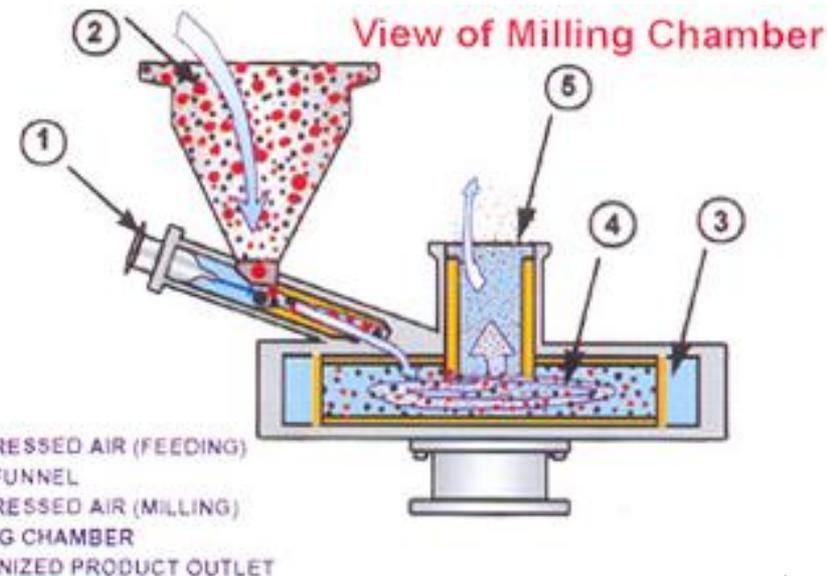
- Compress raw material between two rolls with high contact pressure of $\sim 100\text{-}300$ MPa
- Advantages
 - Good energy utilization
 - Low wear
- Size range reached: $\sim 10\text{-}100$ μm



<http://www.koepfern-international.com/products/comminution/cement/process-technology/>

❑ Jet mill

- High-speed gas flow carrying coarse particles that cause particles to collide with each other and/or the wall
- Advantages
 - Rapid process for producing particles down in 1 μm
 - Can have low contamination
- Size range reached: $\sim 1\text{-}20$ μm



http://www.sreenex.com/html/bulk_airjetmill.htm

Ball Mill

❑ Ball mill

- Use of grinding media (usually balls or short cylinders) to produce compression, impact, and shear that reduce size

❑ Common features

- Size range reached: $\sim 0.5\text{-}10\ \mu\text{m}$
- Running (or rotation) speed
 - Those running at low speed has large balls that depend on potential energy
 - Those running at high speed has small balls that depend on kinetic energy
- Grinding media material
 - As high density as possible: ZrO_2 , WC, steel
- Ball size
 - Smaller balls lead to more collisions/contacts and higher grinding rate
 - Too small balls inefficient due to low mechanical impact force
- Particle size
 - Decreasing particle size lead to decreased rate of grinding



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

https://www.google.com/search?q=grinding+media&biw=985&bih=494&source=lnms&tbn=isch&sa=X&ved=0CAcQ_AUoAmoVChMiiLLegPHLxwIVQ_0eCh0h_wSZ#imgsrc=NSMqBFHAN_d4EM%3A

❑ Disadvantages

- Contamination
- Wear of grinding media

Rahaman (2003), p. 55-61

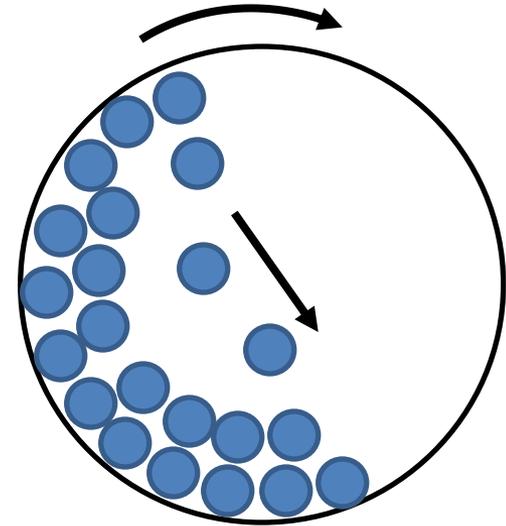
Tumbling Ball Mill

❑ Tumbling ball mill

Low speed rotation of cylinder container that holds grinding media and powders, with the falling ball that cause impact and breakage of the powders

- Critical (rotation) speed is when centrifuge force balance gravity $\frac{(g/a)^{1/2}}{2\pi}$ in unit of Hz
- Typically operated at 75% of critical speed
- Dry milling loading level
 - Media (ball) ~50 vol.% of container
 - Powder ~25 vol.%, i.e., half of ball volume
- Wet milling loading level
 - Media (ball) ~50 vol.% of container
 - Slurry ~40 vol.% of container with slurry solid loading level ~25-40 wt.%

Rahaman (2003), p. 55-61



<http://www.toreuse.com/category/mining-and-geology/equipment-for-underground-mines-open-cast-mines-and-metal-ore-mines/ball-mills/>

http://www.detroitprocessmachinery.com/inventory/Jar_Mills_Pebble_Mills_Ball_Mills_Vibratory_Mills/DPM-291-U.S._Stoneware_Norton_print.html

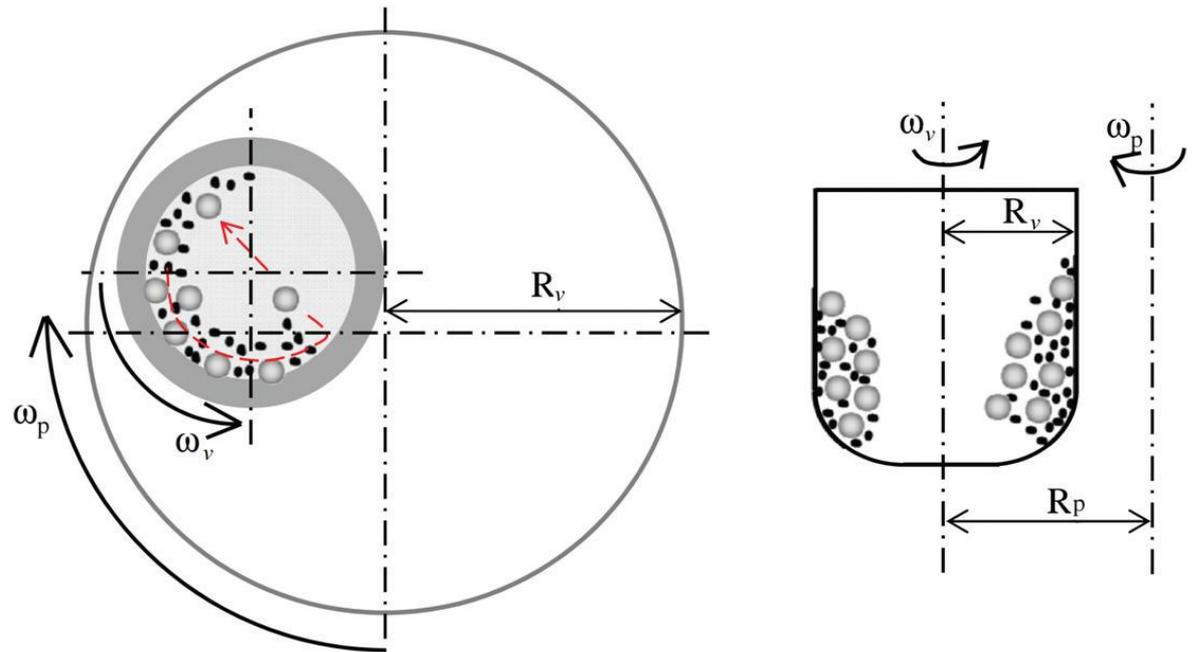
Planetary Ball Mill

□ Planetary ball mill

- Jar holding grinding media and ball and move within a plane like a planet with two types of rotations:
 - one around the jar center axis
 - the other around a common orbit like a planet around the sun
- Lab scale only
- Symmetrical for jar placement



http://ttdspb.com/m_planeta/mpp1-1.html



Majid Abdellahia, Maryam Bahmanpour, Materials Research. 2014; 17(3): 781-791
http://www.scielo.br/pdf/mr/v17n3/aop_matres_255813.pdf

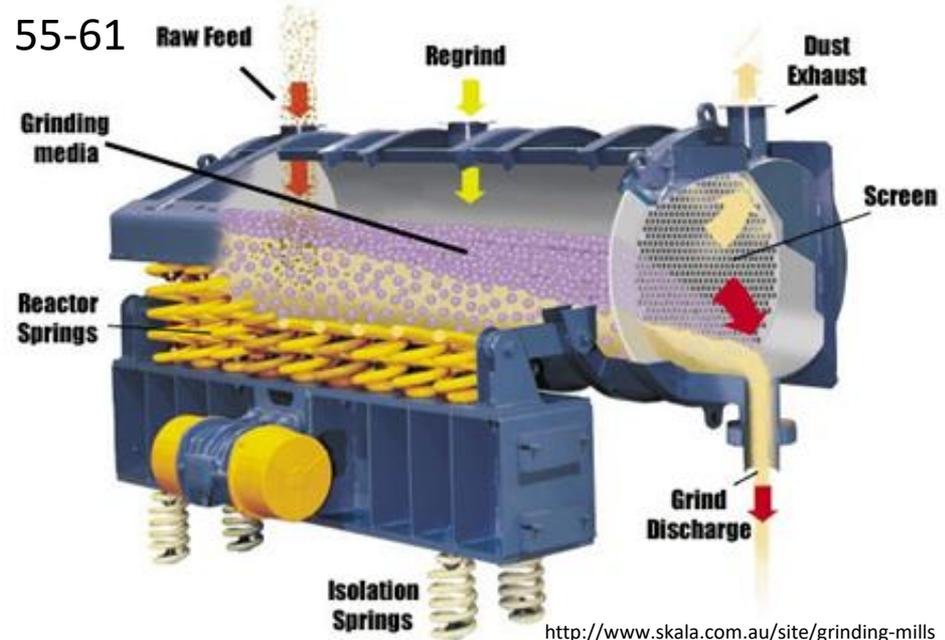
Other Ball Milling Techniques

❑ Vibration ball mill

Rahaman (2003), p. 55-61

Drum almost filled with grinding media and powders and vibrate (not large rotation) at ~10-20 Hz in 3D

- Grinding media usually cylinder shape and occupy 90 vol.%
- Provides higher impact energy compared with tumbling ball mill



❑ Agitated ball mill (also called attrition mill or stirred media mill)

Grinding media and powders are stirred vigorously

- Usually wet milling
- Smaller grinding media of 0.2-10 mm diameter
- Even higher energy efficiency than vibration ball mill



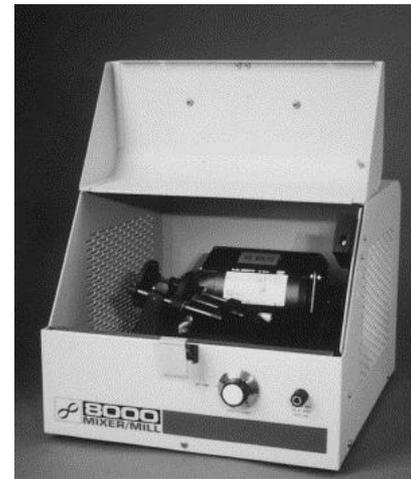
<http://www.machineryautomation.com.au/applications/processing/blending/grinding/#.VdxtRE3H92M>

Mechanochemical Synthesis (1)

□ Description

- Use high-energy ball milling that enhances chemical reactivity of powders for synthesizing compounds of powder form
- Other names:
 - Mechanical alloying
 - Mechanical driven synthesis
- Advantages
 - Relative simple and fast process
 - Ease with adjustment of composition/stoichiometry
- Disadvantages
 - Impurity; Long process (for some); Hard to control (for some); Low productivity
 - Formation mechanism often not very clear
- Equipment used: Spex mill, Planetary ball mill
- Reaction may be self-propagating and very fast when using elements
 - How to get ZrB_2 by mechanical alloying?

Spex Mill



C. Suryanarayana, Progress in Materials Science, Vol 46, 2001, pp.1-184
<http://www.sciencedirect.com/science/article/pii/S0079642599000109>

Rahaman (2003), p. 61-62

Review of Basic Chemistry - Class Example

- To make ZrB_2 , if starting materials are Zr metal powder and B powder, what is the chemical reaction?
 - Balance of mass or species (atoms, ions, molecules, and also electrical charges)



- To make 1 mole of ZrB_2 , assuming no loss in handling:
How much Zr metal powder and B powder (in grams) will be needed?
What is the final product weight? Knowing:

Zr: Atomic number: $Z = 40$, Atomic mass: 91.224 amu (or g/mol)

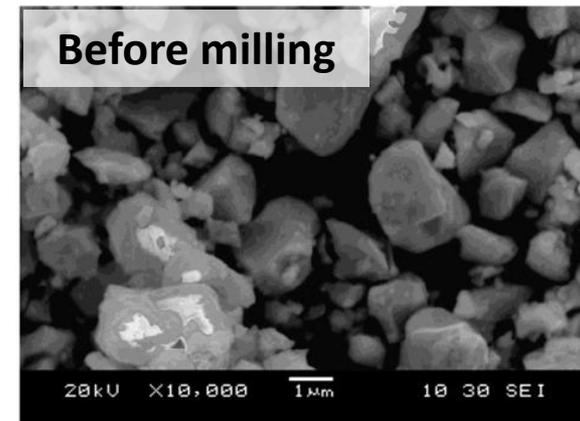
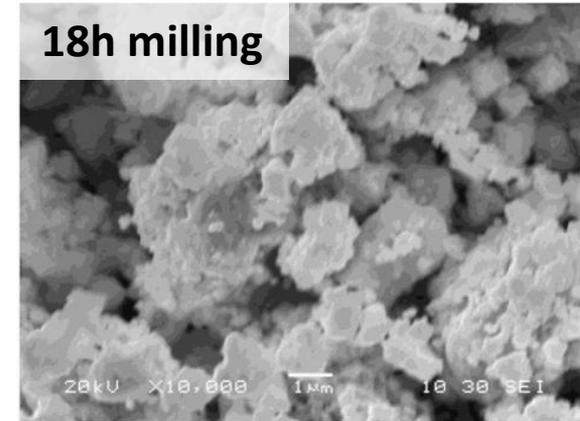
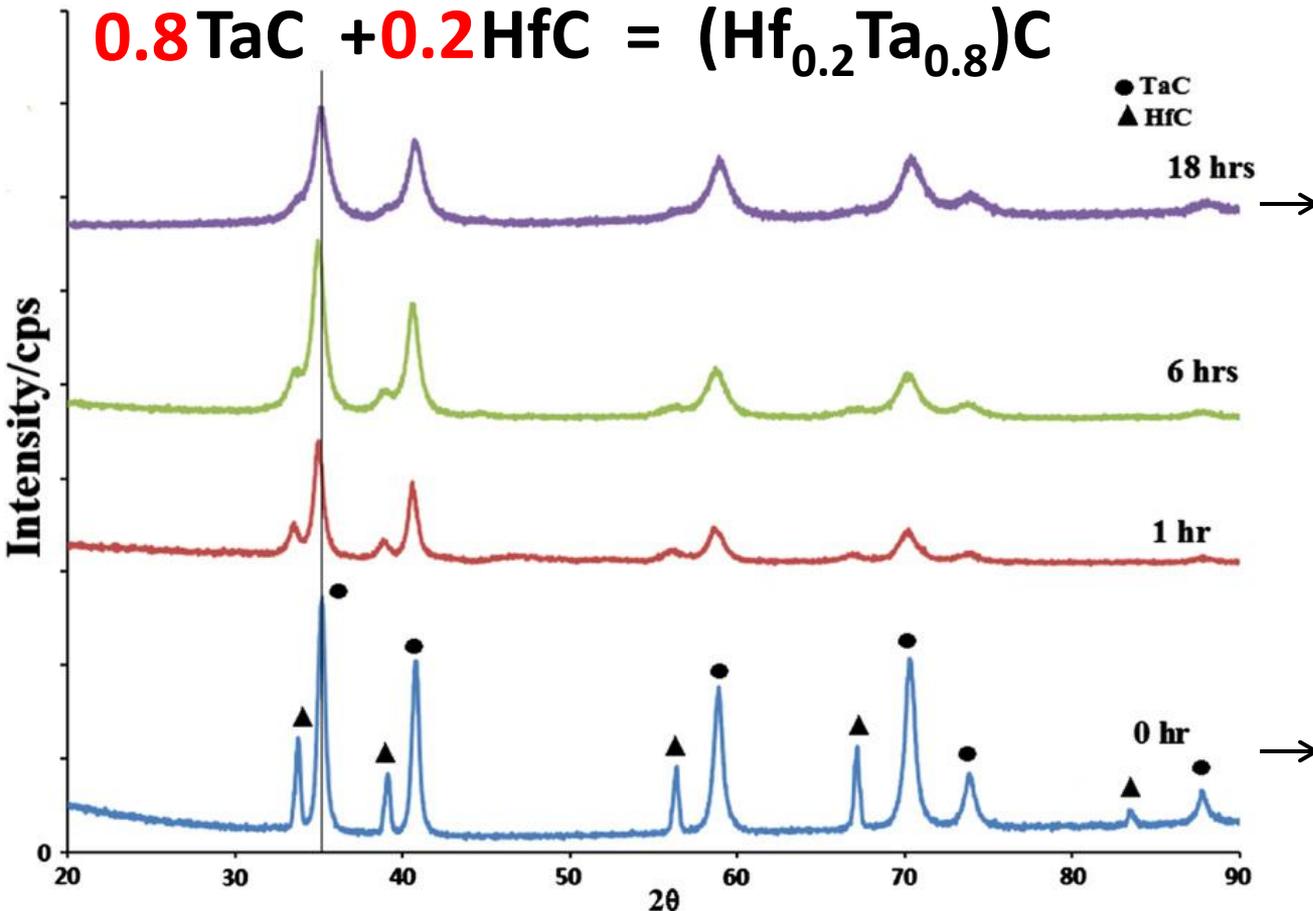
B: Atomic number: $Z = 5$, Atomic mass: 10.811 amu (or g/mol)

	Zr	+	2 B	=	ZrB₂
Molar quantity	1 mol		2 mol		1 mol
Mass (or weight)	91.2 g		10.8 g × 2 = 21.6 g		112.8 g
Check mass balance	91.2 + 10.8 × 2 = 112.8 g				

Mechanochemical Synthesis (2)

□ Mechanical alloying for synthesis of $(\text{Hf}_{0.2}\text{Ta}_{0.8})\text{C}$?

Spex milled in He-atmosphere from 0.2-2 μm commercial TaC and HfC powder mixture



Osama Gaballa et al., Int. Journal of Refractory Metals and Hard Materials 41 (2013) 293–299

Powder Synthesis via Solid-State Reactions (SSR)

Rahaman (2003), p. 63-77

□ Features

- Simple and most widely used
- Foundation for many other synthesis methods (e.g., sol-gel, precipitation)

□ Decomposition

- Some ceramics powders are produced via simple decomposition reaction
- Often produces porous solid products while giving off gas(es)
- E.g., heating MgCO_3 to produce MgO at high temperature? $\text{MgCO}_3 = \text{MgO} + \text{CO}_2$
- Can generate very fine nano particles, depending on reaction condition

□ Reaction between different solids

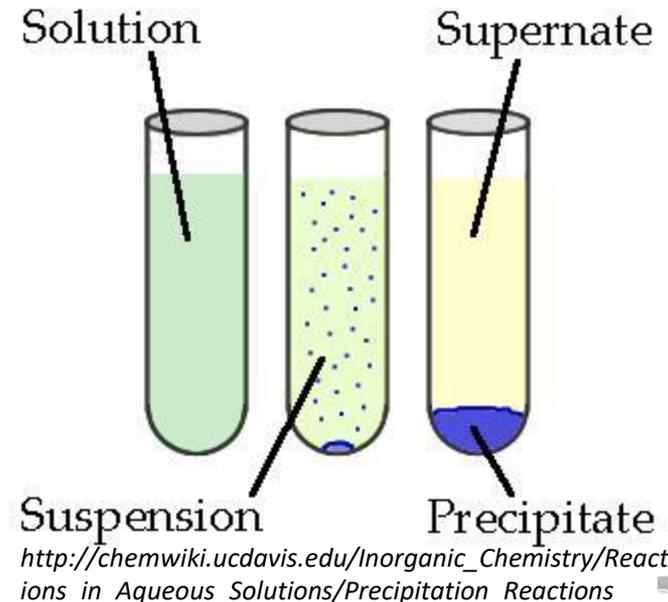
- Reaction between different solids to form another solid phase
- Examples for typical SSR:
 - Reaction between La_2O_3 and Cr_2O_3 to form LaCrO_3 : $\text{La}_2\text{O}_3 + \text{Cr}_2\text{O}_3 = 2\text{LaCrO}_3$
 - Reaction between Li_2TiO_3 and TiO to form LiTiO_2 : $\text{Li}_2\text{TiO}_3 + \text{TiO} = 2\text{LiTiO}_2$
- Examples involving reduction-type SSR
 - Reaction involve reduction (by carbon, boron, or other phases)
 - Produce SiC as well as CO from SiO_2 and C ? $\text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO}$



Powder Synthesis via Precipitation from Solutions

□ Precipitation

- Production of ceramic powder and/or precursors (e.g., oxylates) by precipitation from uniform solution via certain reactions
- Homogeneous nucleation in most cases
- **Precipitation from dissolved metal salts**
 - Example: $\text{NiSO}_4 + 4\text{FeSO}_4 + 5(\text{NH}_4)_2\text{C}_2\text{O}_4 = 5\text{Ni}_{0.2}\text{Fe}_{0.8}\text{C}_2\text{O}_4 \downarrow + 5(\text{NH}_4)_2\text{SO}_4$
- **Precipitation from organometallic compounds (e.g., metal alkoxides)**
 - Example: $\text{Ti}(\text{OC}_2\text{H}_5)_4 + (2+x)\text{H}_2\text{O} = \text{TiO}_2 \cdot x\text{H}_2\text{O} \downarrow + 4\text{C}_2\text{H}_5\text{OH}$
- Factors that influence nucleation & growth, which then determine precipitate size and morphology include
 - Reactants and solvents type
 - Reaction temperature and time (aging)
 - Other: pH, concentration, etc.
- Used extensively for lab scale synthesis of fine especially nano particles



Rahaman (2003), p. 77-100

Powder Preparation via Evaporation of Solvents

□ Evaporation of solvents Rahaman (2003), p. 100-107

- Fast removal of solvent from solution that creates supersaturation and produces powder (precursors)

- **Spray drying** – removal of solvents alone

- Can use solution or suspension Aude Munin and Florence Edwards-Lévy, *Pharmaceutics* 2011, 3, 793-829
- Give ~10 µm agglomerates
- May need subsequent heat treatments

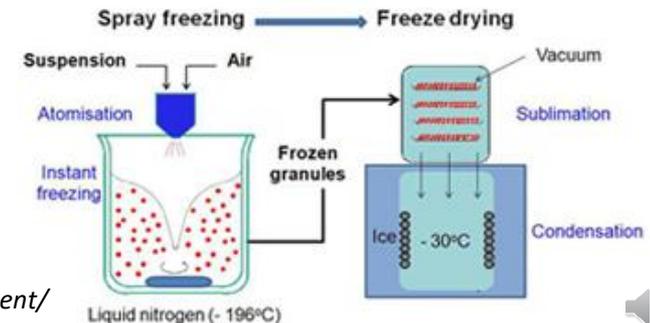
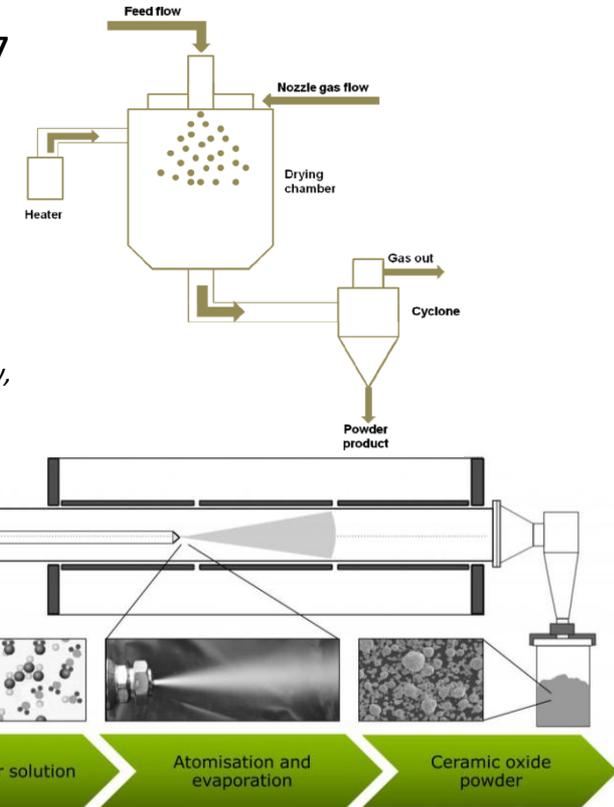
- **Spray pyrolysis** – removal of solvents followed by thermal pyrolysis of precipitated salts

- Direct production of fine powders <http://www.cerpotech.com/node/27>

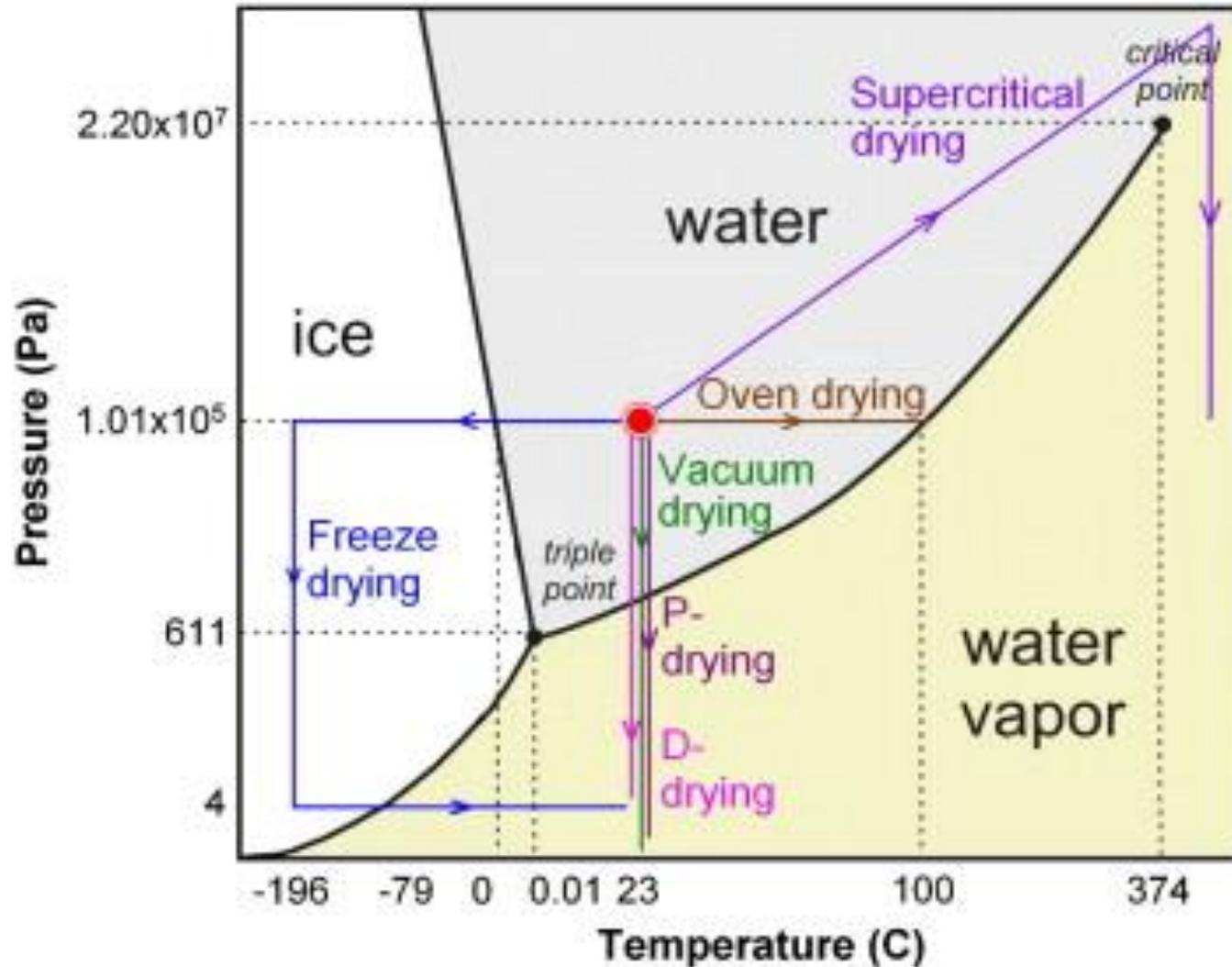
- **Freeze drying** – removal of solvents at below freezing temperature by mixing with cold liquid (e.g., liquid N₂) and followed with vacuum sublimation

- May need subsequent heat treatments

<http://powderpro.se/applications/material-research-and-development/>



Schemes of Solvent Removal



<http://freedryinc.com/page.php?id=30>

Powder Synthesis via Gel Route

□ Sol-gel process

Rahaman (2003), p. 107-110

Solution of metal alkoxides or other organometallics go through hydrolysis and condensation or other gelation reaction to form semi-solid 3D gel consisting of networked nano particles, which, often after thermal treatment, gives ceramic powders (mostly oxides)

□ Examples for additional methods

▪ Pechini method

Similar to sol-gel except that inorganic metal salts may be used with carboxylic acid (e.g., citric acid) and polyhydroxy alcohol (ethylene glycol) to complex it and form gel, which after heat treatments, to give metal oxides

▪ Glycine nitrate process (GNP)

Solution of metal nitrates and glycine is subject to intensive heating, which self-ignites to produce metal oxides



https://engineering.purdue.edu/H2Lab/Sodium_Borohydride/index.html

Vapor Phase Reactions

□ Gas-solid reaction

Rahaman (2003), p. 110-118

- Direct reaction between gas and solid
- Example: $V_2O_5 + 2H_2 = V_2O_3 + 2H_2O$

□ Gas-liquid reaction

- Direct reaction between gas and liquid
- Example: $3SiCl_4 + 4NH_3 = Si_3N_4 + 12HCl$

□ Gas phase reaction

- Reactants are all gas phase
- Examples:
 - $SiH_4 = Si + 2H_2$
 - $TiCl_{4(g)} + O_2 = TiO_{2(s)} + 2Cl_2$

Thermodynamics & Kinetics for Reactions

□ Thermodynamics

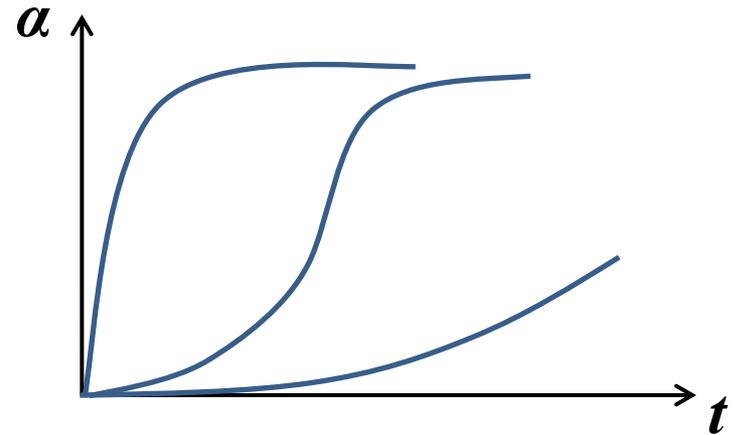
- Standard free energy change & equilibrium constant

$$\Delta G_R = \Delta G_R^0 + RT \ln K \quad K = \exp\left(-\frac{\Delta G_R^0}{RT}\right)$$

- Direction of reaction

□ Kinetics

- Extent of reaction $\alpha = ?$ and rate of reaction $r = ?$
- Kinetic curve: α vs. time
- Kinetic models
 - Nucleation-growth (different variations)
 - Geometric models
 - Diffusion controlled reaction models
 - Reaction order
- Reaction mechanism
 - Rate limiting step, intermediates, and sub-steps
- Impacts of processing factors (temperature, size, scale of mixing)
- Microstructure evolution



Safety Aspects

☐ Personal protective equipment (PPE)

- Gloves, lab coat, goggle, proper shoe, etc.
- Most powders/chemicals are hazardous: corrosive/caustic, reactive, poisonous (including carcinogenic)



<http://ehs.ucr.edu/laboratory/gloves.html>

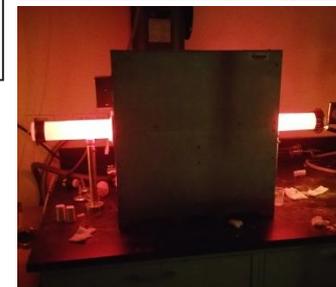
<http://www.dialysisworldnigeria.org/item.php?id=39>

<http://decorationbesto.tk/tag/safety-shoes-italy/>

<http://www.aliexpress.com/item/Anti-smoke-mask-splash-mask-acid-mask-sanding-dust-mask-safety-mask/1828476798.html>

☐ Engineering control

- Warning signs
- Chemical fume hood
- Use minimum quantity
- Special risks:
 - Hot surfaces: proper insulation
 - Gas: EXTREME care; secure cylinder; check for proper exhaust and leakage...
 - Liquid: consider the possibility of splash and have plan...
 - Pressure vessel: EXTREME care and barricade



<http://safe.engineering.asu.edu/safety-notice-hydrofluoric-acid-exposure>