Introduction to Advanced Powder Processing

by

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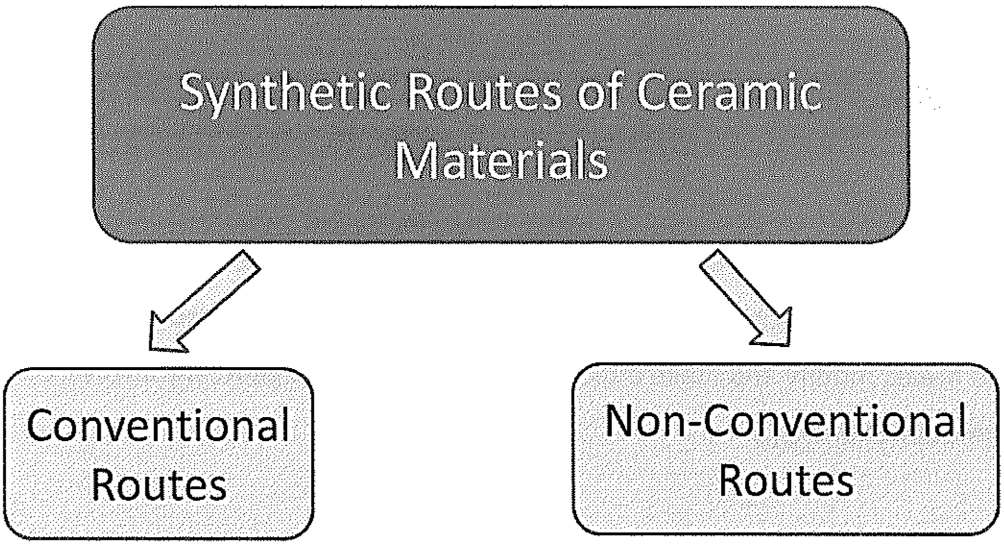
Tentative schedule

- Solid state reaction
  - Chemical reaction between solids
  - Decomposition
  - Reduction
- Liquid phase solution
  - Precipitation from solution
  - Co-Precipitation
  - Sol-Gel Processing
- Vapor phase reaction
  - Gas-solid reaction
  - Liquid-gas reaction
  - Gas-gas reaction



Synthetic Routes of Ceramic Materials

Conventional Routes

Non-Conventional Routes

- Solid state reaction
  - Chemical reaction between solids
  - Decomposition
  - Reduction

- Liquid phase solution
  - Precipitation from solution
  - Co-Precipitation
  - Sol-Gel Processing
- Vapor phase reaction
  - Gas-solid reaction
  - Liquid-gas reaction
  - Gas-gas reaction

Solid State Reactions

Lecture overview

Powder synthesis by solid-state reaction

- Introduction to conventional solid-state reaction routes
- Solid-state reaction rate
- Examples of ceramic powder synthesis by solid-state reaction
- Advantages and disadvantages of solid-state reaction for synthesis of ceramic powder

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Solid State Reactions

Solid-state reaction: Direct reaction of a mixture of non-volatile solid reactants in powder form to produce a solid product at high temperature (500-2000°C)

High temperatures are required to provide the significant amount of energy to overcome the lattice energy so a cation or anion can diffuse into a different site. To break, modify and make multiple bonds of inorganic generally involve a large amount of energy.

$$\text{A (solid)} + \text{B (solid)} \xrightarrow{\text{high temperature}} \text{C (solid)}$$

Solid State Reactions

A large variety of materials can be prepared using the solid-state reaction route:

- Mixed oxide ceramic powders
  - $NiO\ (s) + Al_2O_3\ (s) \rightarrow NiAl_2O_4\ (s)$
  - $ZrO_2\ (s) + SiO_2\ (s) \rightarrow ZrSiO_4\ (s)$
  - $NiO\ (s) + Cr_2O_3\ (s) \rightarrow NiCr_2O_4\ (s)$
  - $MgO\ (s) + Fe_2O_3\ (s) \rightarrow MgFe_2O_4\ (s)$
  - $ZnO\ (s) + Al_2O_3\ (s) \rightarrow ZnAl_2O_4\ (s)$
- Metal carbides by carbothermal reduction
  - $4B\ (s) + C\ (s) \rightarrow B_4C\ (s)$
  - $7C\ (s) + 2B_2O_3 \rightarrow B_4C\ (s) + 6CO\ (g)$
  - $SiO_2\ (s) + 3C\ (s) \rightarrow SiC\ (s) + 2CO\ (g)$
  - $WO_2\ (s) + C\ (s) \rightarrow WC\ (s) + CO_2\ (g)$
- Nitrides
  - $3SiO_2\ (s) + 6C\ (s) + 2N_2\ (g) \rightarrow Si_3N_4\ (s) + 6CO\ (g)$

Products of solid-state reaction are thermodynamically stable compounds.

The driving force is the difference between the free energies of formation of products and reactants.

Ring T. A. Fundamentals of ceramic powder processing and synthesis, Academic Press, 1996, p.166

General rule of solid-state synthesis

"Shake and Bake"

Mix powder thoroughly

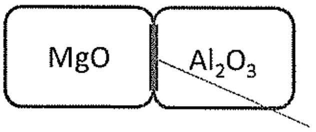
↓

Press powder into the pellets

↓

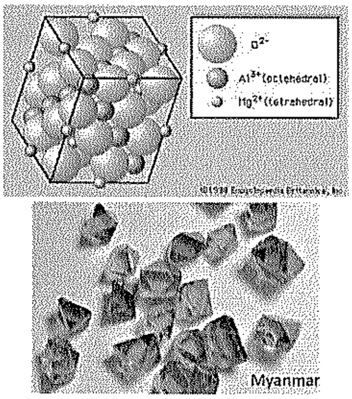
Heat for long time

Formation of $MgAl_2O_4$ spinel



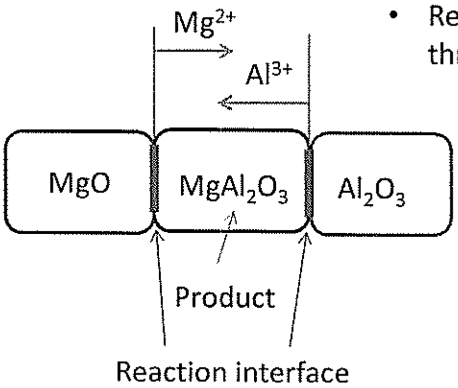
Contact between grains of solid reactants

- Reaction only takes place at contact point between grains
- Nucleation starts near contact points
- Growth of product layer
- Reaction requires ion diffusion through the product layer



http://inlovewithgeosciences.tumblr.com/page/43

Ion diffusion through product layer to reaction interface



Ion diffusion
- Diffusion rate is very slow
- Reaction rate decreases with time due to the growing product layer

Reaction is diffusion limited

Solid State Reactions

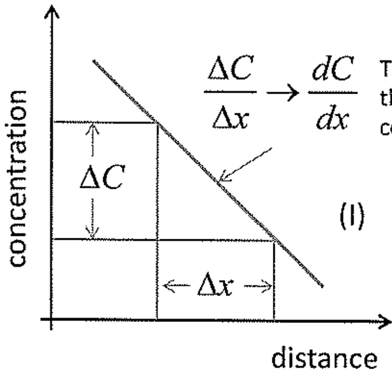
- Diffusion frequently is the rate limiting step (slow) in solid state reactions

Diffusion is the mass transport resulting in mixing of reactants .

Diffusion rate: Flux = (conductivity) × (driving force)

Diffusion coefficient (diffusivity)
Reflects the mobility of diffusing species

Concentration gradient
Variation of concentration as a function of distance



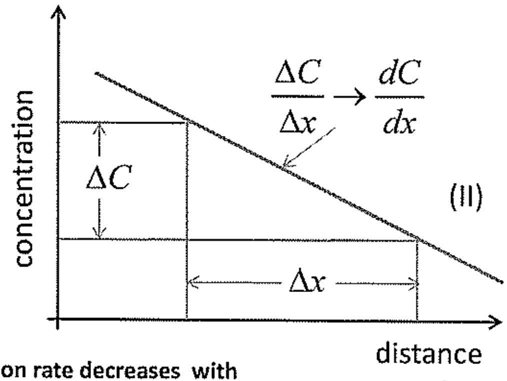
The concentration gradient is the rate of change of the concentration with distance

$$\Delta C\,(I) = \Delta C\,(II)$$

$$\Delta x\,(I) < \Delta x\,(II)$$

$$\Downarrow$$

$$\frac{\Delta C}{\Delta x}(I) > \frac{\Delta C}{\Delta x}(II)$$

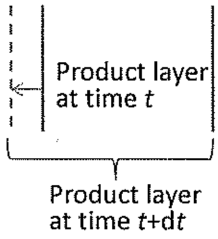


Diffusion rate decreases with increasing distance, Δx

Solid State Reactions

- Fick's first law: Diffusion rate is proportional to concentration gradient

$$J = -D \cdot \frac{dc}{dx}$$



J – diffusion flux (moles $cm^{-2}\ s^{-1}$), (atoms $cm^{-2}\ s^{-1}$), etc.
D - diffusion coefficient ($m^2 s^{-1}$)

The flux can be related to the change of the product layer thickness $\frac{dx}{dt}$,

$$J = (k \cdot \rho) \cdot \frac{dx}{dt} = -D \cdot \frac{dc}{dx} \cong -D \frac{\Delta c}{x} \longrightarrow xdx = Kdt,\ K = -\frac{D \Delta c}{k \rho}$$

where ρ is the molar density of product and k is the conversion factor.
Here we assume that Δc is approximately constant.

Integration results in $\int xdx = \int Kdt,\quad \frac{x^2}{2} = K \cdot t,\quad x^2 = 2 \cdot K \cdot t = K' \cdot t$

Parabolic rate law: $\boxed{x = \sqrt{K'} \cdot \sqrt{t}}$ The thickness of the planar layer increases with the square root of time

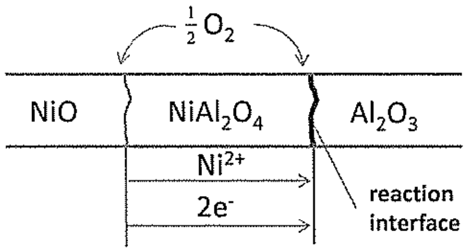
Describes the kinetics of processes for which the limiting step is the mass transport through a reaction layer

Formation of nickel aluminate spinel

$NiO + Al_2O_3 \rightarrow NiAl_2O_4$

Possible reaction paths:

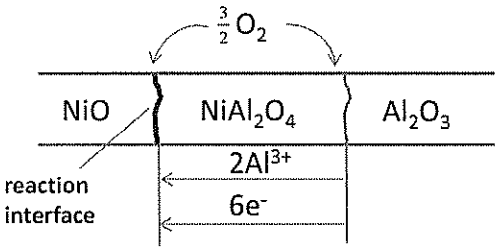
1. Reaction occurs at $NiAl_2O_4 - Al_2O_3$ interface



Oxygen gas phase transport
+
Ion Ni^{2+} and electron e^- transport through $NiAl_2O_4$
+
Reaction at $NiAl_2O_4 - Al_2O_3$ interface:

$Ni^{2+} + 2e^- + \frac{1}{2}O_2 + Al_2O_3 = NiAl_2O_4$

2. Reaction occurs at NiO - $NiAl_2O_4$ interface



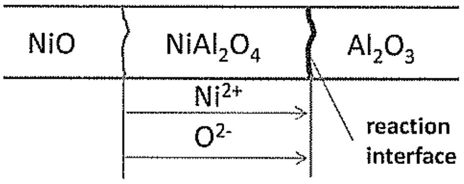
Oxygen gas phase transport
+
Ion Al^{3+} and electron e^- transport through $NiAl_2O_4$
+
Reaction at NiO-$NiAl_2O_4$ interface:

$2Al^{3+} + 6e^- + \frac{3}{2}O_2 + NiO = NiAl_2O_4$

W.D.Kingery, et al. Introduction to ceramics, J.Wiley & Sons, 1991, p 387-391.

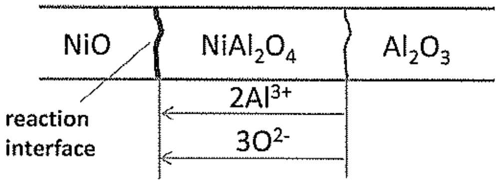
Formation of nickel aluminate spinel
Possible reaction paths:

3. Reaction occurs at $NiAl_2O_4 - Al_2O_3$ interface



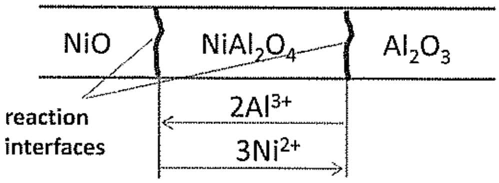
Oxygen O^{2-} and Ni^{2+} diffuse through $NiAl_2O_4$
+
Reaction at $NiAl_2O_4 - Al_2O_3$ interface:
$Ni^{2+} + O^{2-} + Al_2O_3 = NiAl_2O_4$

4. Reaction occurs at $NiO - NiAl_2O_4$ interface



Oxygen O^{2-} and Al^{3+} diffuse through $NiAl_2O_4$
+
Reaction at $NiO-NiAl_2O_4$ interface:
$2Al^{3+} + 3O^{2-} + NiO = NiAl_2O_4$

5. Reaction occurs at $NiAl_2O_4 - Al_2O_3$ and $NiO - NiAl_2O_4$ interfaces

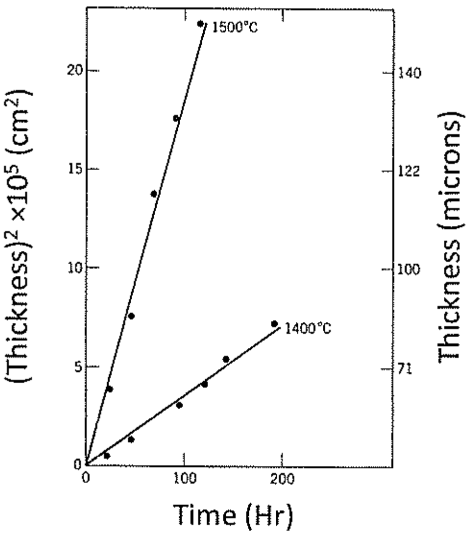


Both cations (Al^{3+} and Ni^{2+}) diffuse through $NiAl_2O_4$
+
Reaction at $NiO-NiAl_2O_4$ interface:
$2Al^{3+} + 4NiO = NiAl_2O_4 + 3Ni^{2+}$
+
Reaction at $NiAl_2O_4 - Al_2O_3$ interface:
$3Ni^{2+} + 4Al_2O_3 = 3NiAl_2O_4 + 2Al^{3+}$

Formation of nickel aluminate spinel

The rate of spinel formation could be controlled by the diffusion of Ni^{+2}, Al^{+3} or O^{2-} ions, by the transport of electrons (holes), by the transport of O_2 gas, or by the interface reactions.

Figure shows the parabolic time dependence for $NiAl_2O_4$ formation at two different temperatures.



The experimental data can be fitted by a line as (thickness)^2 vs. time.

The rate limiting step is the ion diffusion through the product layer

Solid State Reactions

Chemical decomposition reaction: solid reactant is heated to produce a solid product and a gas

Used for the production of simple oxides from carbonates, hydroxides, nitrates, sulfates, acetates, oxalates and other metal salts.

Decomposition of calcium carbonate (calcite) to produce calcium oxide and carbon dioxide gas:

$$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g)$$

The **reaction** is strongly **endothermic** with the standard heat of reaction at 298K, ΔH_R^o = 44.3 kcal/mol.

⇓

Heat should be supplied for reaction to proceed

Rahaman M.N. Ceramic processing, CRC, 2007, p.46

Solid State Reactions

Chemical decomposition reaction

Theory: Assuming that compounds become unstable when the partial pressure of the gaseous product above the solid equals the partial pressure of the gas in the surrounding atmosphere, we can calculate that $CaCO_3$ become unstable above 810 K.

Practice: These compounds are observed to be stable at much higher temperatures.

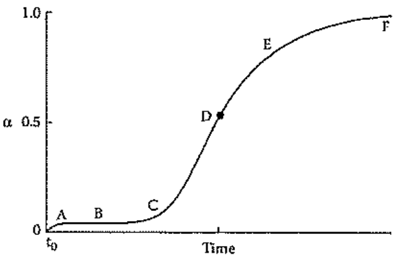
⇓

The decomposition is controlled by kinetic factors and not by thermodynamics

Weight loss at time *t*

$$\alpha = \frac{\Delta W}{\Delta W_{max}}$$

Maximum weight loss



A: initial reaction, decomposition of impurities or unstable materials
B: induction period, formation of stable nuclei
C: acceleratory period of growth of nuclei and further nucleation
D: maximum rate of reaction
E: decay period due to impingement of growing nucleus and consumption of reactant
F: completion of reaction

FIGURE 2.9 Generalized α vs. time plot summarizing characteristic kinetic behavior observed for isothermal decomposition of solids. α represents the weight loss divided by the maximum weight loss.

Solid State Reactions

Chemical decomposition reaction

molar volume of solid product < molar volume of solid product ⇨ product forms a porous layer around nonporous reactant

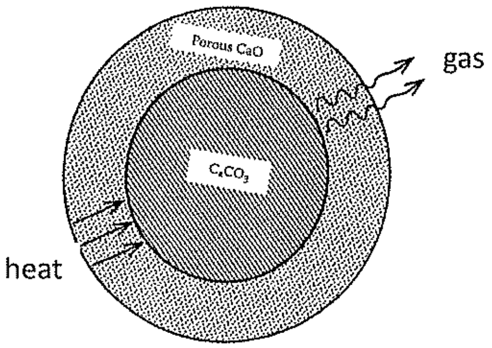


Fig. Schematics of the decomposition of calcium carbonate

The rate of reaction may be controlled by :

1. The reaction at the interface between the reactant and the solid product
2. Heat transfer to the reaction surface
3. Gas diffusion from the reaction surface through the porous product layer

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Solid State Reactions

Chemical decomposition reaction

Reaction rate equations for the analysis of kinetic data in decomposition reaction

Nucleation

Power law	$\alpha^{1/n} = Kt$	(1)	Reaction at interface is rate controlling
Exponential law	$\ln \alpha = Kt$	(2)	
Avrami–Erofe'ev	$[-\ln(1-\alpha)]^{1/2} = Kt$	(3)	
	$[-\ln(1-\alpha)]^{1/3} = Kt$	(4)	
	$[-\ln(1-\alpha)]^{1/4} = Kt$	(5)	
Prout–Tompkins	$\ln[\alpha/(1-\alpha)] = Kt$	(6)	

Geometrical Models

Contracting thickness	$\alpha = Kt$	(7)	Reaction is fast and rate depends on the geometry
Contracting area	$1-(1-\alpha)^{1/2} = Kt$	(8)	
Contracting volume	$1-(1-\alpha)^{1/3} = Kt$	(9)	

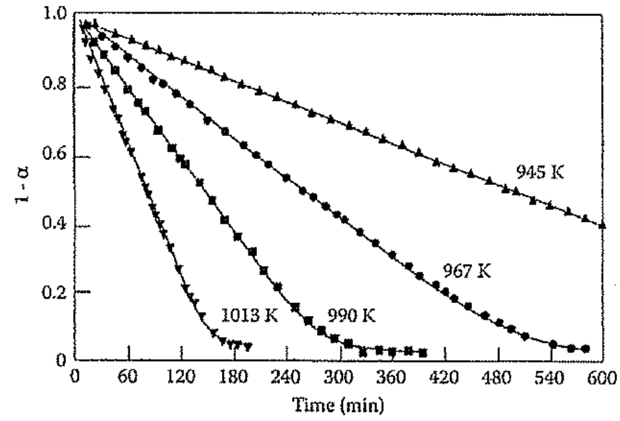
Diffusion

One dimensional	$\alpha^2 = Kt$	(10)	Diffusion is rate controlling
Two dimensional	$(1-\alpha)\ln(1-\alpha)+\alpha = Kt$	(11)	
Three dimensional	$[1-(1-\alpha)^{1/3}]^2 = Kt$	(12)	
Ginstling–Brounshtein	$[1-(2\alpha/3)]-(1-\alpha)^{2/3} = Kt$	(13)	

Solid State Reactions

Chemical decomposition reaction

- Decomposition kinetics of **thin** calcite crystals



Equation (7)
Contracting thickness:

$$\alpha = K \cdot t$$

FIGURE 2.11 Isothermal decomposition kinetics of calcite ($CaCO_3$) single crystal. (From Beruto, D. and Searcy, A.W., Use of the Langmuir method for kinetic studies of decomposition reactions: calcite ($CaCO_3$), *J. Chem. Soc., Faraday Trans. I*, 70, 2145, 1974. With permission.)

- Decomposition kinetics of **large** calcite is usually controlled by the rate of removal of gaseous product or the rate of heat transfer

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Solid State Reactions

Chemical decomposition reaction

The microstructure of the solid product is dependent on the decomposition conditions.

- Vacuum: Product particles are often of the same size and shape as reactant particles
  Product particles are aggregates of fine particles with fine internal pores
  → large surface area.
  The decomposition of $CaCO_3$ particles of 1 to 10 microns at 923K in vacuum results in CaO product of very high surface area of ~100 m^2/g with fine particles smaller than 10 nm and fine pores

- Atmospheric: The atmospheric gas catalyzes the sintering of fine particles, leading to larger particles and a reduction of the surface area.
  The decomposition of $CaCO_3$ particles at 1 atm N_2 results in CaO particles with low surface area of ~3 to 5 m^2/g

Solid State Reactions

Chemical reduction reaction

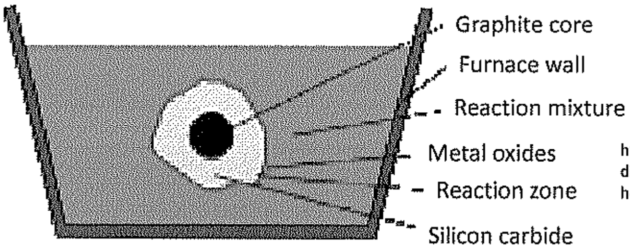
Industrial synthesis of carbides, nitrides, borides from oxides.

Reduction of oxides by carbon. Carbon is used for the elimination of oxygen.

Acheson process for the preparation of SiC powder (silicon carbide or carborundum): Silica is mixed with carbon and the mixture is heated electrically to temperatures of ~2500°C. The product is obtained after several days of reaction. Aggregates are crushed, washed, ground and classified to desired particle sizes.

$SiO_2 + 3C \rightarrow SiC + 2CO$

$C + SiO_2 \rightarrow SiO\ (g) + CO\ (g)$
$SiO_2 + CO \rightarrow SiO + CO_2\ (g)$
$C + CO_2 \rightarrow 2CO$
$2C + SiO \rightarrow SiC + CO$



http://en.wikipedia.org/wiki/Acheson_process

In the furnace, an electric current passes through a graphite core, surrounded by sand, salt, and carbon. The electric current heated the graphite and other materials, allowing them to react, producing a layer of silicon carbide around the graphite core.

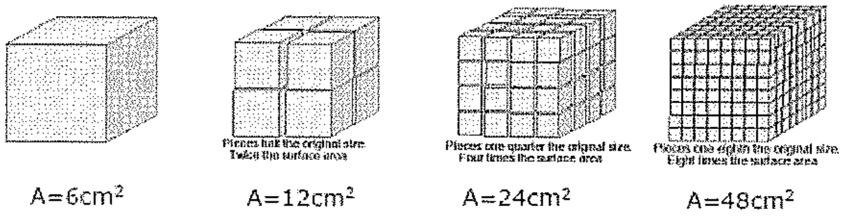
Solid State Reactions

Improving reactions rates

(1) Increase area ↑ of contact between reacting solids by decreasing particle size ↓

If the volume of solid reactant = 1 cm^3

- Edge length of cubic crystal = 1 cm, No of crystals = 1, surface area = 6 cm^2
- Edge length of cubic crystal = 0.5 cm, No of crystals = 8, surface area = 1.5*8=6 cm^2



(2) Thorough mixing to obtain a homogeneous mixture (decrease diffusion distance)

(3) Make pellets to decrease inter-particle void space

(4) Increase temperature

Diffusion is a thermally activated process: $D = D_o \cdot e^{-\frac{E_a}{RT}}$ **T ↑ → D ↑**

Solid State Reactions

Improving reactions rates

(4) Increase temperature

Tamman's rule: temperature of about 2/3 of the melting point of the lower melting reactant is required to have reaction to occur in a reasonable time

(5) Introduce defects by starting with reagents that decompose prior to or during reaction, such as carbonates or nitrates.

- vacancies (Schottky defects)
- interstitials (Frenkel defects)
- structural defects: dislocations, grain boundaries

(6) Continuously reground reaction mixture to bring fresh surfaces in contact

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Steps in Conventional Solid State Synthesis

http://www.ch.ntu.edu.tw/~sfcheng/HTML/material95/Solid_synthesis.pdf

1). Select appropriate starting materials
  a) Fine grain powders to maximize surface area
  b) Reactive starting reagents are better than inert
  c) Well defined compositions
2). Weigh out starting materials
3). Mix starting materials together
  a) Agate mortar and pestle (organic solvent optional)
  b) Ball Mill (Especially for large preps > 20g)
4). Pelletize
5). Select sample container
  Reactivity, strength, cost, ductility are all important
  a) Ceramic refractories (crucibles and boats)
    Al_2O_3 1950 °C \$30/(20 ml)
    ZrO_2/Y_2O_3 2000 °C \$94/(10 ml)
  b) Precious Metals (crucibles, boats and tubes)
    Pt 1770 °C \$500/(10 ml)
    Au 1063 °C \$340/(10 ml)
  c) Sealed Tubes
    SiO_2-Quartz, Au, Ag, Pt

Steps in Conventional Solid State Synthesis

http://www.ch.ntu.edu.tw/~sfcheng/HTML/material95/Solid_synthesis.pdf

6) Heat
   a) Factors influencing choice of temperature for volatilization
   b) Initial heating cycle to lower temperature can help to prevent spillage and volatilization
   c) Atmosphere is also critical
      Oxides (Oxidizing Conditions) –Air, O_2, Low Temps
      Oxides (Reducing Conditions) –H_2/Ar, CO/CO_2, High T
      Nitrides –NH_3 or Inert (N_2, Ar, etc.)
      Sulfides –H_2S
      Sealed tube reactions, Vacuum furnaces
7) Grind product and analyze (x-ray powder diffraction)
8) If reaction incomplete, return to step 4 and repeat.

Solid State Reactions

Advantages

- Solid-state reactions can be used for preparation of large number of components
- Relatively simple and old method

Disadvantages

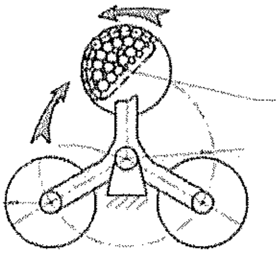
- High temperatures are required
- Reaction may proceed very slowly
- Product often impure and impurities difficult to separate
- Product can cover unreacted reactant and yield to incomplete reaction → impure final product
- Possible grain coarsening due to high temperature

Solid State Reactions

Mechanochemical Synthesis of Ceramics

Reaction milling

Mechanism: repeated deformation, fracture, and welding of the powder during collisions of the grinding media. Low temperature. Fracture exposes fresh reacting surfaces in close contact (short diffusion distance) to promote reaction. Diffusion rates are also enhanced by the high concentration of lattice defects.



Planetary ball mill

Oxide materials : $LiMn_2O_4$
perovskite structure of BT, PT, PZT,
PZN, PMN

Nonoxide materials : carbide and nitride
TiC, TiN etc

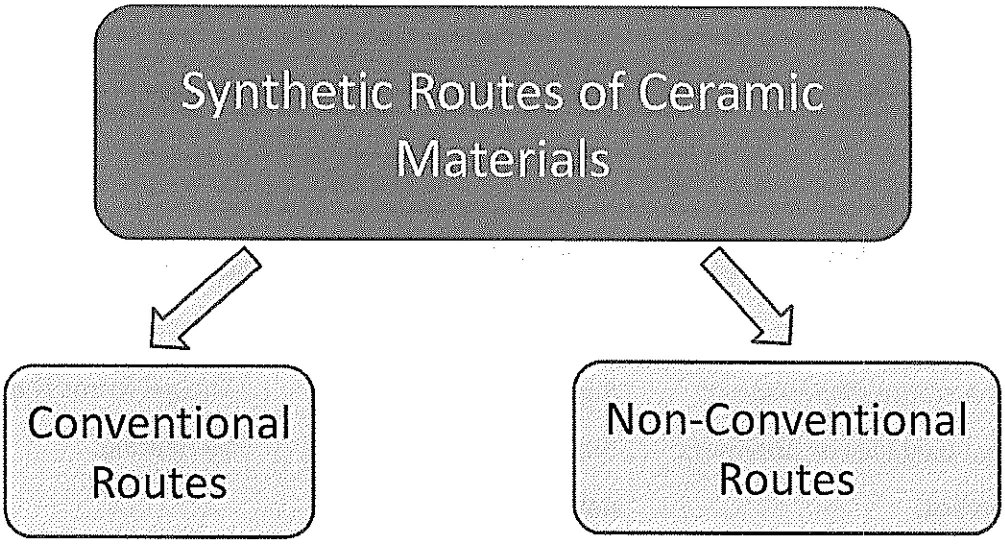
$2V+N_2=2VN$

$ZrO_2 + B_2O_3 + 5Mg = ZrB_2 + 5MgO$

Ultrafine particles: Possible to produce powder with minimal agglomeration as product fine particles are dispersed in by-product salt. $ZnCl_2 + Na_2CO_3 \rightarrow ZnO$

Composite powder: Alumina reinforced intermetallic compounds - the new high temperature structural materials, Ti_5Si_3-Al_2O_3

Wu H., Li Q., Journal of Advanced Ceramics, 1, 130-137, 2012
Dodd A.C. in Chemical Processing of Ceramics, 2 ed., p65-75,2005



Synthetic Routes of Ceramic Materials

Conventional Routes

- Solid state reaction
  - Chemical reaction between solids
  - Decomposition
  - Reduction

Non-Conventional Routes

- **Liquid phase solution**
  - Precipitation from solution
  - Co-Precipitation
  - **Sol-Gel Processing**
- Vapor phase reaction
  - Gas-solid reaction
  - Liquid-gas reaction
  - Gas-gas reaction

Sol Gel Processing

Lecture overview

- Introduction to sol-gel processing
- Mechanism of sol-gel processes
- Examples of ceramic synthesis by sol-gel method
- Advantages and disadvantages of sol-gel method for synthesis of ceramic materials

Introduction to sol-gel processing

Sol-gel process: Formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid

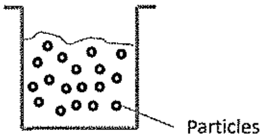
SOL → Heat or aging → GEL → Calcination → PRODUCT

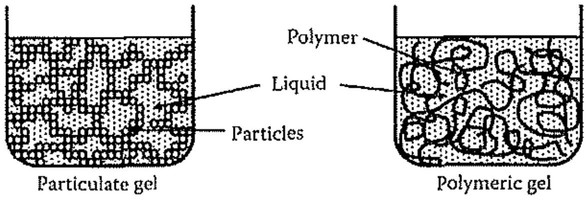
A **sol** is a stable dispersion of colloidal particles or polymers in a solvent.

A **gel** consists of a three dimensional continuous network of colloidal particles or polymeric chains.

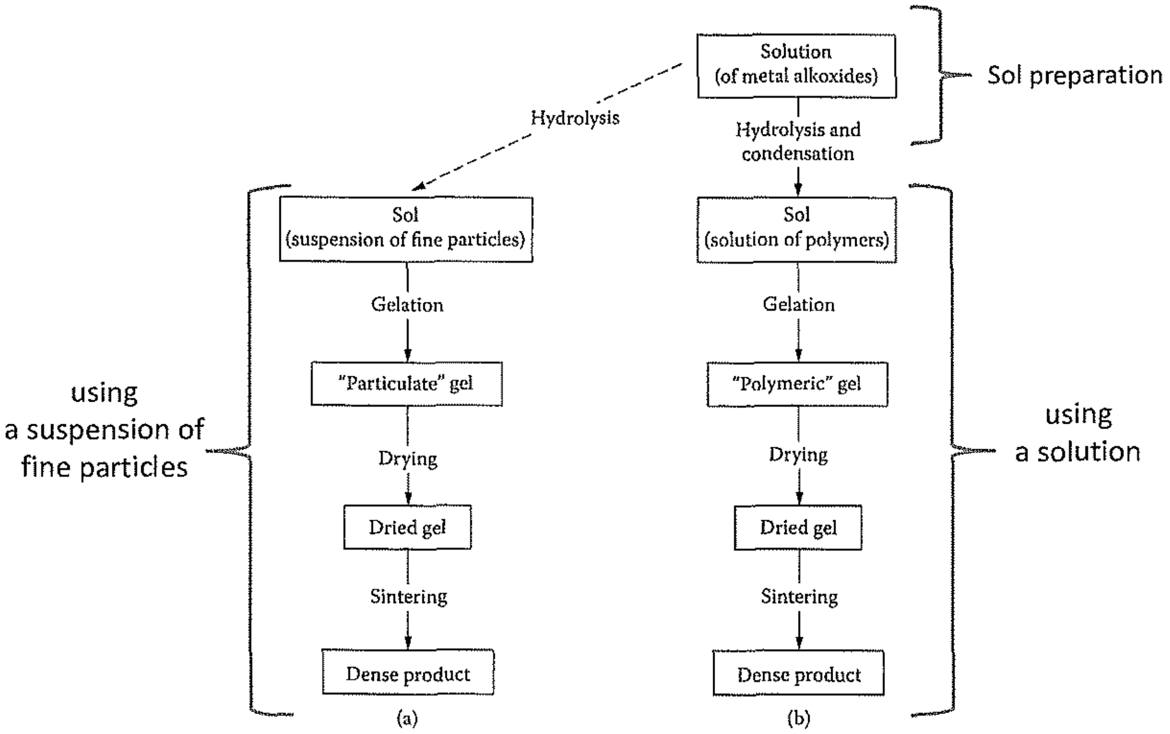
The gel forms the **product** by heating.

Colloid: a material consisting of solid particles (1nm to 1 µm) dispersed in a solution.





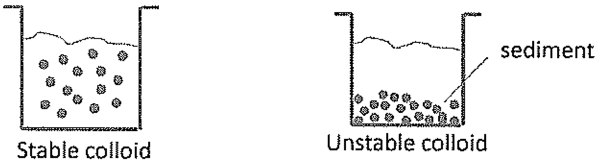
Basic flowchart of sol-gel processing



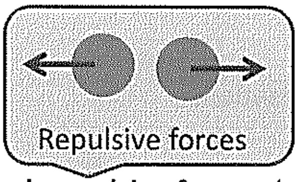
Rahaman. Ceramic Processing, p13

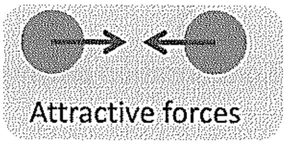
Introduction to sol-gel processing

A **sol** is a **stable** dispersion of colloidal particles.

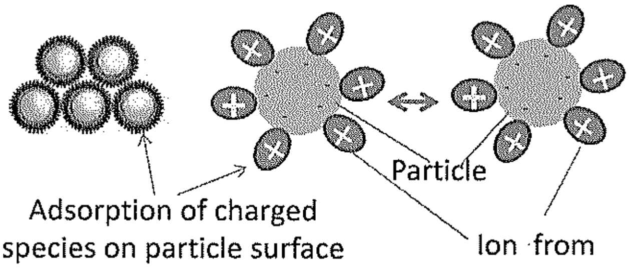


Agglomeration of small particles are due to the van der Waals forces (attractive) + tendency to decrease the total surface energy.





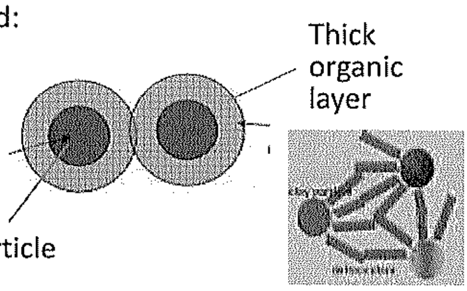
To make a **stable sol, repulsive forces** should be involved:



Adsorption of charged species on particle surface

Ion from solution

(a) **Electrostatic repulsion**



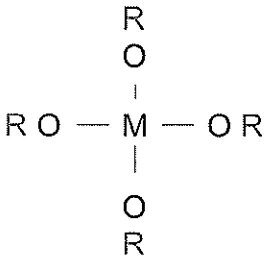
Adsorption of a thick layer of organic molecules

(b) **Steric hindrance**

Starting materials for sol-gel processing

Typical precursors (starting materials) to form a sol: Metal Alkoxides

Metal alkoxides are metal–organic compounds having the general formula $M(OR)_z$, where M is a metal of valence z and R is an alkyl group.



$$\begin{array}{c} R \\ O \\ | \\ RO - M - OR \\ | \\ O \\ R \end{array}$$

M – metal cation (Si^{4+}, Ti^{4+} ...)

R - alkyl group (CH_3, C_5H_5, C_3H_7 etc.)

Methoxide	$R{=}CH_3$	$B(OCH_3)_3$
Ethoxide	$R{=}C_2H_5$	$Si(OC_2H_5)_4$
Propoxide	$R{=}C_3H_7$	$Ti(O^iC_3H_7)_4$ (n-, iso-)
Butoxide	$R{=}C_4H_9$	$Al(O^sC_4H_9)_3$ (n-, iso-, sec-, tert-)

the superscripts n, t, s, and i refer to normal, tertiary, and secondary or iso alkyl chains

Preparation of metal alkoxides:

1. Reaction between metals and alcohols

   $M + z\,ROH \rightarrow M(OR)z + (z/2)\,H_2$

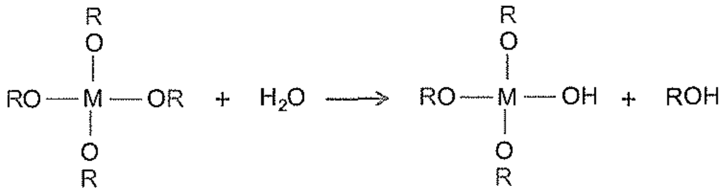
2. Reaction involving metal chlorides

   $MClz + z\,ROH + NH_3 \rightarrow M(OR)z + z\,NH_4Cl\downarrow$

Basic mechanism of sol-gel reaction

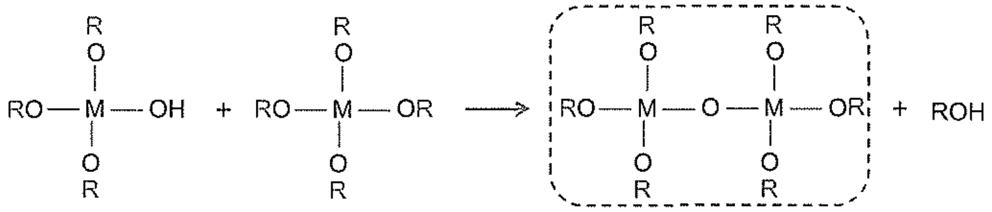
Formation of sol by hydrolysis-polycondensation reaction of metal alkoxides:

- Hydrolysis of alkoxide by controlling addition of water



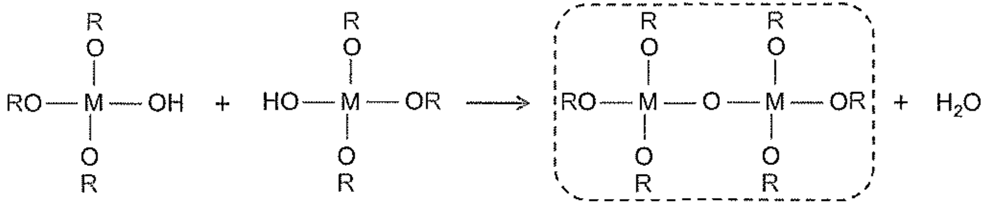
$$\mathrm{RO{-}\underset{\underset{R}{O}}{\overset{\overset{R}{O}}{M}}{-}OR} + \mathrm{H_2O} \longrightarrow \mathrm{RO{-}\underset{\underset{R}{O}}{\overset{\overset{R}{O}}{M}}{-}OH} + \mathrm{ROH}$$

- Condensation polymerization (alcohol condensation)



$$\mathrm{RO{-}\underset{\underset{R}{O}}{\overset{\overset{R}{O}}{M}}{-}OH} + \mathrm{RO{-}\underset{\underset{R}{O}}{\overset{\overset{R}{O}}{M}}{-}OR} \longrightarrow \boxed{\mathrm{RO{-}\underset{\underset{R}{O}}{\overset{\overset{R}{O}}{M}}{-}O{-}\underset{\underset{R}{O}}{\overset{\overset{R}{O}}{M}}{-}OR}} + \mathrm{ROH}$$

- Condensation polymerization (water condensation)

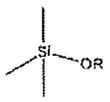


$$\mathrm{RO{-}\underset{\underset{R}{O}}{\overset{\overset{R}{O}}{M}}{-}OH} + \mathrm{HO{-}\underset{\underset{R}{O}}{\overset{\overset{R}{O}}{M}}{-}OR} \longrightarrow \boxed{\mathrm{RO{-}\underset{\underset{R}{O}}{\overset{\overset{R}{O}}{M}}{-}O{-}\underset{\underset{R}{O}}{\overset{\overset{R}{O}}{M}}{-}OR}} + \mathrm{H_2O}$$

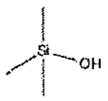
Basic mechanism of sol-gel synthesis of SiO_2

- ***Starting reagent*** *for the* ***sol-gel synthesis of*** SiO_2

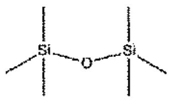
Aqueous silicates (silicic acid) or silicon alkoxides (Tetraethylorthosilicate, ***TEOS****)*



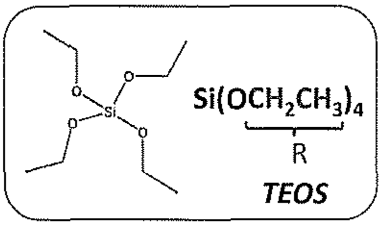
alkoxide



silanol



siloxane



- ***Reaction mechanism*** *of the* ***sol-gel synthesis of*** SiO_2

$$\underset{\text{alkoxide}}{\equiv\mathrm{Si\text{-}OR}} + \mathrm{H_20} \xrightarrow[\text{esterification}]{\text{hydrolysis}} \underset{\text{silanol}}{\equiv\mathrm{Si\text{-}OH}} + \mathrm{R0H}$$

} hydrolysis

$$\underset{\text{silanol}}{\equiv\mathrm{Si\text{-}OH}} + \underset{\text{alkoxide}}{\equiv\mathrm{Si\text{-}OR}} \xrightarrow[\text{alcoholysis}]{\text{alcohol condensation}} \underset{\text{siloxane}}{\equiv\mathrm{Si\text{-}O\text{-}Si}\equiv} + \mathrm{R0H}$$

$$\underset{\text{silanol}}{\equiv\mathrm{Si\text{-}OH}} + \underset{\text{silanol}}{\equiv\mathrm{Si\text{-}OH}} \xrightarrow{\text{water condensation}} \underset{\text{siloxane}}{\equiv\mathrm{Si\text{-}O\text{-}Si}\equiv} + \mathrm{H_2O}$$

]— condensation

Sol-gel synthesis of SiO_2

Acid (HCl) or base (NH_3) catalysts are frequently used for synthesis of silica gels.

TABLE 5.4
Sol–Gel Silicate Compositions for Bulk Gels, Fibers, Films, and Powders

	Mole %					
SiO_2 Gel Types	TEOS	EtOH	H_2O	HCl acid	NH_3 base	H_2O/Si (*w*) w
Bulk						
One-step acid	6.7	25.8	67.3	0.2	—	10
One-step base	6.7	25.8	67.3	—	0.2	10
Two-step acid-base						
First-step acid	19.6	59.4	21.0	0.01	—	1.1
Second-step acid (A2)	10.9	32.8	55.7	0.6	—	5.1
Second-step base (B2)	12.9	39.2	47.9	0.01	0.016	3.7
Fibers	11.31	77.26	11.31	0.11	—	1.0
Films	5.32	36.23	58.09	0.35	—	10.9
Monodisperse spheres	0.83	33.9	44.5	—	$\boxed{20.75}$	53.61

Particle base w ↑
Polymer acid w ↓

Rahaman. Ceramic Processing, p.208

Sol-gel transformation

Formation of rigid or semi-rigid porous solid by destabilization of stable sol:

Reduction of distance between particles

⇩

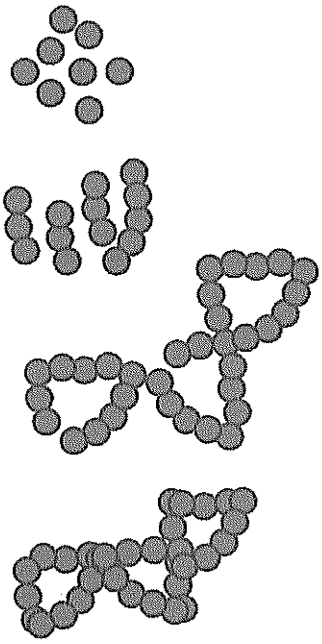
formation of particle clusters

⇩

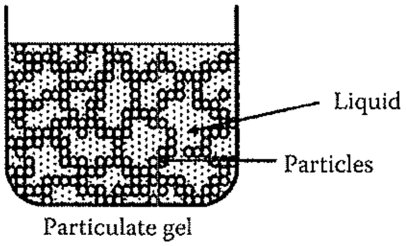
linking clusters into network

⇩

aging of gel: strengthening , stiffening and shrinkage of network



Particulate gel



Viscosity sharply increases when the sol–gel transition occurs.

Hydrogel: Particulate gels consists of a network in which pores are filled with water

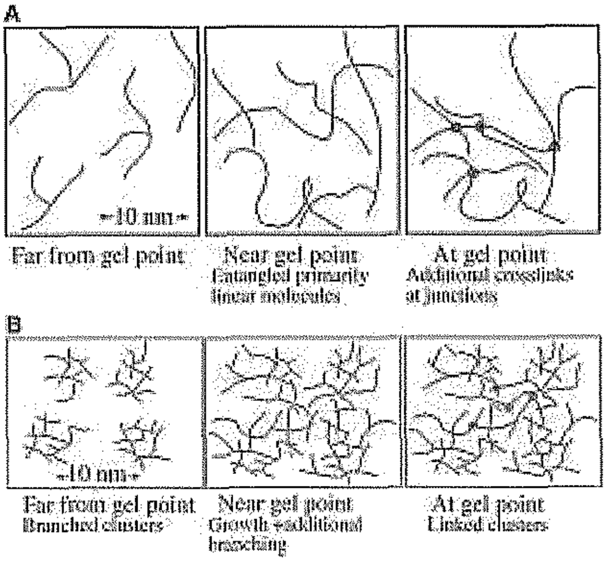
Sol-gel transformation

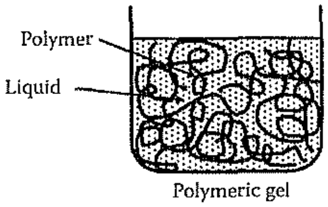
polymeric gel

The **structural changes** that occur during **gelation** of **polymeric gel** for acid-catalyzed and base-catalyzed reactions

acid-catalyzed

base-catalyzed





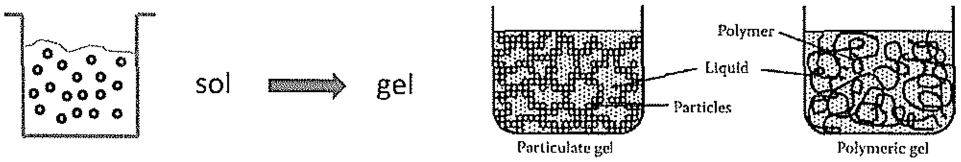
Alcogel: weak amorphous solid structures containing interconnected network of fine pores filled with alcohol (polymeric gels)

Carter, Norton, Ceramic Materials: Science and Engineering, p. 416

Sol-gel transformation

The **kinetics of the hydrolysis** of the sol to form a gel and the **gel structure** are **influenced** by:

- Alkoxide concentration
- Reaction medium
- Concentration of catalyst
  The rates of hydrolysis and condensation can be affected by the addition of small amounts of acid (e.g., HCl) or base (e.g., NH4OH)
- Temperature



Drying of gel

Slow drying under **controlled conditions** is important for formation of crack free product

Xerogel: gel produced by conventional drying. Dried gel has 40-60% of the fired density and contains small pores (nm) .

Aerogel: gel produced by removal liquid under supercritical conditions. Network of ~95% porosity.

Cryogel: gel produced by freeze-drying. Fine powder, not suitable for producing monolithic ceramics.

Drying is a complex process involving the interaction of independent **processes:**

(1) Evaporation

(2) Shrinkage

(3) Fluid flow in the pores

Drying is divided into two **stages:**

(1) constant-rate period where the evaporation rate is constant

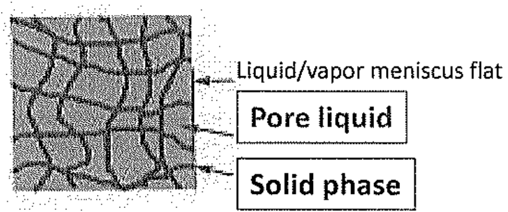
(2) falling-rate period where the evaporation rate decreases with time or the amount of liquid remaining in the body

Rahaman. Ceramic Processing, p217

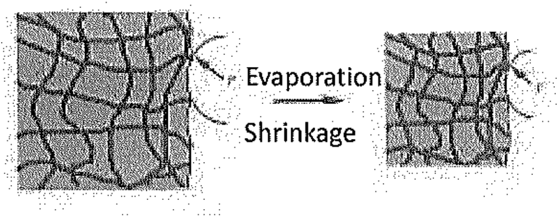
Drying of gel

Stages of drying

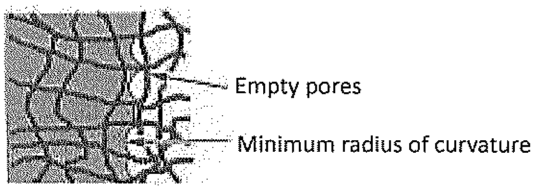
(a) Initial condition



(b) Constant rate period



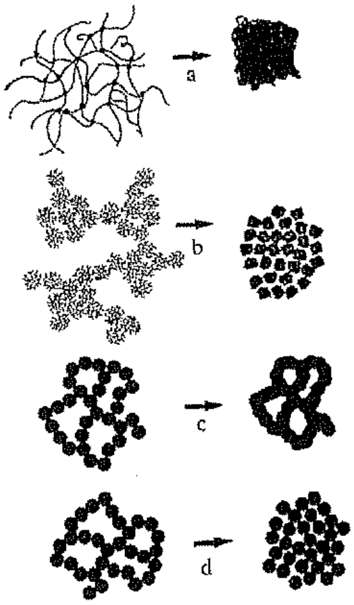
(c) Falling rate period



Rahaman. Ceramic Processing, p217

Drying of gel

Structural changes during drying of gel



Polymeric gel, acid catalyzed

Weakly cross-linked → easily to collapse
High density and fine pores

Polymeric gel, base catalyzed

strongly cross-linked → difficult to collapse
Relatively low density and large pores

Particulate gel of high silica solubility

Large pores , less shrinkage than in polymeric gel

Particulate gel of weakly bonded particles

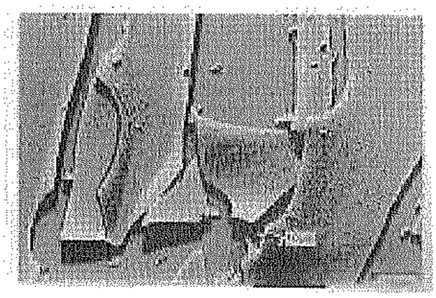
Rahaman. Ceramic Processing, p229

Drying of gel

Slow drying under **controlled conditions** is import for formation of crack free product

A number of **procedures** have been developed to **increase drying rates** while **avoiding cracking:**

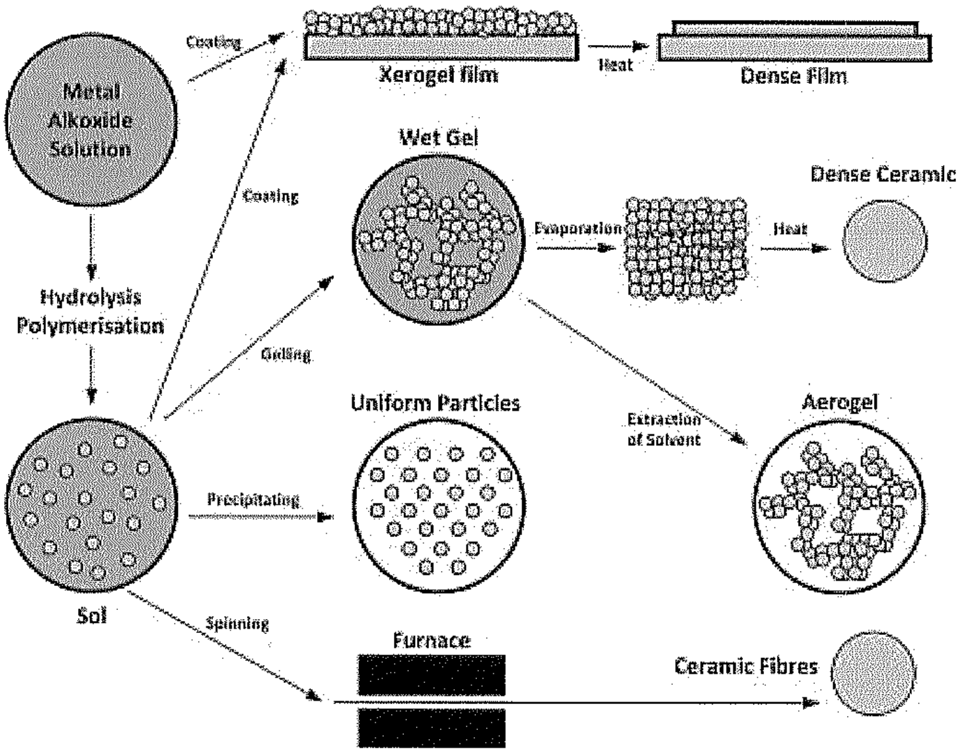
- Increase the pore size of the gel.
- Decrease the liquid/vapor interfacial energy (e.g., use a solvent with a low γ_{lv}).
- Strengthen the gel.
- Use supercritical (hypercritical) drying:
  the liquid is removed above its critical temperature, T_c, and critical pressure, p_c. The values of T_c and p_c for the commonly used sol–gel liquids are: water 647 K and 22 MPa; ethanol 516 K and 6.4 MPa.



Cracked silica coating on glass substrate
Segal. Chemical synthesis of adv, cer.., p.81

Carter, Norton, Ceramic Materials: Science and Engineering, p. 417

Routes of Sol-Gel Processing



http://en.wikipedia.org/wiki/Sol-gel

Applications of Sol Gel Processing

I. Powder

Powder can be obtained via a sol–gel process using metal alkoxides or a combination of metal alkoxides and metal salts.

- Powders are chemically homogeneous, because the mixing of the constituents is achieved at a molecular level.
- Powders produced by the sol–gel method are usually amorphous.
- Powders produced by the sol-gel method are of high surface area.
- Powder can be sintered to nearly full density at lower temperatures than are normally required when the particles have been made by other techniques.

  For example, gel-derived mullite powders can be sintered to full density at <1300°C. The sintering temperature is ~1600°C for crystalline mullite powder produced by conventional method.
- High cost of the raw materials.

Carter, Norton, Ceramic Materials: Science and Engineering.

Applications of Sol Gel Processing

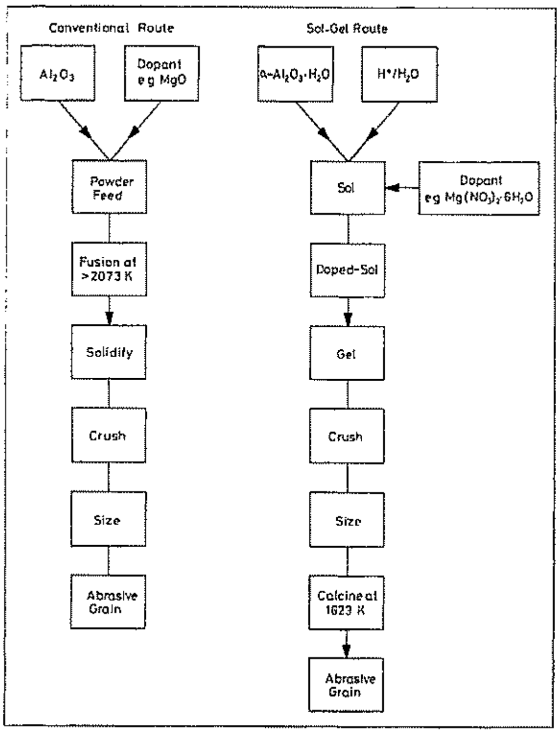
I. Powder

Manufacturing of **alumina-based abrasive grain** used in grinding wheels and coated paper

Conventional route:

- Fusion of Al_2O_3 with dopant at 2073 K
- Solidification of melt

Variations in cooling rate result in a product with a wide distribution of crystallite sizes of one phases in a matrix of second phase.



Segal, Chemical synthesis of advanced ceramic materials.

Sol-gel route:

- An aqueous peudo-boehmite sol is doped with the second phase in the form of oxide powder or salt solution.
- Sintering of gel at 1623K.

The brittle gel transforms to a continuous phase of randomly oriented crystallites of alumina (~300nm) containing a secondary phase.

Small crystals of narrow size distribution

⇓

Improved abrasive properties

Applications of Sol Gel Processing

I. Powder

Suspension of dense nanoparticles

Suspensions of **dense nanoparticles** (silica, ceria) are used as abrasive materials for **chemical mechanical polishing** process of materials used in fabrication of microelectronic devices.

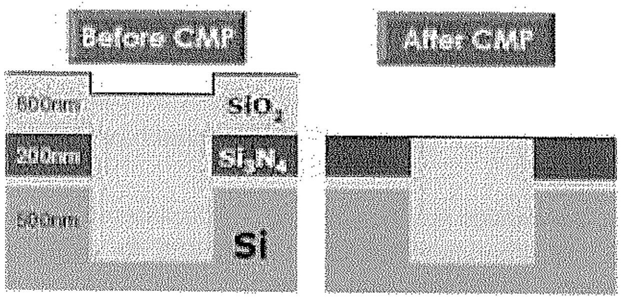


Figure 1: Structure of STI and planarization by CMP process

Y.Hong, G.R. Yi, Industrial Applications of Sol-Gel Technology, Solid State Phenomena, Vols. 124-126, p 619, 2007

Applications of Sol Gel Processing

I. Powder

Nanoparticles as fillers for flat panel display

Nanoparticles under 50nm are used as fillers for flat panel display coatings since they are optically transparent when they are incorporated into nanocomposites. The conductive nanoparticles such as indium tin oxide are using for antistatic function layer. SiO_2 and TiO_2 are also most common nanoparticles to adjust reflective index in the display films.

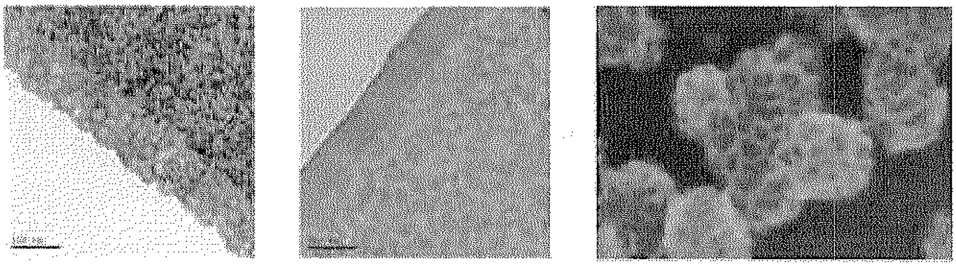


Figure 2. TEM/SEM images of functionalized transparent nanoparticles.

Y.Hong, G.R. Yi, Industrial Applications of Sol-Gel Technology, Solid State Phenomena, Vols. 124-126, p 619, 2007

Applications of Sol Gel Processing

I. Powder

Nanoparticles as active component

TiO_2 nanoparticles are used in personal care products due to UV protecting function. The photo catalytic activation of TiO_2 have been applied to self-cleaning applications for removing dirt or other substances to adhere to the surface.

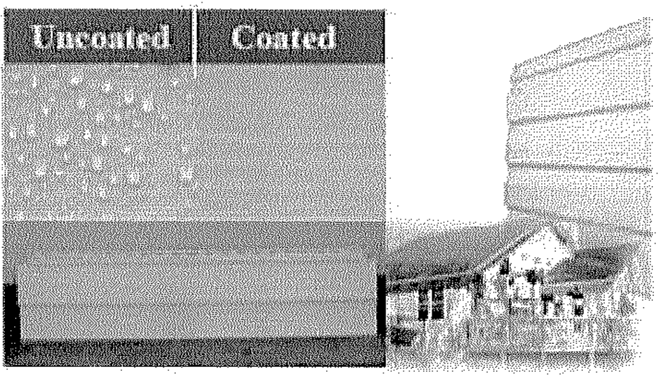


Figure 3. Effect of vinyl siding coated silica based self cleaning material.

Y.Hong, G.R. Yi, Industrial Applications of Sol-Gel Technology, Solid State Phenomena, Vols. 124-126, p 619, 2007

Applications of Sol Gel Processing

II. Fiber

Fibers can be drawn directly from viscous sols, which are usually made by acid-catalyzed hydrolysis using low H2O:M ratios.

Applications for sol–gel derived *fibers* include:

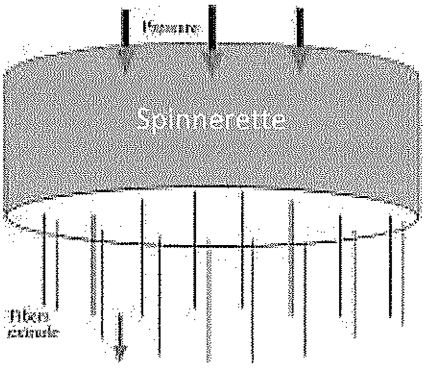
- Reinforcement in composites
- Refractory textiles
- High-temperature superconductors

Examples of fibers produced by sol–gel are:

- SiO_2
- SiO_2–TiO_2 (10–50 mol% TiO_2)
- SiO_2–Al_2O_3 (10–30 mol% Al_2O_3)
- SiO_2–ZrO_2 (10–33 mol% ZrO_2)
- SiO_2–Na_2O–ZrO_2 (25 mol% ZrO_2)

Sol-gel spinning process

Sol



Carter, Norton, Ceramic Materials: Science and Engineering.

Applications of Sol Gel Processing

II. Fiber

Manufacturing of aluminosilicate ceramic fiber (95 wt,% Al_2O_3, 5 wt.% SiO_2):

Basic aluminium chloride solution with polymeric cationic species

+

Polymer (polyvinyl alcohol) 2 wt%

+

Silica source

Extrude through spinneret holes (100-200 μm)

↓

Calcination

Fiber of 3 μm in diameter

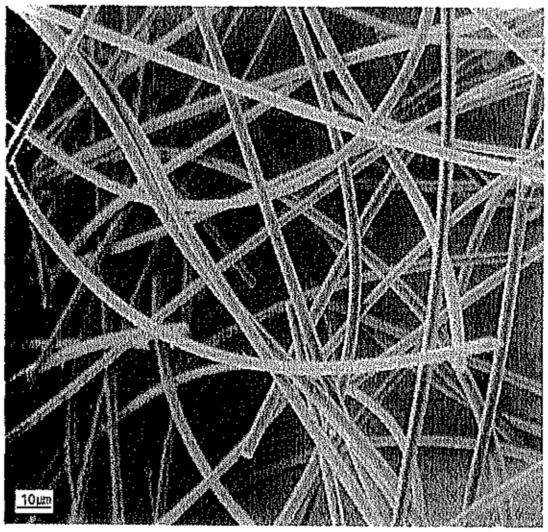


Figure 4.13. Scanning electron micrograph for Saffil alumina fibre. (Courtesy of Imperial Chemical Industries.)

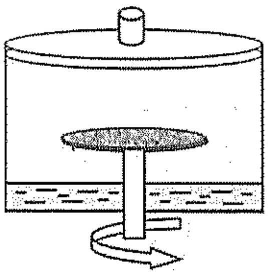
Application: high-temperature thermal insulation in chemically reactive environment (wall linings in furnaces for the glass and steel industries)

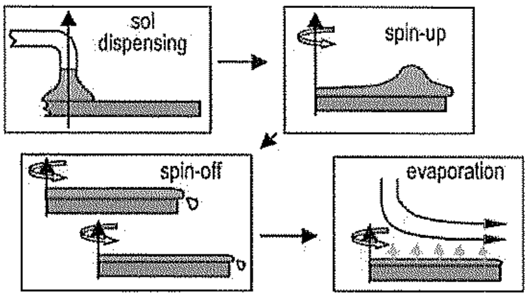
Segal, Chemical synthesis of advanced ceramic materials.

Applications of Sol Gel Processing

III. Thin films and coatings

Spin coating





- Deposition of sol on substrate
- Spin-up: liquid flows radially due to centrifugal force generated by the rotating substrate
- Spin-off: excess liquid flows to the perimeter of the substrate, leaving as droplets
- Evaporation

⇓

Thin uniform films

http://homepages.rpi.edu/~plawsky/Research/images/

Applications of Sol Gel Processing

III. Thin films and coatings

Spin coating

The **advantages** of forming **coatings** via sol–gel reactions are:

- Large areas
- Uniform composition
- High purity
- Microstructural control—i.e., pore volume (0–65%), pore size (<0.4 to >5.0 nm), and surface area (<1 to 250 m2/g)
- Less expensive than vapor-phase processes such as chemical vapor deposition and sputtering

Spinning is widely used for applying sol–gel coatings:

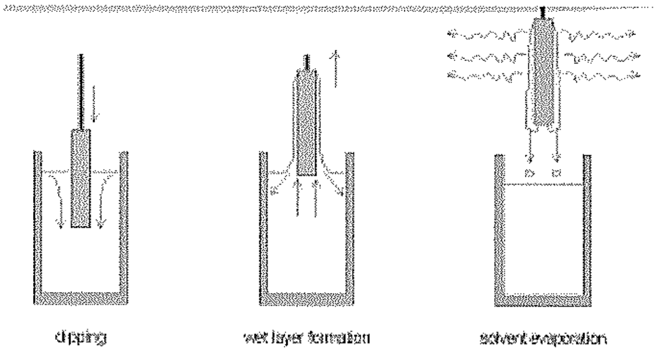
- thin coatings of PZT for micro-electro-mechanical systems (MEMS).
- antireflective layers on glass substrates and solar reflecting coatings on flat glass.

Carter, Norton, Ceramic Materials: Science and Engineering.

Applications of Sol Gel Processing

III. Thin films and coatings

Dip coating



- An accurate and uniform coating thickness depends on precise speed control and minimal vibration of the substrate and fluid surface.
- The coating thickness is mainly defined by the withdrawal speed, the solid content and the viscosity of the liquid.

- Immersion : the substrate is immersed in the solution
- Start-up: the substrate has remained inside the solution for a while and is starting to be pulled up
- Deposition: The thin layer deposits itself on the substrate while it is pulled up with a well-defined withdrawal speed under controlled temperature and atmospheric conditions
- Drainage: Excess liquid will drain from the surface.
- Evaporation: The solvent evaporates from the liquid, forming the thin layer.

http://en.wikipedia.org/wiki/Dip-coating
http://www.ceramicindustry.com/articles/advances-in-sol-gel-technology

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Applications of Sol Gel Processing

III. Thin films and coatings

TABLE 22.7 Applications of Sol–Gel Films and Coatings

Field	*Property*	*Examples*
Electronic	Ferroelectric	$BaTiO_3$, PZT
	Piezoelectric	PZT
	High-T_c superconductor	$YBa_2Cu_3O_7$
	Ferrimagnetic	Doped Fe_2O_3
	Transparent conductors	Indium tin oxide
Optical	Antireflective	TiO_2/SiO_2
	Solar reflecting	TiO_2/Pd
	Electro-optic	PLZT
Protective	Corrosion resistant	SiO_2
	Abrasion resistant	Organic modified silicates
	Barrier films	YSZ
Biomaterials	Bone cell regeneration	Calcium apatites

PLZT lead-lanthanum-zirconate-titanate, *PZT* lead zirconate titanate, *YSZ* yttria-stabilized zirconia.

Carter, Norton, Ceramic Materials: Science and Engineering.

Advantages and disadvantages of sol-gel processing

Advantages

- High purity raw materials
- Low process temperature
- Good homogeneity
- Production of multicomponent composite products
- Fabrication of special products such as films and fibers

Disadvantages

- Relatively high cost of raw materials
- Large shrinkage during processing
- Residual pores
- Possibility of cracking during drying
- Long processing times
- Special handling of raw materials usually required
- Health hazards of organic solvents

Sol Gel Processing

Applications

ORMOSIL

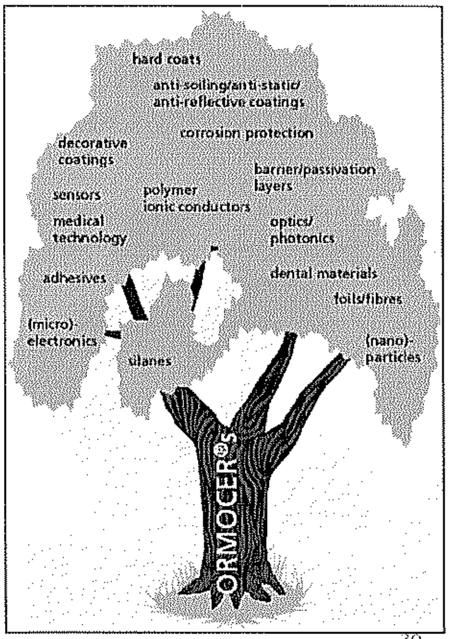
ORganically MOdified SILicate

ORMOCER

ORganically MOdified CERamic

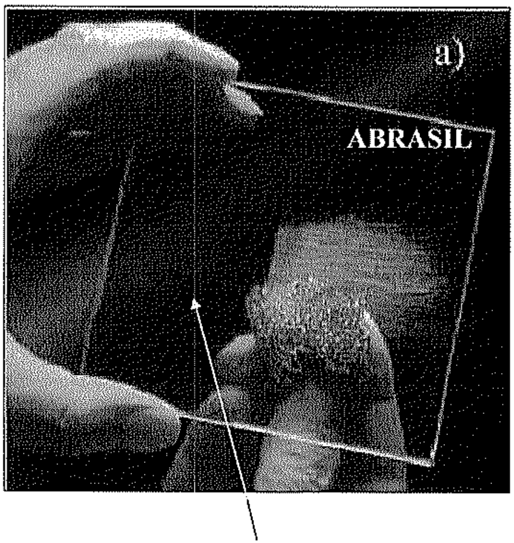
CERAMER

CERAmic polyMER

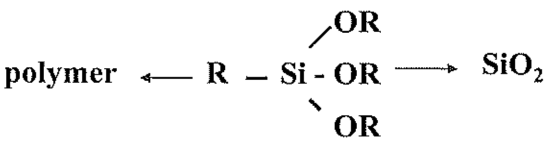


http://www.labos.upmc.fr/lcmcp/files/livage/Cours_Amiens_2008-2009/3._Sol-Gel_Hybrids.ppt
Pierre-and-Marie-Curie University

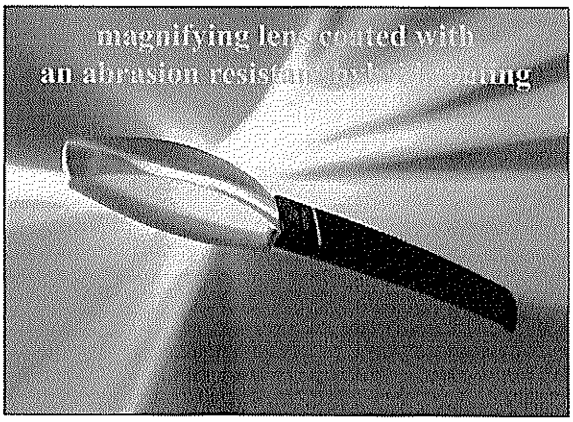
Scratch resistant coatings on plastics



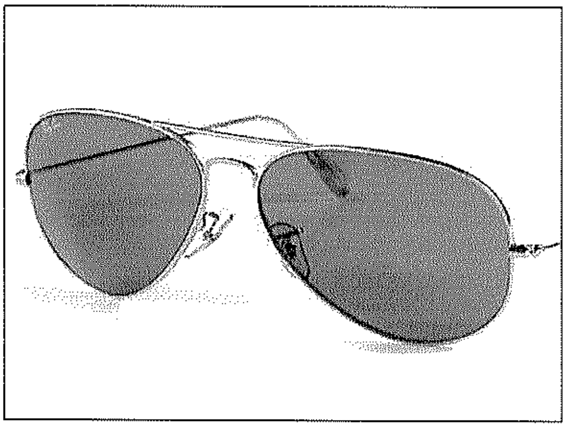
Sol-gel coating



$$\text{polymer} \longleftarrow \text{R} - \underset{\text{OR}}{\overset{\text{OR}}{\text{Si}}} - \text{OR} \longrightarrow \text{SiO}_2$$



magnifying lens coated with
an abrasion resistant hybrid coating



http://www.labos.upmc.fr/lcmcp/files/livage/Cours_Amiens_2008-2009/3._Sol-Gel_Hybrids.ppt
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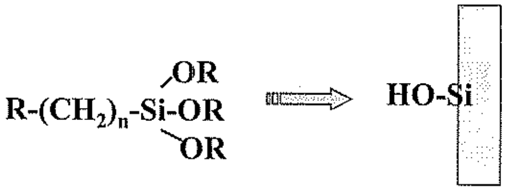
hydrophobic coatings on windshields

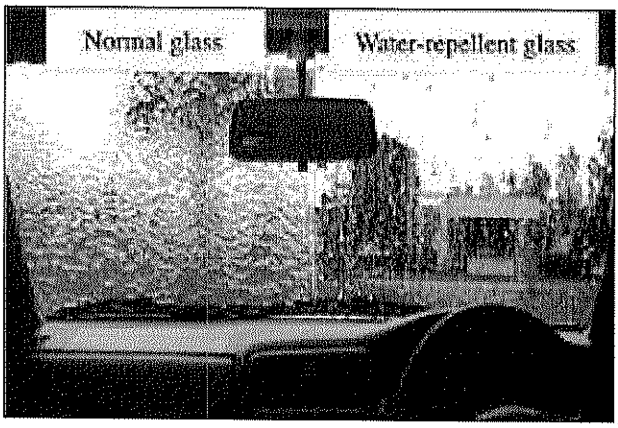


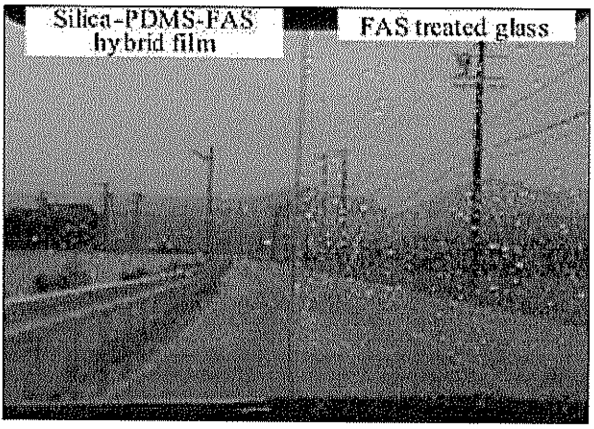
$$\text{R-(CH}_2)_n\text{-}\underset{\text{OR}}{\overset{\text{OR}}{\text{Si}}}\text{-OR} \Longrightarrow \text{HO-Si}$$

R = hydrophobic group : CF_3, CH_3, …

Hybride PDMS + TEOS : « sliding effect »
Hybride PDMS + TEOS + FAS : against rain

FAS = $CF_3\text{-}(CF_2)_7\text{-}CH_2\text{-}CH_2\text{-}Si\text{-}(OCH_3)_3$





Central Glass Japan

http://www.labos.upmc.fr/lcmcp/files/livage/Cours_Amiens_2008-2009/3._Sol-Gel_Hybrids.ppt
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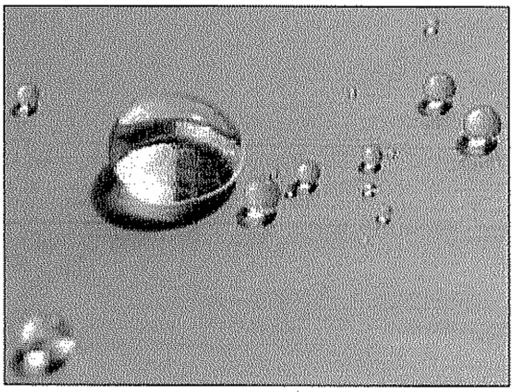
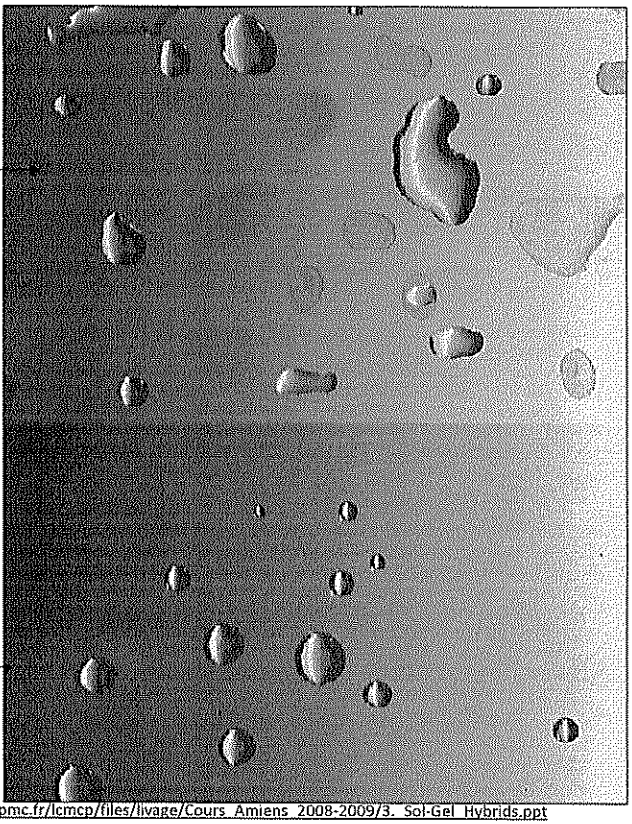
Sol-gel hydrophobic coatings

G. Schottner, Chem. Mater. 13 (2001) 3422

Stainless steel without coating





Stainless steel with an abrasion resistant fluorinated hybrid coating

http://www.labos.upmc.fr/lcmcp/files/livage/Cours_Amiens_2008-2009/3._Sol-Gel_Hybrids.ppt
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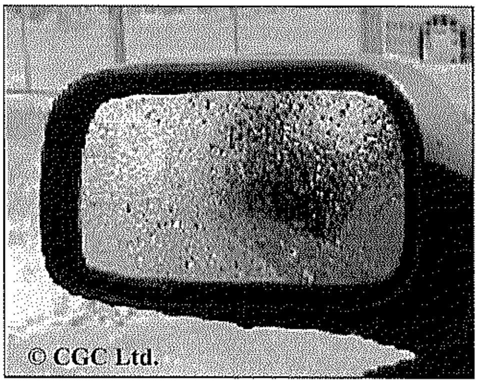
Hydrophilic and photocatalytic coatings

Two layers :

- **SiO_2 : hydrophilic, scratching resistant**
- **TiO_2 : photocatalytic effect under UV irradiation**
- **Thermal treatment at 600°C**



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http://www.labos.upmc.fr/lcmcp/files/livage/Cours_Amiens_2008-2009/3._Sol-Gel_Hybrids.ppt
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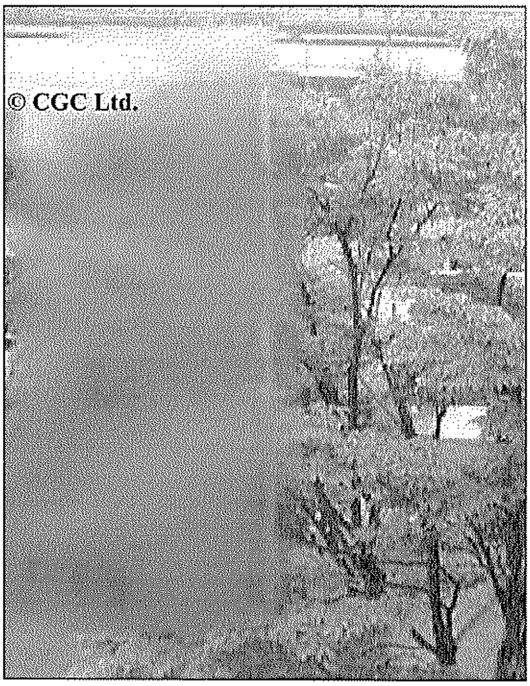
‘anti-mist’ coatings

Central Glass - Japon

To avoid moisture condensation on a cold surface

SiO_2-ZrO_2

Nobuyuki.Itakura,
Glass Research Center, Central Glass Co. Ltd.,
1510 Ohkuchi-cho, Matsusaka-shi, Mie, 515-0001 Japan
E-mail nobuyuki.itakura@cgco.co.jp



SiO_2 / ZrO_2 colloïdal + top-layer SiO_2 ou

Gel = isocyanate + ethylene oxide/propylene oxide + PEG + PC polyol

dépôt par spin-coating + traitement thermique (@150°C); ép. 20µm

http://www.labos.upmc.fr/lcmcp/files/livage/Cours_Amiens_2008-2009/3._Sol-Gel_Hybrids.ppt
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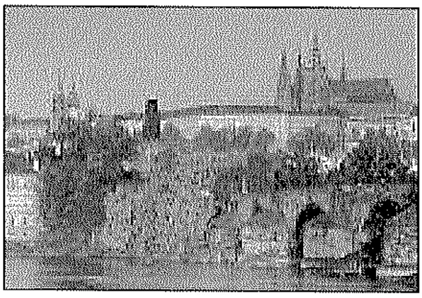
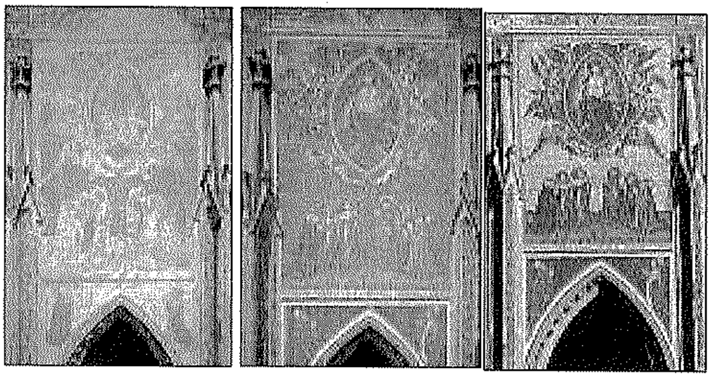
Cathedral of Pragua

Protection of the mosaic by an hybrid coating



before



after

Getty Museum - Los Angeles

http://www.labos.upmc.fr/lcmcp/files/livage/Cours_Amiens_2008-2009/3._Sol-Gel_Hybrids.ppt
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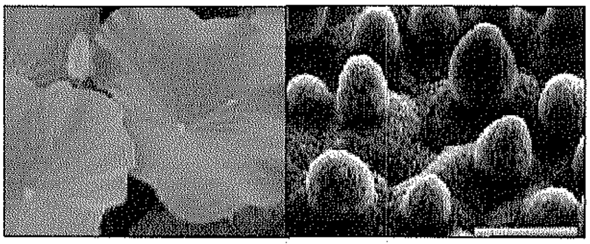
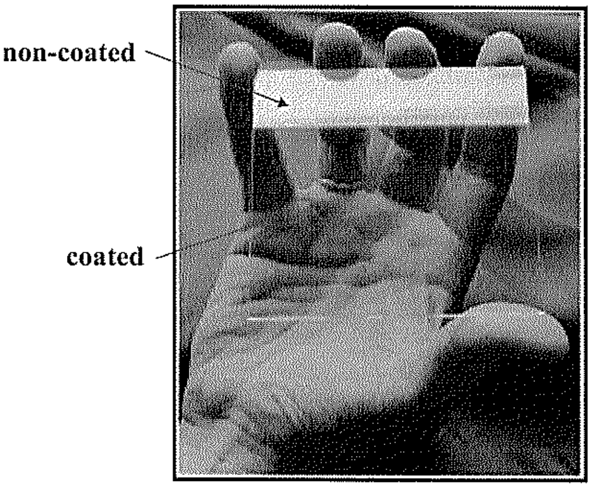
Nano-patterned films

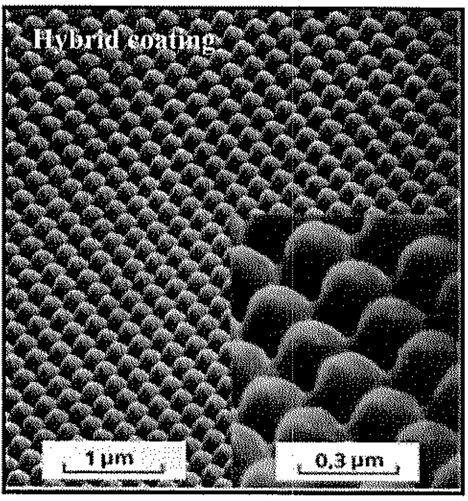
produced by embossing a hybrid coating



' *lotus* ' *effect*

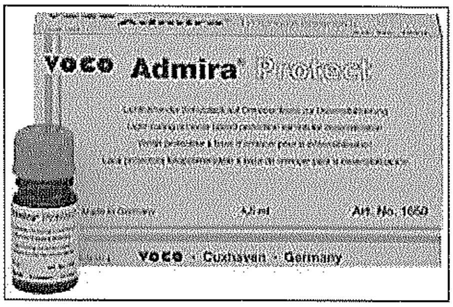
Periodic microstructure leading to a gradient in the refractive index



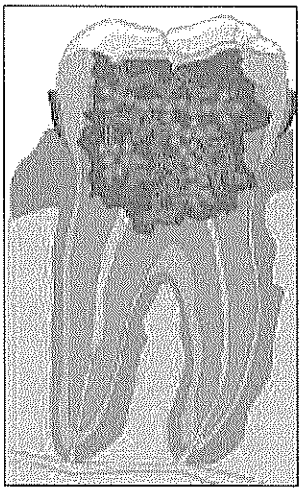


Filling composites for dental applications

Reduction of polymerization shrinkage



Definite® & Admira® resins
(Fraunhofer ISC - VOCO GmbH)



http://www.labos.upmc.fr/lcmcp/files/livage/Cours_Amiens_2008-2009/3._Sol-Gel_Hybrids.ppt
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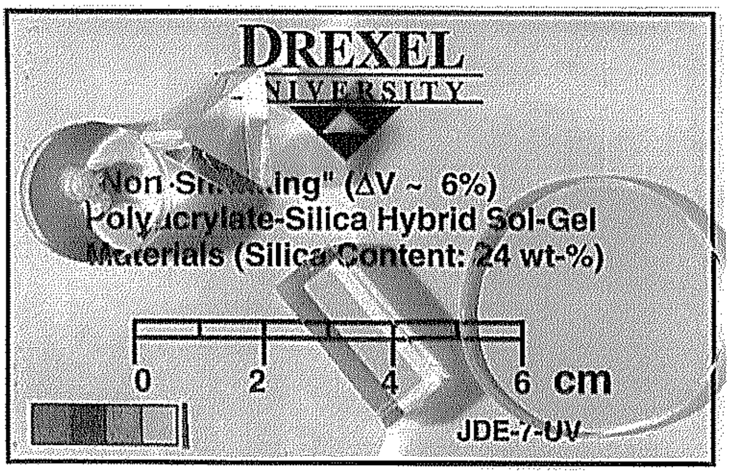
sol-gel optics

bulk pieces

no crack or shrinkage upon drying (hydrophobic organics)

easily shaped materials (molding, polishing)

nano-composite = transparency



http://www.labos.upmc.fr/lcmcp/files/livage/Cours_Amiens_2008-2009/3._Sol-Gel_Hybrids.ppt
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Synthetic Routes of Ceramic Materials

Conventional Routes

- Solid state reaction
  - Chemical reaction between solids
  - Decomposition
  - Reduction

Non-Conventional Routes

- **Liquid phase solution**
  - **Precipitation from solution**
  - **Coprecipitation**
  - Sol-Gel Processing
- Vapor phase reaction
  - Gas-solid reaction
  - Liquid-gas reaction
  - Gas-gas reaction

Precipitation from Solution

Lecture overview

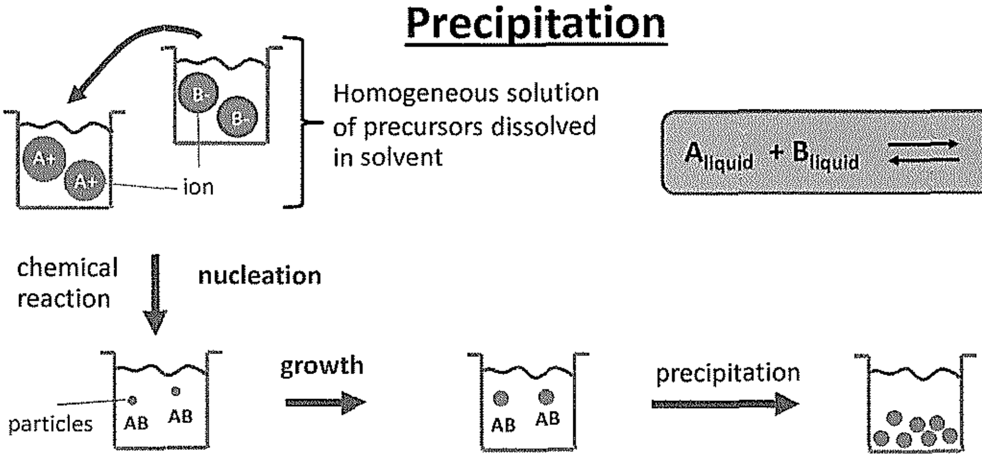
- Introduction to precipitation processes
- Mechanism of precipitation process
- Examples of ceramic synthesis by precipitation method
- Advantages and disadvantages of precipitation method for synthesis of ceramic materials

Production of powdered material from a solution

Evaporation of liquid

Precipitation by adding a chemical reactant that reacts with the solution

Precipitation



$A_{liquid} + B_{liquid} \rightleftharpoons AB_{solid}$

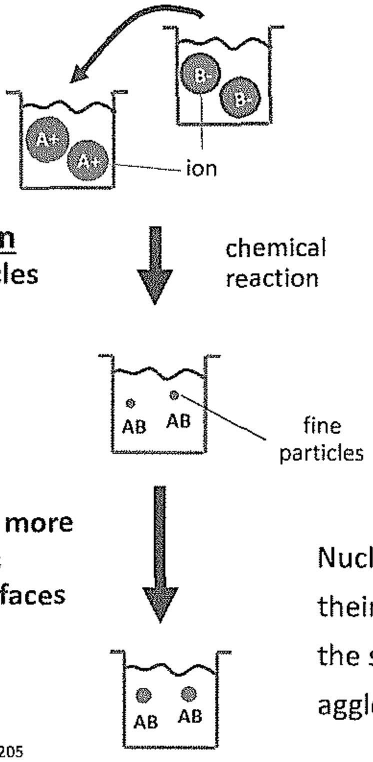
Precipitation from a solution

Precipitation from solution consists of two basic steps:

$A_{liquid} + B_{liquid} \rightleftharpoons AB_{solid}$

(1) **Nucleation** of fine particles

(2) **Growth** by addition of more materials to particle surfaces



Nucleation of fine particles and their growth determine the size, size distribution, shape and agglomeration of product particles.

Precipitation from solution

Compound in the solid state is in chemical equilibrium with a solution of that compound

$$\boxed{A_{\text{liquid}} + B_{\text{liquid}} \underset{\text{dissolution}}{\overset{\text{precipitation}}{\rightleftharpoons}} AB_{\text{solid}}}$$

$$\underbrace{\text{dynamic equilibrium}}_{\text{rate of dissolution} \;=\; \text{rate of precipitation}}$$

⇓

the **solution** is said to be **saturated**

The concentration of the solute in a saturated solution is known as the **solubility** or the **saturation concentration**, Cs.

$C = Cs$
saturation

A solution containing a higher concentration of solute than the solubility is said to be **supersaturated**.

$C > Cs$
supersaturation

Solubility is temperature dependent.

Driving force for precipitation

The thermodynamic driving force for nucleation and growth is the reduction of the Gibbs free energy of a supersaturated solution by forming a solid phase and maintaining an equilibrium concentration in the solution.

Supersaturation ratio:

$$S = \frac{\text{Actual concentration in solution, } C}{\text{Saturation concentration, } Cs}$$

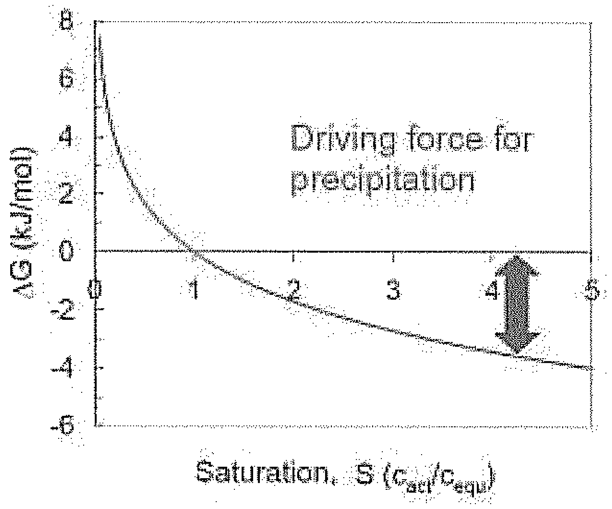
At constant temperature and pressure:

$$\boxed{\Delta G = -RT \ln S}$$

$$\underbrace{\Delta G}_{\text{molar Gibbs free energy}}$$

$\Delta G = 0$ for $S = 1$

$\Delta G < 0$ for $S > 1$



The larger the supersaturation S, the larger the driving force for precipitation.

S ⇑ ⇔ driving force ⇑

Driving force for precipitation

$$\underbrace{\Delta G^o}_{\text{standard free energy}} = \underbrace{\Delta H_{RXN}}_{\text{enthalpy of reaction}} - \underset{\text{temp.}}{T}\ \underbrace{\Delta S_{RXN}}_{\text{entropy change of reaction}}$$

$$\underbrace{\Delta G_{RXN}}_{\text{total free energy}} = \underset{\text{standard free energy}}{\Delta G^o} + \underset{\text{gas constant}}{R}\ T \ln \underset{\text{distribution coefficient}}{K}$$

For equilibrium reaction: $\Delta G_{RXN} = 0$

$$\Delta G^o = -R_g T \ln K_e$$

Castellan, Physical Chemistry

$$\boxed{\Delta G = -RT \ln \underset{\text{Supersaturation ratio}}{S}}$$

Driving force for precipitation

The thermodynamic driving force for nucleation and growth is the reduction of the overall Gibbs free energy of a supersaturated solution by forming a solid phase and maintaining an equilibrium concentration in the solution.

Supersaturation ratio:

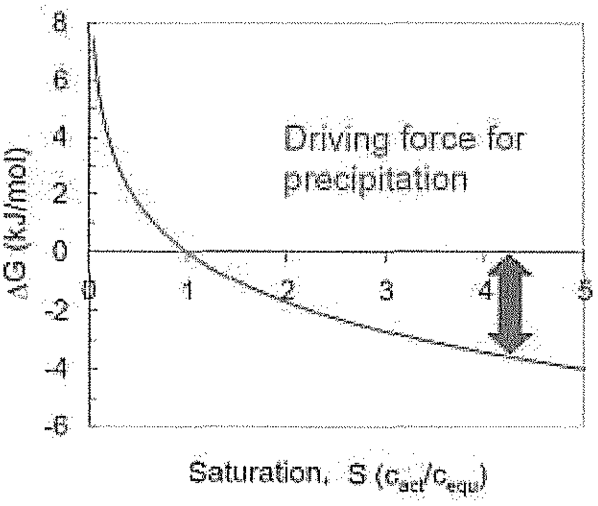
$$\boxed{S = \frac{\text{Actual concentration in solution, C}}{\text{Saturation concentration, Cs}}}$$

At constant temperature and pressure:

$$\boxed{\underbrace{\Delta G}_{\text{molar Gibbs free energy}} = -RT \ln S}$$

$\Delta G = 0$ for $S = 1$

$\Delta G < 0$ for $S > 1$

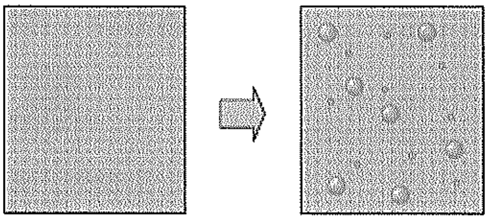


The larger the supersaturation S, the larger the driving force for precipitation.

S ↑ ⟺ driving force ↑

Principles of precipitation

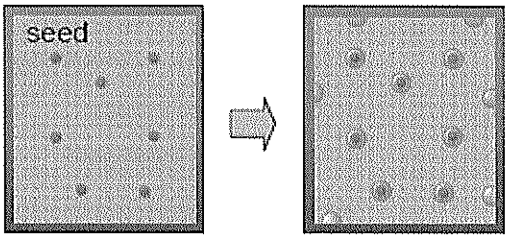
(I) Nucleation



Homogeneous solution

Homogeneous nucleation

Formation of nucleus (fine particles) is taking place in a **homogeneous solution** **without** **foreign inclusions** in the solution or on the walls of reactor



Inclusions (seed) in solution

Heterogeneous nucleation

Foreign inclusions in the solution (i.e. seed) act to assist the nucleation

n.ethz.ch/~rysj/.../Keramik
Rahaman, Ceramic Processing, p.59

Principles of precipitation

(Ia) Homogeneous nucleation

Supersaturated solution consisting of ions (e.g. hydrated metal ions)

Random local variations in concentration ↓

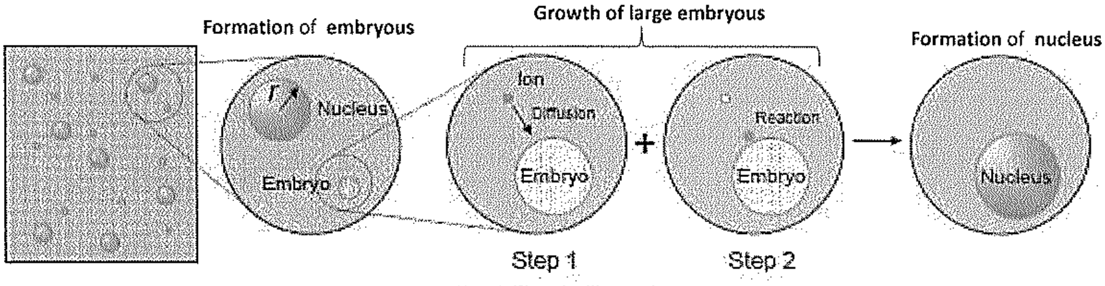
Formation of clusters of ions (**embryous**) by polymerization process

Dissolution of small embryous r < r* ↑

Growth of large embryous, r > r* ↓

Formation of solid **nuclei**

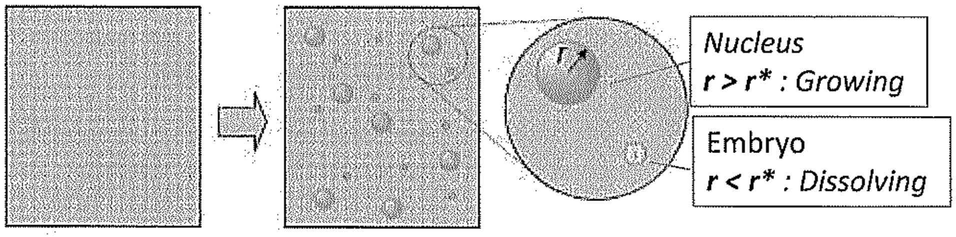
Critical size *r**



n.ethz.ch/~rysj/.../Keramik

Principles of precipitation

(Ia) Thermodynamics of homogeneous nucleation



$$\Delta G = -RT\ln S$$

Surface free energy

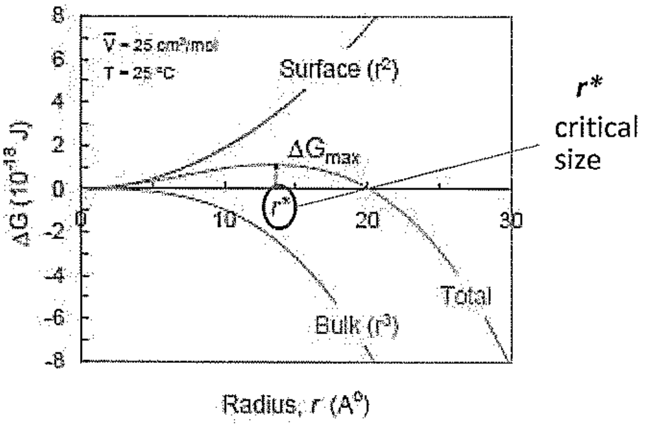
$$\Delta G = -\frac{v}{\bar{V}}RT\ln S + \gamma A$$

v = Volume of the aggregate

$\bar{V}$ = Molar volume of the precipitate

γ = Surface free energy

A = Area of the aggregate



If the particle/aggregate is a sphere:

$$\Delta G = \underbrace{\ominus\frac{4\pi r^3}{3\bar{V}}RT\ln S}_{\text{Bulk („Interior")}} \oplus \underbrace{4\pi r^2\gamma}_{\text{Surface}}$$

S < 1: ΔG always positive

S > 1: ΔG with maximum at r* (critical size)

Principles of precipitation

(Ia) Homogeneous nucleation

To increase nucleation:

(a) Increase supersaturation

Nucleation rate strongly depends on supersaturation ratio S

S ↑ ⇔ nucleation ↑

(b) Decrease surface free energy

γ ↓ ⇔ nucleation ↑

If the particle/aggregate is a sphere:

$$\Delta G = \underbrace{\ominus\frac{4\pi r^3}{3\bar{V}}RT\ln S}_{\text{Bulk („Interior")}} \oplus \underbrace{4\pi r^2\gamma}_{\text{Surface}}$$

Principles of precipitation

(Ib) Heterogeneous nucleation

- **Heterogeneous nucleation** takes only place as long as there are **seeds present**
- **Heterogeneous nucleation** takes place at **lower saturation ratio** in comparison with homogeneous nucleation
- **Heterogeneous nucleation:**

  Better control over particle size distribution, because the nucleation rate is almost independent of S
- **Homogeneous nucleation:**

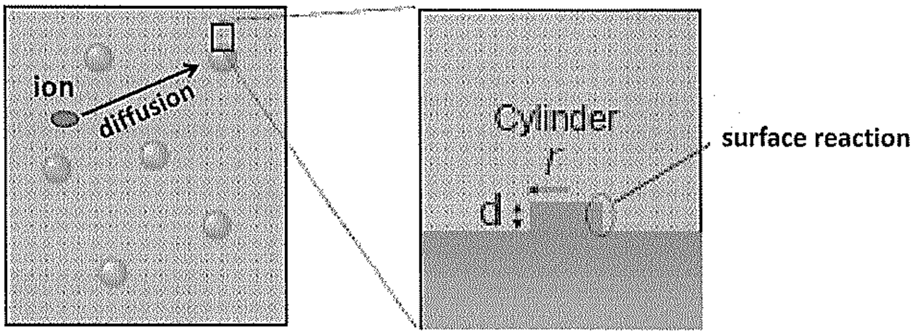
  Very sensitive to slight changes in S, **difficult to control**

Principles of precipitation

(II) Particle growth by solute precipitation

The **rate-determining step** in the **growth** of particles can be:

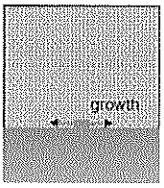
1. **Diffusion of solute species** toward the particle
2. Addition of new material to the particle surface by a **surface reaction**



Principles of precipitation

(II) Particle growth by solute precipitation

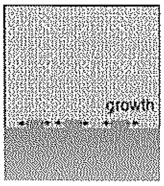
2. Addition of new material to the particle surface by a **surface reaction**



Mononuclear growth

Once a nuclear step is formed on the particle surface,
a layer has the time to completion before a new step appears

Layer by layer growth

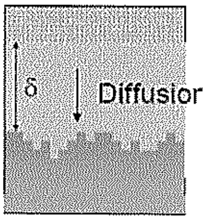


Polynuclear growth

Formation of nucleation steps on the particle surface
is fast enough to create a new layer before the
previous one been completed

Principles of precipitation

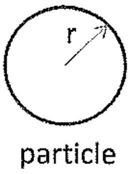
Particle growth rate

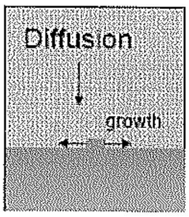


Diffusion Controlled (low γ, high S)

$$\boxed{\frac{\mathrm{d}r}{\mathrm{d}t} \propto \frac{1}{r}}$$

Growth rate is
inversely
proportional to r



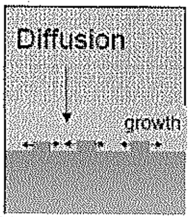


Nucleation controlled (high γ, low S)

Mononuclear

$$\boxed{\frac{\mathrm{d}r}{\mathrm{d}t} \propto r^2}$$

Growth rate is
proportional to r^2



Polynuclear

$$\boxed{\frac{\mathrm{d}r}{\mathrm{d}t} \propto r^0 = X}$$

Growth rate does
not depend on r

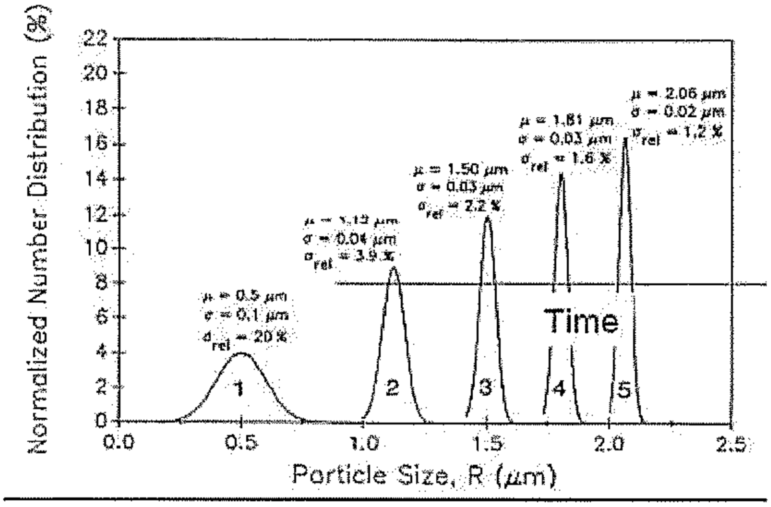
Principles of precipitation

(II) Particle growth by solute precipitation

Size distribution of particles

Diffusion Controlled (low γ, high S)

$$\boxed{\frac{\mathrm{d}r}{\mathrm{d}t} \propto \frac{1}{r}}$$



Particle size distribution narrows with growth time, i.e., smaller particles grow faster than the larger ones.

Ring Fundamentals of ceramic powder processing and synthesis

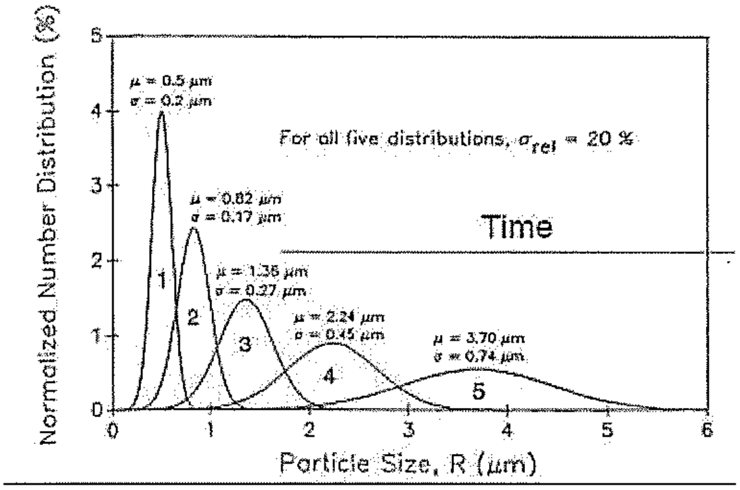
Principles of precipitation

(II) Particle growth by solute precipitation

Size distribution of particles

Mononuclear growth

$$\boxed{\frac{\mathrm{d}r}{\mathrm{d}t} \propto r^2}$$



Particle size distribution broadens with growth time, i.e., larger particles grow faster than the small ones.

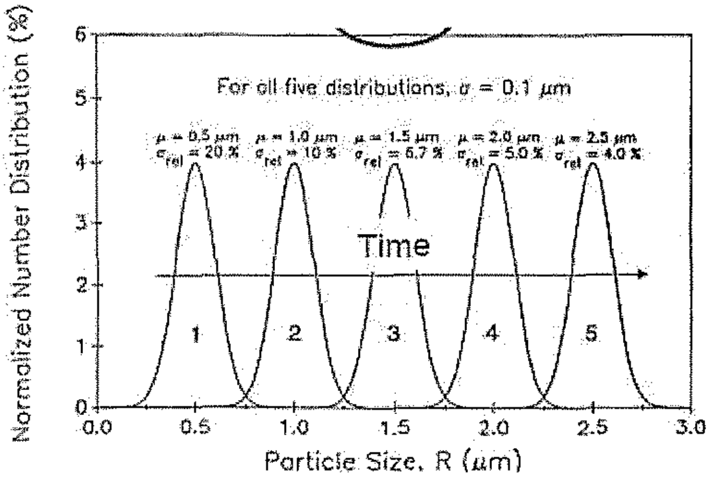
Ring Fundamentals of ceramic powder processing and synthesis

Principles of precipitation

(II) Particle growth by solute precipitation

Size distribution of particles

Polynuclear growth

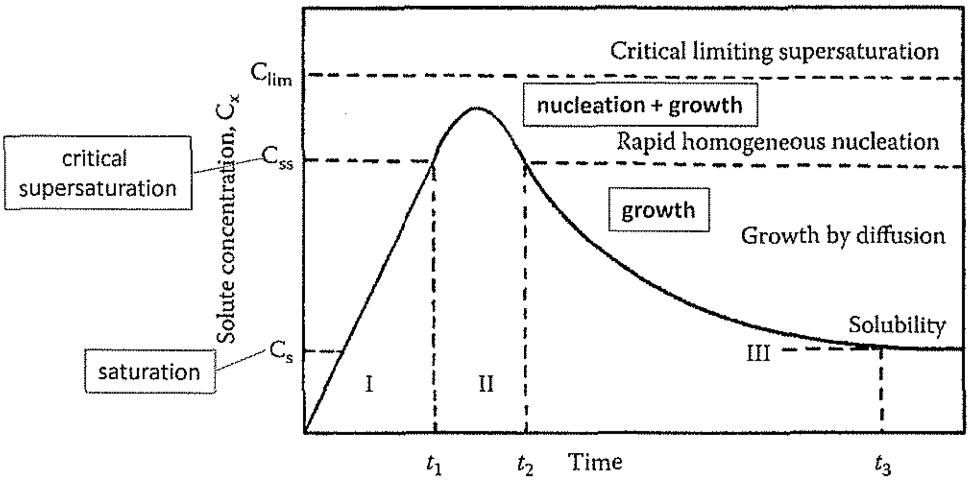


$$\boxed{\frac{\mathrm{d}r}{\mathrm{d}t} \propto r^0 = X}$$

Particle size distribution remains constant with growth time, i.e., all particles grow with the same speed.

Ring Fundamentals of ceramic powder processing and synthesis

LaMer diagram for precipitation from solution



I – as reaction proceed, the concentration of the solute increases to or above the saturation value Cs.

II – a critical supersaturation concentration, Css, will be reached at time t_1 and homogeneous nucleation and growth of solute particles start.
Concentration decreases to a value below Css after a time t_2

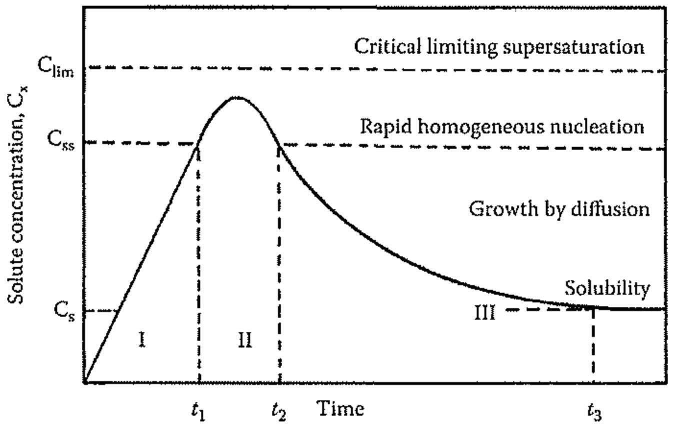
III – particle grow by diffusion of solute through liquid and precipitation on to the particle surfaces. Particle growth stops after a time t_3 when C=Cs

Rahaman, Ceramic Processing, p.63

LaMer diagram for precipitation from solution

To produce particles of uniform sizes:

- Nucleation: Nucleation should occur in a short time interval, t_2-t_1. Use a low reactant concentration
- Growth: Supply solute slowly to avoid nucleation and to provide uniform growth



Example of precipitation from solution

Hydrolysis of solutions of metal salts

Hydrolysis: Metal salt + water

- Metal ions are **hydrated** in aqueous solutions

$$Me^{z+} + H_2O \rightarrow \text{hydrated metal ions} \quad [Me(OH_2)_n]^{z+}$$

- Reaction of **deprotonation** of hydrated cation at ~ 100 °C

$$\underset{\text{hydrated cation}}{[Me(OH_2)_n]^{z+}} \leftrightarrow \underbrace{\underset{\text{hydroxylated complex}}{[Me(OH)_y(OH_2)_{n-y}]^{z+}}}_{\text{Precursor to the nucleation of particles}} + \underset{\text{proton}}{yH^+}$$

- Nucleation and growth of uniform particles by adjustment of temperature and pH

Rahaman, Ceramic Processing, p.67

Example of precipitation from solution

Hydrolysis of solutions of metal salts

Hydrolysis: Metal salt + water

- **Mixing** of $Al(NO_3)_2$ and $Al_2(SO_4)_3$:
  pH = 4.1
  $[Al^{3+}]$ to $[SO_4^{2-}]$ molar ratio = 0.5~1,
  Al concentration = $2 \cdot 10^{-4} \sim 5 \cdot 10^{-3}$ mol/dm^3
- **Heating (aging)** of mixture of $Al(NO_3)_2$ and $Al_2(SO_4)_3$
  at 98°C for up to 84 h, pH = 3.1

⇩

Particles with uniform sizes

✓ Reaction is very sensitive to temperature: no particles at T< 90°C
✓ Particle size distribution depends on pH, reactants molar ratio and concentration

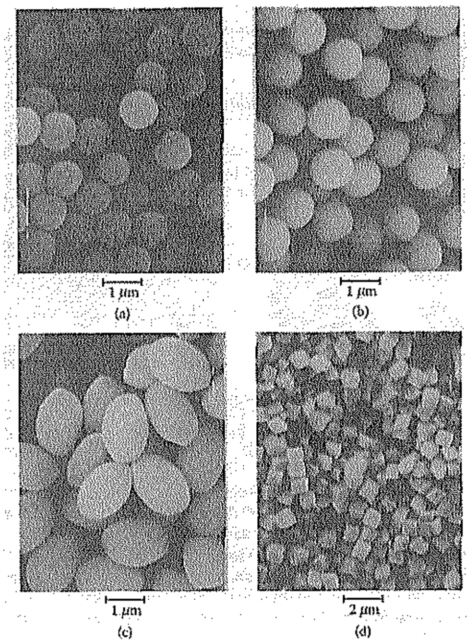
Rahaman, Ceramic Processing, p.67

Example of precipitation from solution

Precipitation of particles of various shapes

(a) Hematite
α-Fe_2O_3

(c) Iron oxide



(b) Cadmium
sulfide

(d) Calcium
carbonate

FIGURE 2.23 Examples of the sizes, shapes, and chemical compositions for powders prepared by precipitation form metal salt solutions, showing particles of (a) hematite (α-Fe_2O_3), (b) cadmium sulfide, (c) iron (III) oxide, and (d) calcium carbonate. (From Matijevic, E., Monodispersed colloidal metal oxides, sulfides, and phosphates, in *Ultrastructure Processing of Ceramics, Glasses, and Composites*, Hench, L.L. and Ulrich, D.R., Eds., Wiley, New York, 1984, chap. 27. With permission.)

Example of precipitation from solution

Shape and size distribution of particles are **sensitive** to:

- temperature
- aging time
- composition of salts
- concentration of metal salts
- pH of solution

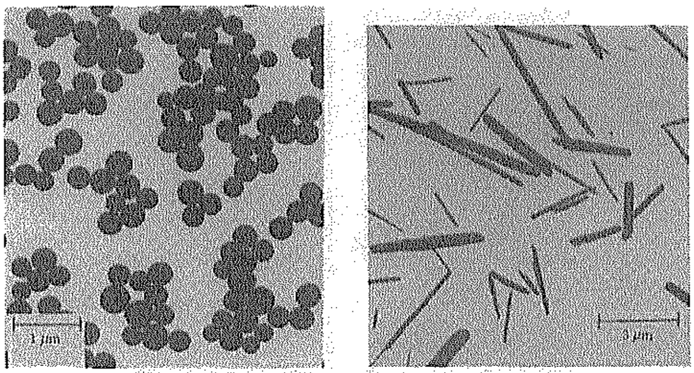


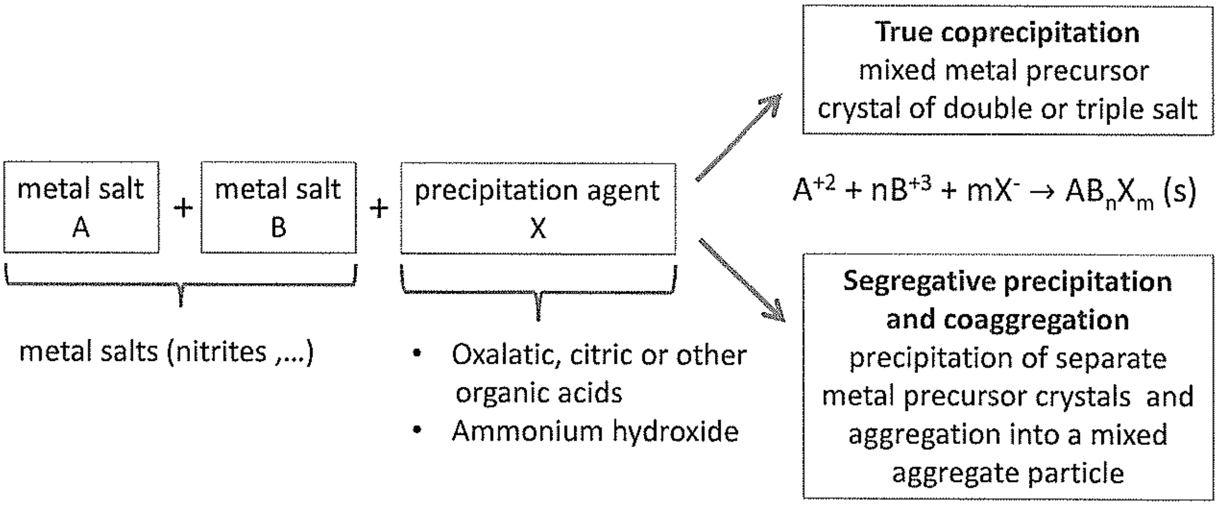
FIGURE 2.24 Particles obtained (a) by aging for 2.5 h at 90°C a solution of 1.5×10^{-2} mol/dm^3 YCl_3 and 0.5 mol/dm^3 urea and (b) by aging for 18 h at 115°C a solution of 3.0×10^{-3} mol/dm^3 YCl_3 and 3.3 mol/dm^3 urea. (From Aiken, B., Hsu, W.P., and Matijevic, E., Preparation and properties of monodispersed colloidal particles of lanthanide compounds, *J. Am. Ceram. Soc.*, 71, 845, 1988. With permission.)

Rahaman, Ceramic Processing, p.68

Coprecipitation from solution

Precipitation of complex oxides

Complex oxides are oxides that contain more than one type of metal, $BaTiO_3$.



True coprecipitation
mixed metal precursor
crystal of double or triple salt

metal salt A + metal salt B + precipitation agent X

$$A^{+2} + nB^{+3} + mX^{-} \rightarrow AB_nX_m\ (s)$$

metal salts (nitrites ,…)

- Oxalatic, citric or other organic acids
- Ammonium hydroxide

Segregative precipitation and coaggregation
precipitation of separate metal precursor crystals and aggregation into a mixed aggregate particle

$$A^{+2} + 2X^{-} \rightarrow AX_2\ (s)$$
$$B^{+3} + 3X^{-} \rightarrow BX_3\ (s)$$
$$AX_2\ (s) + BX_3\ (s) \rightarrow AB_nX_m\ (s)$$

aggregation

Ring. Fundamentals of ceramic powder processing and synthesis

Coprecipitation from solution

True coprecipitation

metal salt A + metal salt B + precipitation agent X ⟶

True coprecipitation
mixed metal precursor
crystal of double or triple salt

$A^{+2} + nB^{+3} + mX^{-} \rightarrow AB_nX_m\ (s)$

Examples:

Double metal hydroxides

$Co_3(AsO_4)2 \cdot 8H_2O$

$CdSeO_4 \cdot 2H_2O$

$LiMnO_4 \cdot 3H_2O$

$ZnCr_2O_4 \cdot 2H_2O$

$Co_2Fe(CN)_6 \cdot xH_2O$

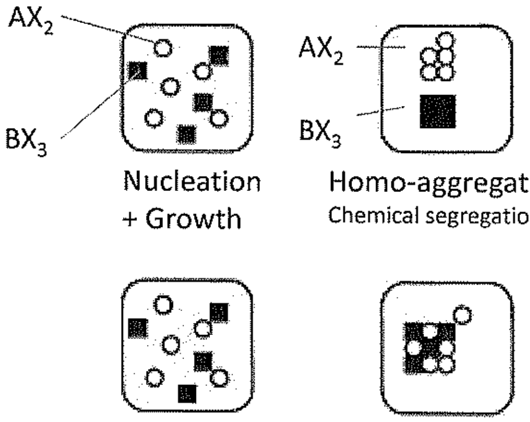
Very good (atom level) mixing of metal components

Coprecipitation from solution

Segregative precipitation and coaggregation

metal salt A + metal salt B + precipitation agent X ⟶

Segregative precipitation and coaggregation
precipitation of separate metal precursor crystals and aggregation into a mixed aggregate particle



Nucleation + Growth

Homo-aggregation
Chemical segregation on aggregate scale

Nucleation + Growth

Hetero-aggregation
Chemical segregation on particle scale

$A^{+2} + 2X^{-} \rightarrow AX_2\ (s)$
$B^{+3} + 3X^{-} \rightarrow BX_3\ (s)$

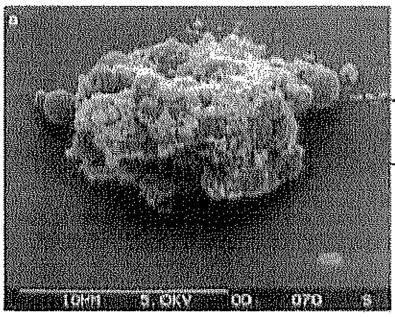
To decrease segregation use particles of small sizes

Coprecipitation from solution

Segregative precipitation and coaggregation

Example: $Ba(NO_3)_2 + Y(NO_3)_2 + Cu(NO_3)_2 + C_6H_8O_7 \rightarrow BaY_2Cu_3$oxalate

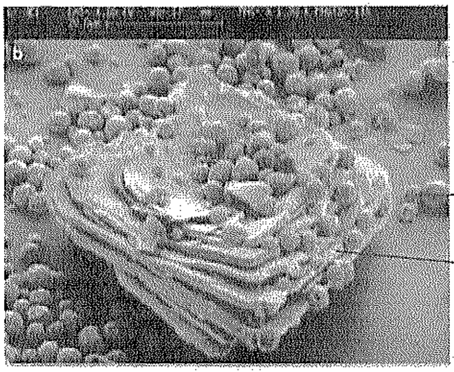
Oxalic acid



Samples taken 5 min after mixing

Copper oxalate (large spheres)

Yttrium barrium oxalate mixture (small particles)



Samples taken 2 days after mixing

Copper oxalate (large spheres)

Yttrium barrium oxalate mixture coaggregated with copper oxalate (crystal)

Ring Fundamentals of ceramic powder processing and synthesis

Advantages and disadvantages of precipitation method

Advantages

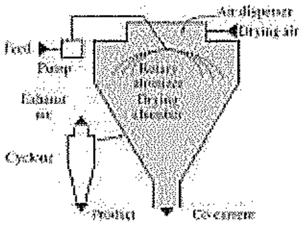
- High degree of homogeneity
- Low reaction temperature
- High purity raw materials
- Possible production of particles with uniform size

Disadvantages

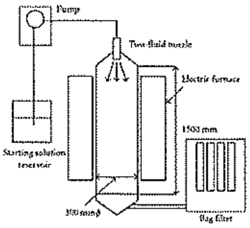
- Relatively high cost of raw materials
- Difficult to control particle average size, size distribution and shape (sensitive to process parameters)
- Special handling of raw materials usually required

Production of powdered material from a solution by evaporation

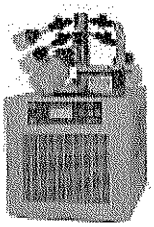
Spray drying



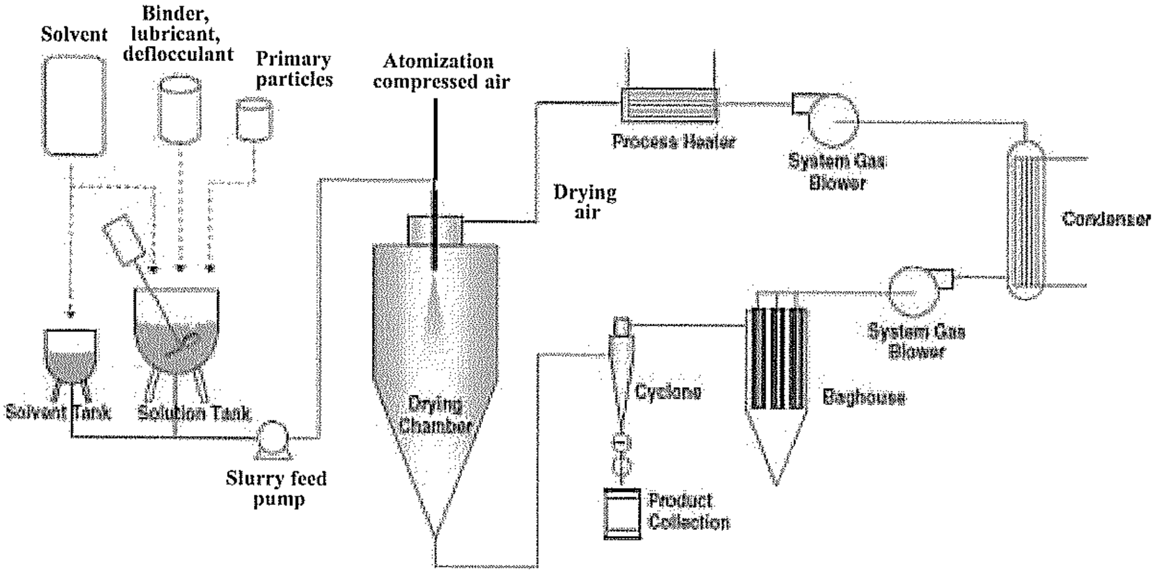
Spray pyrolysis



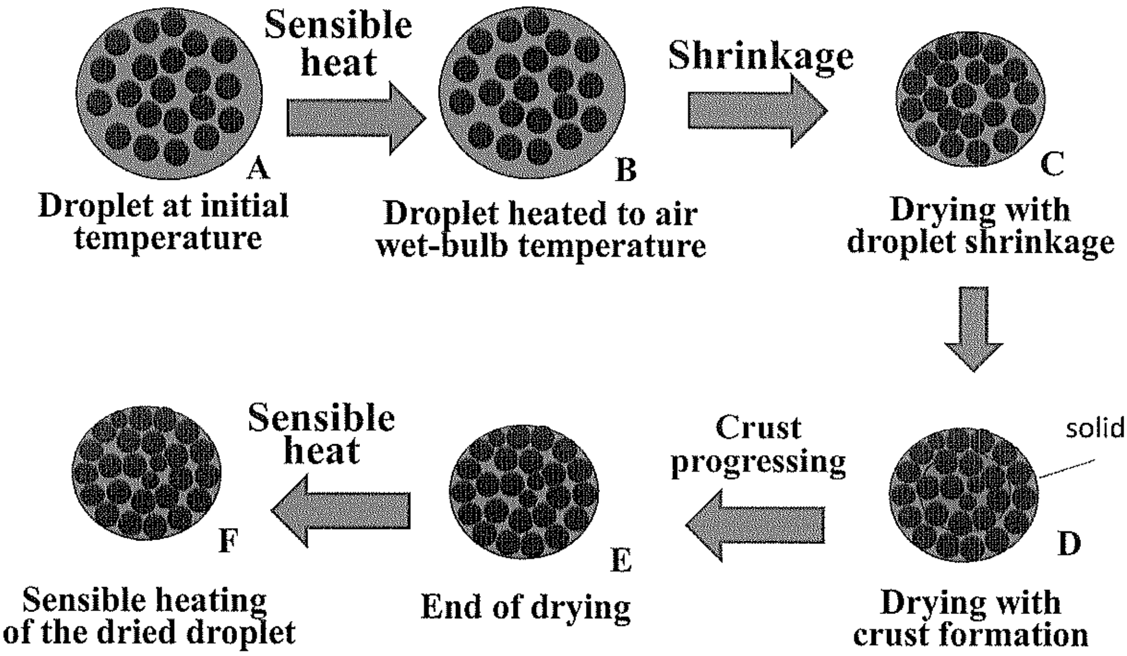
Freeze drying



General Spray-drying Equipment Configuration



Mechanism of drying of a slurry droplet



Sensible heat

Shrinkage

A
Droplet at initial temperature

B
Droplet heated to air wet-bulb temperature

C
Drying with droplet shrinkage

solid

D
Drying with crust formation

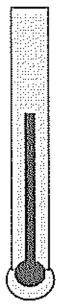
Crust progressing

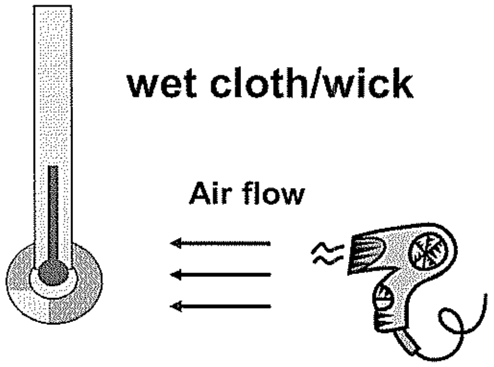
E
End of drying

Sensible heat

F
Sensible heating of the dried droplet

Dry-bulb and wet-bulb temperature

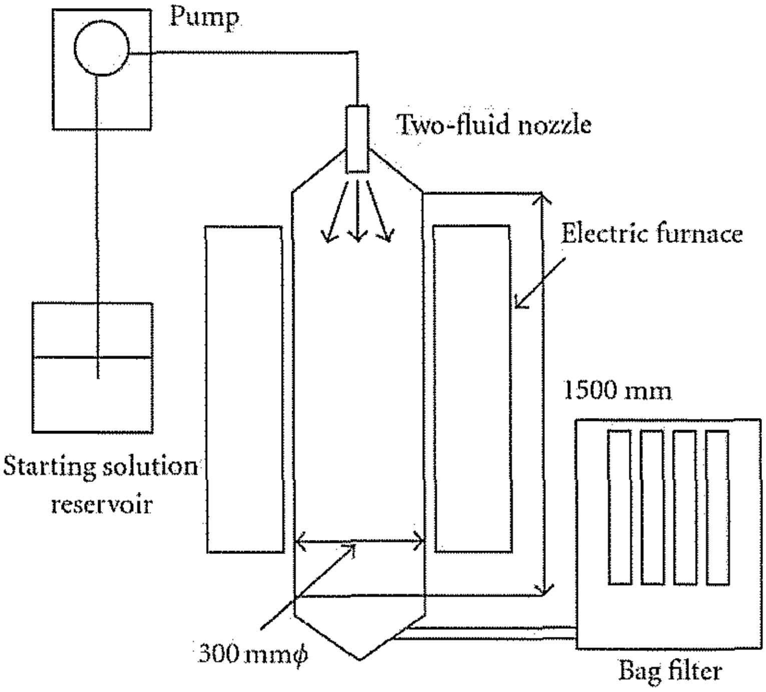




Dry bulb temperature: the ordinary temperature you measure with a thermometer

Evaporation requires energy. The wick and therefore the thermometer bulb decreases in temperature below the dry-bulb temperature until the rate of heat transfer from the warmer air to the wick is just equal to the rate of heat transfer needed to provide for the evaporation of water from the wick into the air stream.
The temperature reached is called the **wet-bulb temperature**

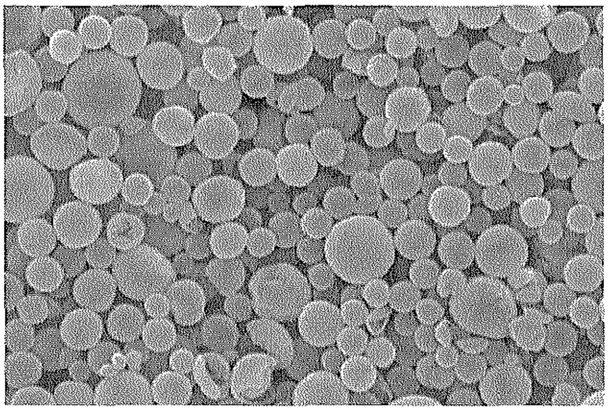
General Spray-pyrolysis Equipment Configuration



Akao et al. International Journal of Chemical Engineering, 2010, Article ID 175914

Mass Production of LiFePO4/C Powders by Large Type Spray Pyrolysis Apparatus and Its Application to Cathode for Lithium Ion Battery

Starting reagents: $LiNO_3$, $Fe(NO_3)_3 \cdot 9H_2O$, and H_3PO_4.
Source of C: Various types of organic compounds such as sucrose, fructose, white sugar, and citric acid
Pyrolysis temperature: 500°C
As-prepared LiFePO4/C powders were heat treated at 700°C for 2 hours in the electric furnace under argon (95%)/hydrogen (5%) atmosphere



Akao et al. International Journal of Chemical Engineering, 2010, Article ID 175914

Synthetic Routes of Ceramic Materials

Conventional Routes

- Solid state reaction
  - Chemical reaction between solids
  - Decomposition
  - Reduction

Non-Conventional Routes

- Liquid phase solution
  - Precipitation from solution
  - Co-Precipitation
  - Sol-Gel Processing
- **Vapor phase reaction**
  - **Gas-solid reaction**
  - **Liquid-gas reaction**
  - Gas-gas reaction

Solid State Reactions

Lecture overview

Powder synthesis by fluid-solid reaction

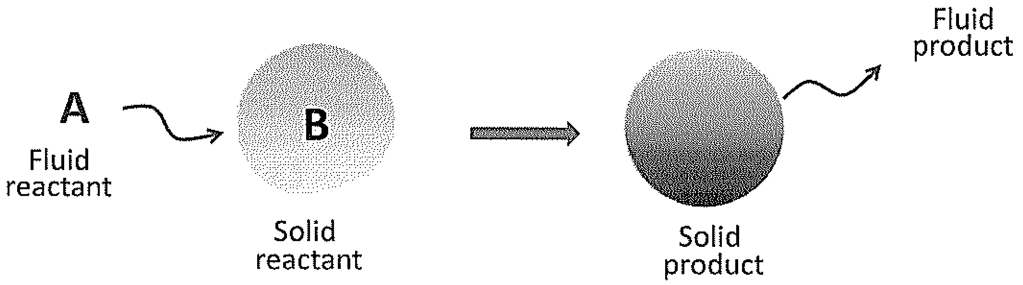
- Introduction to fluid-solid reaction
- Examples of ceramic powder synthesis by gas-solid reaction
- Mechanism of gas-solid reactions
- Examples of ceramic powder synthesis by liquid-gas reaction
- Advantages and disadvantages of fluid-solid reaction for synthesis of ceramic powder

Fluid Solid Reactions

Fluid-solid reaction: Heterogeneous reactions in which a gas or liquid contacts a solid reactant, reacts with solid reactant, and transforms it into product

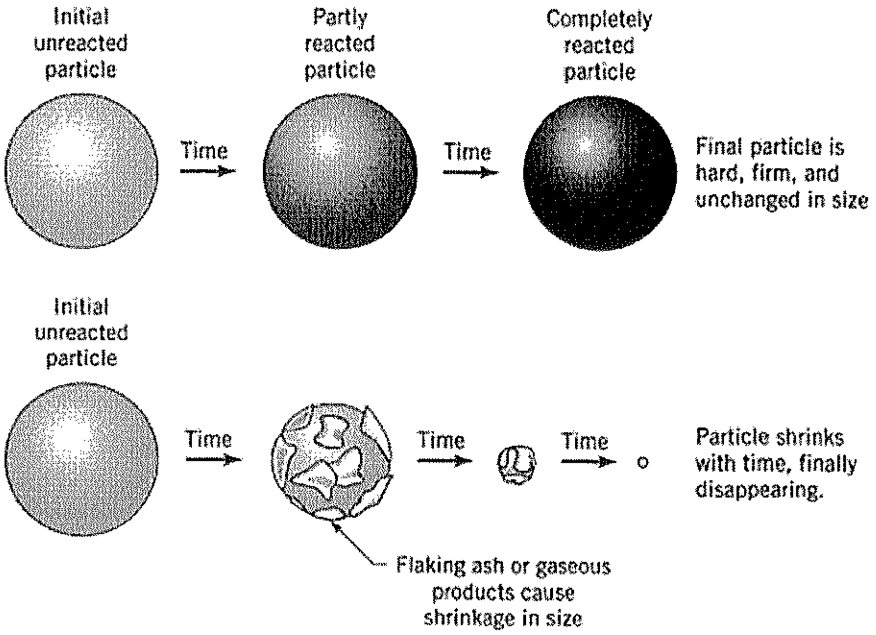
$$\text{A(fluid)} + b\text{B(solid)} \rightarrow \text{solid products}$$

$$\boxed{\text{A(fluid)} + b\text{B(solid)} \rightarrow \text{fluid and solid products}}$$



Fluid Solid Reactions

Different behavior of reacting solid particles



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Examples of gas-solid reactions

- Oxidation of sulfide ores to produce metal oxides

  Preparation of zinc oxide

  $2ZnS(s) + 3\,O_2(g) \rightarrow 2ZnO\,(s) + 2SO_2\,(g)$ — Strongly exothermic

  Preparation of iron oxide

  $4FeS_2(s) + 11\,O_2(g) \rightarrow 2Fe_2O_3\,(s) + 8SO_2\,(g)$

- Reduction of metal oxides with hydrogen

  $Fe_3O_4(s) + 4H_2\,(gas) \rightarrow 3Fe\,(s) + 4H_2O\,(g)$

- Oxidation of metals

  $O_2(g) + 4/3\,Al\,(s) \rightarrow 2/3\,Al_2O_3\,(s)$ — Strongly exothermic

- Nitridation of metals

  $N_2(g) + 3/2\,Si\,(s) \rightarrow 1/2\,Si_3N_4\,(s)$ — Strongly endothermic

  $N_2(g) + 2\,Al\,(s) \rightarrow 2\,AlN\,(s)$

  $N_2(g) + 2\,B\,(s) \rightarrow BN\,(s)$

- Carburization of metals

  $N_2(g) + TiC\,(s) \rightarrow TiN(s) + C(s)$

  $N_2(g) + MgC_2(s) \rightarrow MgCN_2(s) + C(s)$

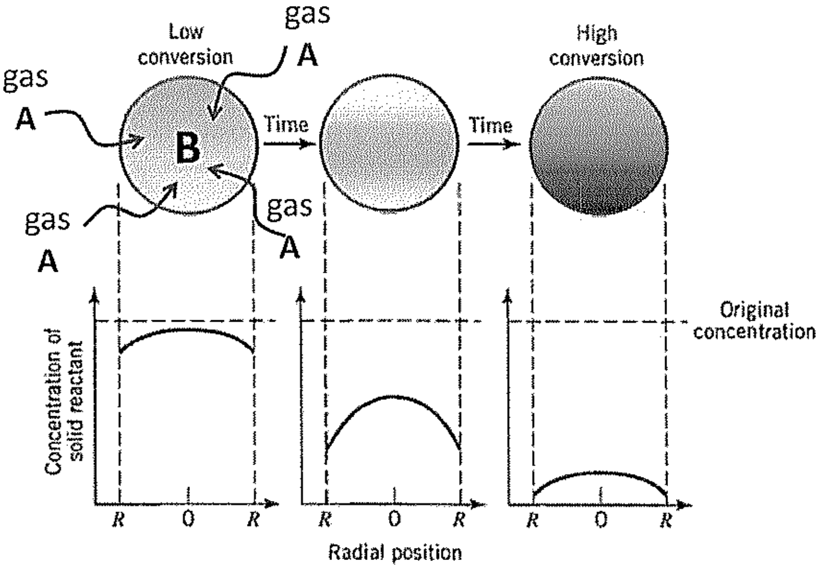
Ring Fundamentals of ceramic powder processing

Mechanism of fluid-solid reactions

$A(fluid) + bB(solid) \rightarrow$ fluid and solid products

Progressive-Conversion Model

- **Reactant gas** enters and reacts **throughout the particle** at all times
- **Solid reactant** is converted continuously and progressively **throughout the particle**



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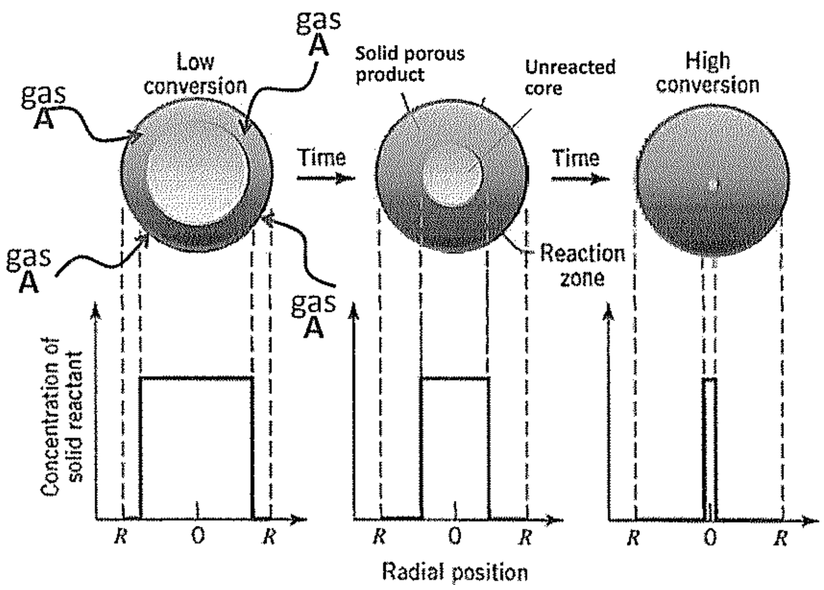
Mechanism of fluid-solid reactions

A(fluid) + bB(solid) → fluid and solid products

Shrinking-Core Model

- **Reaction** occurs first at the **outer surface** of the **particle**. The reaction zone then moves into solid, leaving behind completely converted material and inert solid product, so called 'ash'.
- At any time there exists an **unreacted core** of material which shrinks in size during reaction



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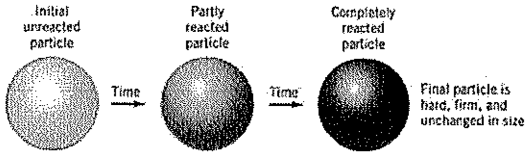
Shrinking-Core Model for Spherical Particles of Unchanged Size



Five steps occurring in succession during reaction

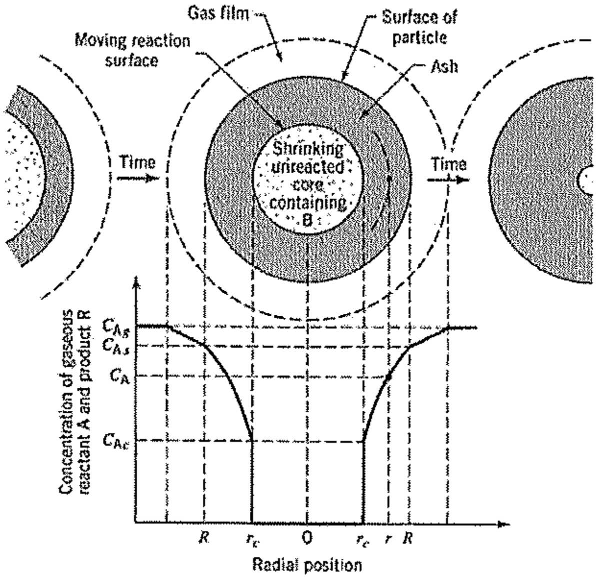
Step 1. Diffusion of gaseous reactant A through film surrounding particle to the surface of solid.

Step 2. Diffusion of A through layer of ash (product) to the surface of the unreacted core.

Step 3. Reaction of gaseous A with solid at this reaction surface.

Step 4. Diffusion of gaseous products through the product layer back to exterior surface of solid.

Step 5. Diffusion of gaseous products through gas film back into the main body of fluid.



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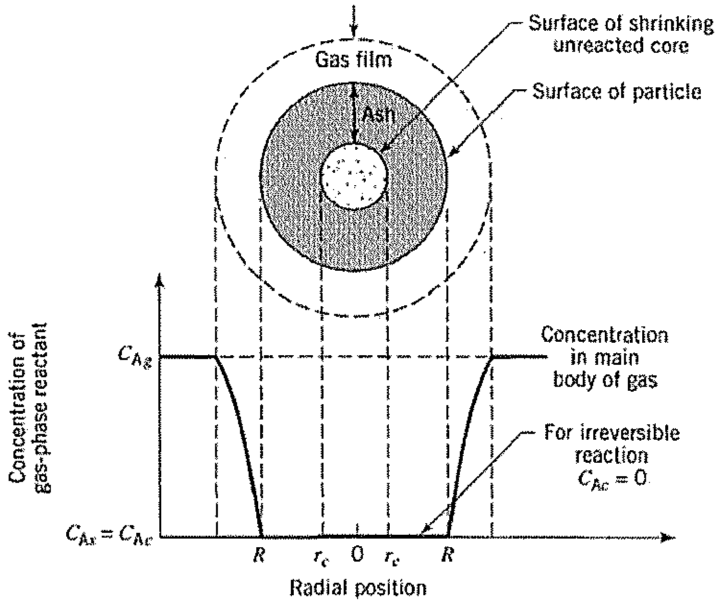
Shrinking-Core Model for Spherical Particles of Unchanged Size

Rate limiting step:

(1) Diffusion through gas film



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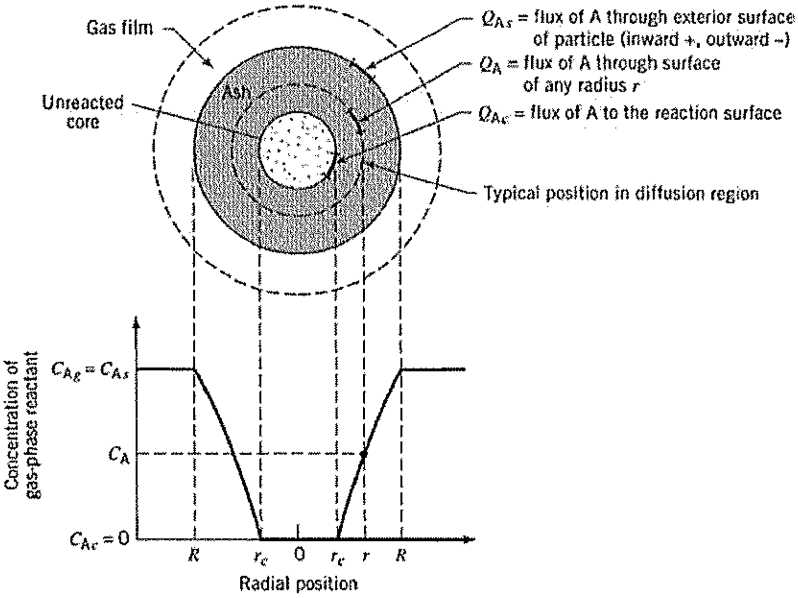
Shrinking-Core Model for Spherical Particles of Unchanged Size

Rate limiting step:

(2) Diffusion through product layer



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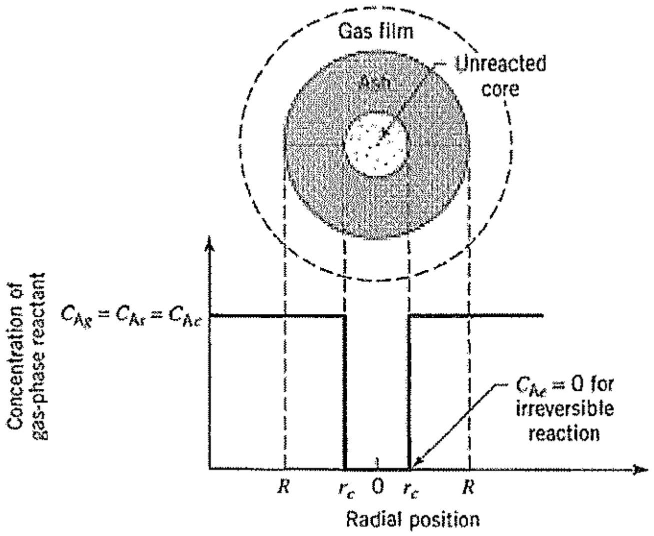
Shrinking-Core Model for Spherical Particles of Unchanged Size

Rate limiting step:

(3) Chemical reaction



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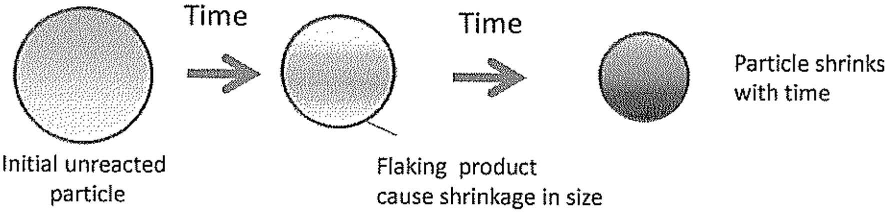
Model of shrinking spherical particles

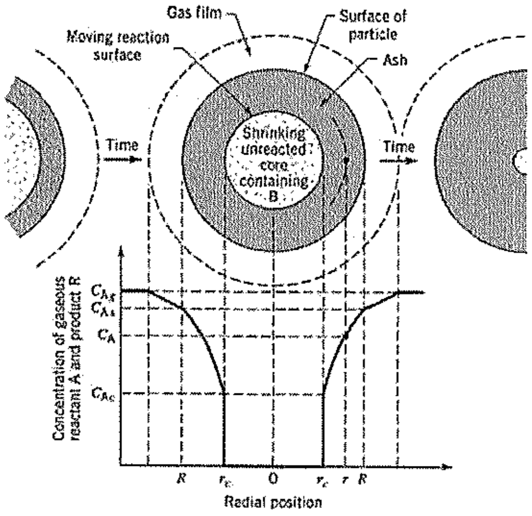


Three steps occurring in succession during reaction

Step 1. Diffusion of gaseous reactant A through film surrounding particle to the surface of solid.

Step 2. Reaction of gaseous A with solid at this reaction surface.

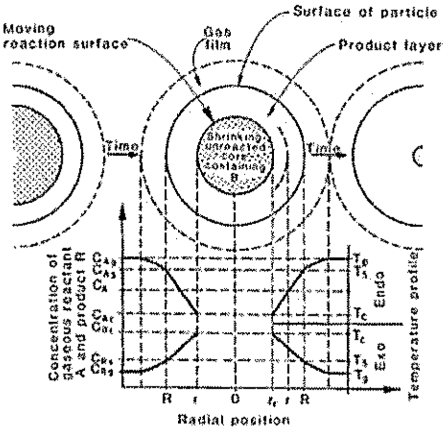
Step 3. Diffusion of gaseous products through gas film back into the main body of fluid.



Fluid-solid reaction kinetics

Possible rate determining steps:

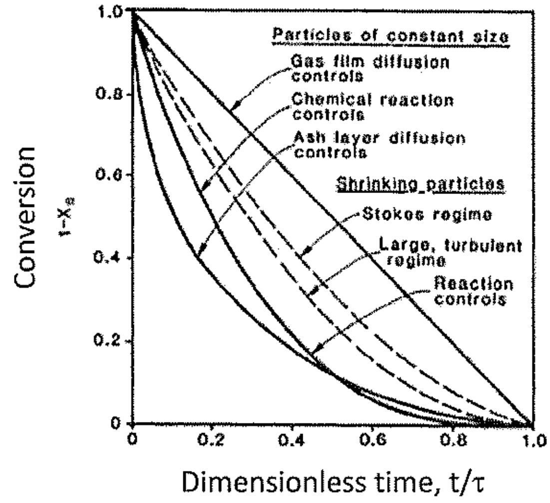
- Surface reaction
- Mass transfer in the boundary layer surrounding the particle
- Diffusion in the product layer
- Heat transfer in the boundary layer surrounding the particle
- Heat conduction in the product layer



Ring Fundamentals of ceramic powder processing

Fluid-solid reaction kinetics

Conversion versus time of a single spherical particle reacting with a surrounding gas



τ time for complete conversion

$t \alpha R^{1.5-2.0}$ for boundary layer mass transfer or boundary layer heat transfer (the exponent drops as the Reynolds number rises, i.e. turbulent flow),

$t \alpha R^2$ for product layer diffusion control or product layer heat conduction control,

$t \alpha R$ for chemical reaction control.

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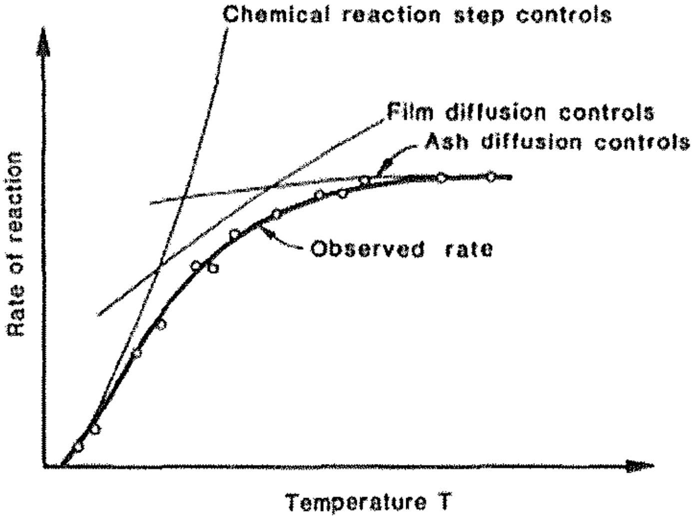
Fluid-solid reaction kinetics

Rate of reaction versus temperature



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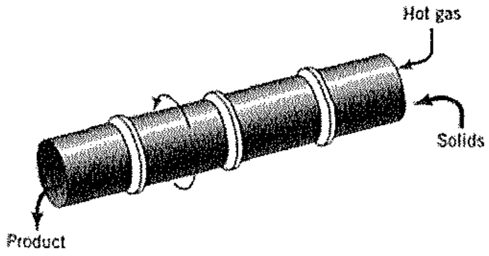
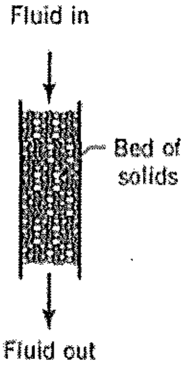
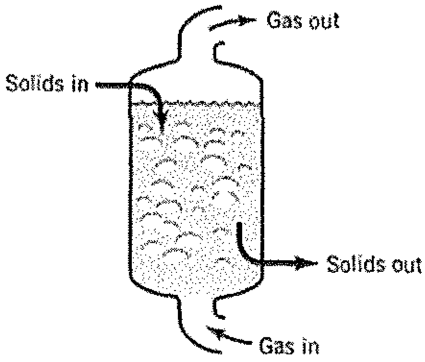
Fluid-solid reactors



Rotary dryer



Packed or moving bed



Fluidized bed

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Liquid-gas reaction

Synthesis of Si_3N_4

T=273 K

$SiCl_4$ (liq) + $6NH_3$ (g) → $Si(NH)_2$ + $4NH_4Cl$

Silicon tetrachloride ammonia silicon diimide ammonium chloride

(polymeric species)

Polymerization, T=633K T=673K

$Si(NH)_2 \rightarrow 6[Si(NH)_2]_f \rightarrow 2[Si_3(NH)_3N_2]_f + 2f\,NH_3$

silicon diimide

T=923K

$2[Si_3(NH)_3N_2]_f \rightarrow 3[Si_2(NH)N_2]_f + f\,NH_3$

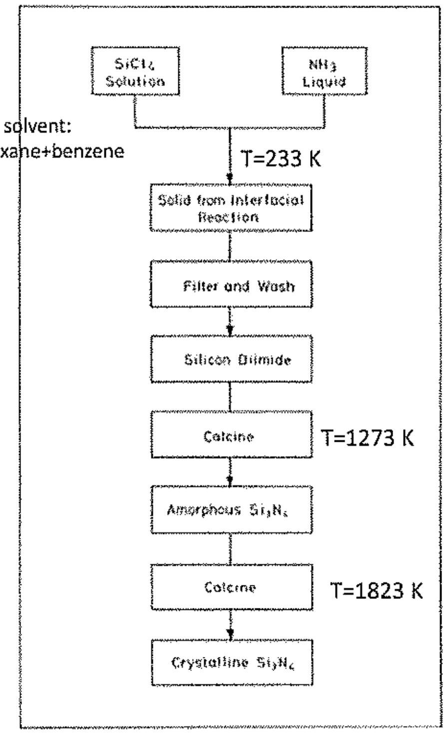
$$\downarrow \text{T=1473-1673K}$$

α-Si_3N_4

Segal Chemical synthesis of advanced ceramic materials, p92

Liquid-liquid reaction

Synthesis of Si_3N_4 (UBE process)



Organic solvent: Cyclohexane+benzene

T=233 K

T=1273 K

T=1823 K

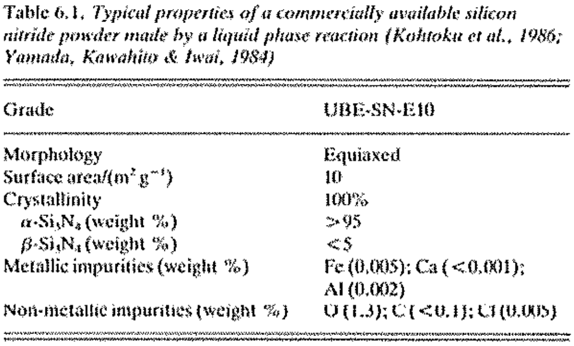
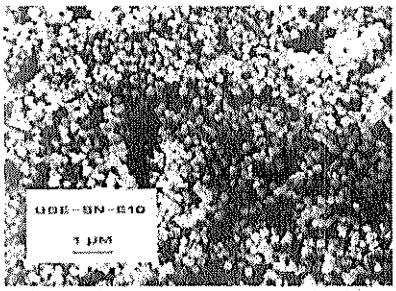


Table 6.1. *Typical properties of a commercially available silicon nitride powder made by a liquid phase reaction (Kohtoku et al., 1986; Yamada, Kawahito & Iwai, 1984)*

Grade	UBE-SN-E10
Morphology	Equiaxed
Surface area/($m^2\,g^{-1}$)	10
Crystallinity	100%
α-Si_3N_4 (weight %)	>95
β-Si_3N_4 (weight %)	<5
Metallic impurities (weight %)	Fe (0,005); Ca (<0,001); Al (0,002)
Non-metallic impurities (weight %)	O (1,3); C (<0,1); Cl (0,005)



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Segal Chemical synthesis of advanced ceramic materials

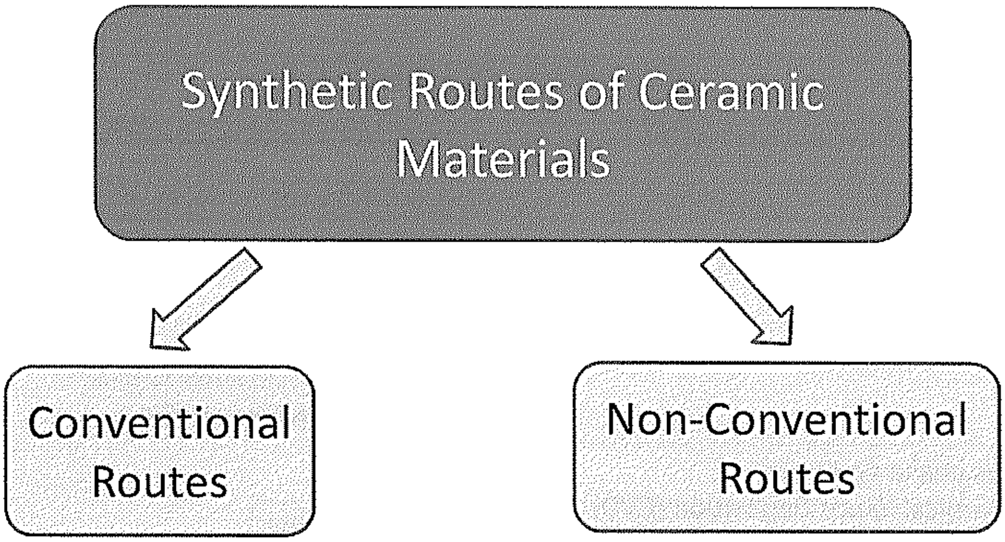
Fluid-Solid Reactions

Advantages

- Inexpensive for particles of large size
- Relatively simple reactor systems
- Suitable for large scale production

Disadvantages

- Low purity
- Product can cover unreacted reactant and yield to incomplete reaction → impure final product
- Relatively expensive for fine powder



Synthetic Routes of Ceramic Materials

Conventional Routes

Non-Conventional Routes

- Solid state reaction
  - Chemical reaction between solids
  - Decomposition
  - Reduction

- Liquid phase solution
  - Precipitation from solution
  - Co-Precipitation
  - Sol-Gel Processing
- **Vapor phase reaction**
  - Gas-solid reaction
  - Liquid-gas reaction
  - **Gas-gas reaction**

Synthesis of ceramic materials with gas phase reactants

Lecture overview

- Introduction to gas phase processing
- Mechanism of gas phase processes
- Typical reactor configurations
- Examples of ceramic synthesis by gas phase method
- Advantages and disadvantages of gas phase method for synthesis of ceramic materials

Introduction to gas phase synthesis of ceramic materials

Gas phase synthesis involves the dissociation and/or chemical reactions of volatile reactants in gas phase or on a growth surface in a activated (flame, heat, light, plasma) environment, followed by the formation of a stable solid product.

Gas phase synthesis
Chemical Vapor Deposition (CVD)

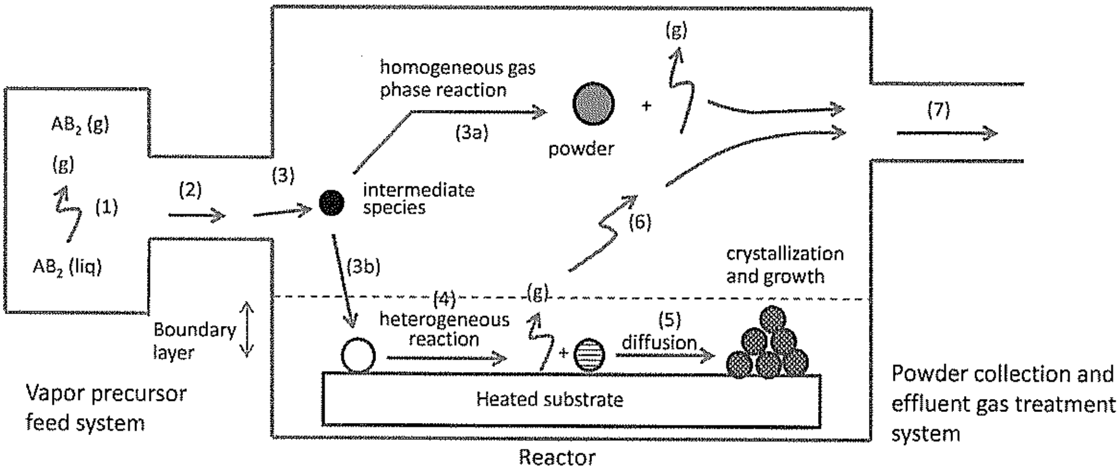
→ Powder production

Titania, Silica, alumina

→ Coating

- semiconductors (e.g. Si, Ge, III–V, II–VI
- dielectrics (e.g. SiO_2, AlN, Si_3N_4, etc.)
- refractory ceramic materials (e.g. TiB_2, SiC, B_4C, BN, TiN, Al_2O_3, ZrO_2, $MoSi_2$, diamond, etc.)
- ceramic fibres (e.g. SiC and C) and ceramic matrix composites (e.g. SiC/SiC,SiC/C)

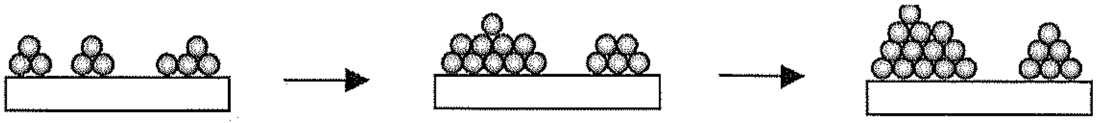
Mechanism of gas phase synthesis of ceramic materials



(1) Generation of active gaseous reactant species.
(2) Transport of the gaseous species into the reaction chamber.
(3) Gaseous reactants undergo gas phase reactions forming intermediate species:
  (a) homogeneous gas phase reaction forming powders and volatile by-products in the gas phase.
  (b) diffusion/convection of the intermediate species across the boundary layer close to the substrate surface.
(4) Absorption of gaseous reactants onto the heated substrate and the heterogeneous reaction at the gas–solid interface (i.e. heated substrate) which produces the deposit and by-product species.
(5) Diffusion of deposits along the heated substrate surface, formation of the crystallization center and growth of the film.
(6) Gaseous by-products are removed from the boundary layer through diffusion or convection.
(7) Transport of unreacted gaseous precursors and by-products away from the deposition chamber.

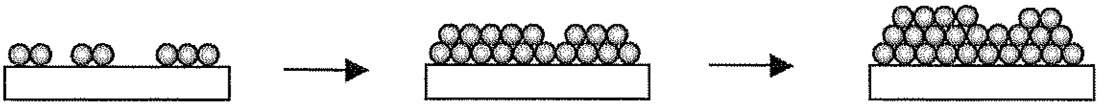
K.L. Choy / Progress in Materials Science 48 (2003) 57–170

Mechanism of initial nucleation in film growth



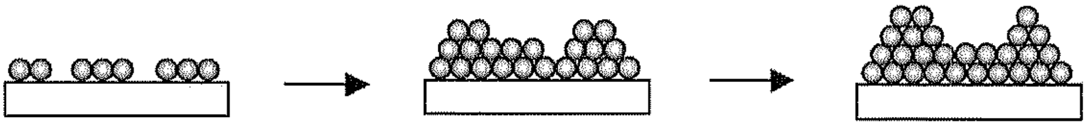
Island or Volmer-Weber growth

Island growth occurs when the growth species are more strongly bonded to each other than to the substrate. Subsequent growth results in the coalescence of islands to form a continuous film.



Layer or Frank- van der Merwe growth

Layer growth occurs when the growth species are more strongly bonded to the substrate than to each other. First, a complete monolayer is formed, then the deposition of a second layer occurs.



Island-layer or Stranski-Krastonov growth

Island-layer growth is a combination of layer growth and island growth. Such a growth mode typically involves stress, which is developed during the formation of nuclei or films.

Chemical processing of ceramics, p 512

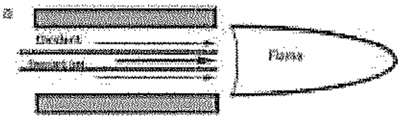
Typical chemical reactions

- **Pyrolysis or thermal decomposition:**
  SiH_4 (g) → Si (s) + $2H_2$ (g) at 650°C
  $Ni(CO)_4$ (g) → Ni (s) + 4CO (g) at 180°C
- **Reduction:**
  $SiCl_4$ (g) + $2H_2$ (g) → Si (s) + 4HCl (g) at 1200°C
  WF_6 (g) + $3H_2$ (g) → W (s) + 6HF (g) at 300°C
- **Oxidation:**
  SiH_4 (g) + O_2 (g) → SiO_2 (s) + $2H_2$ (g) at 450°C
  $4PH_3$ (g) + $5O_2$ (g) → $2P2O_5$ (s) + $6H_2$ (g) at 450°C
- **Compound formation:**
  $SiCl_4$ (g) + CH_4 (g) → SiC (s) + 4HCl (g) at 1400°C
  $TiCl_4$ (g) + CH_4 (g) → TiC (s) + 4HCl (g) at 1000°C
- **Disproportionation:**
  $2GeI_2$ (g) → Ge (s) + GeI_4 (g) at 300°C
- **Reversible transfer:**
  As_4 (g) + As_2 (g) + 6GaCl (g) + $3H_2$ (g) → 6GaAs (s) + 6HCl (g) at 750°C

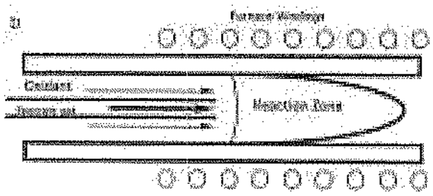
Chemical processing of ceramics, p 512

Schematics of gas phase reactors

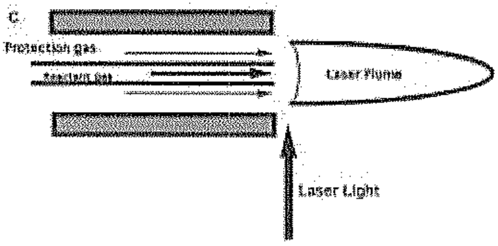
Flame reactor



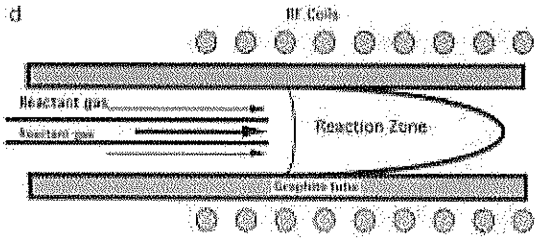
Furnace reactor



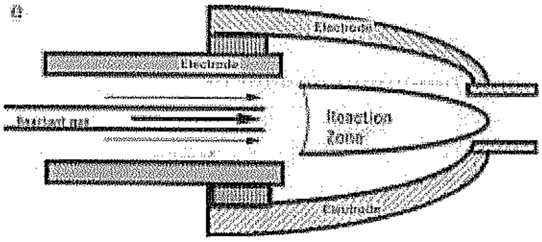
Laser reactor



Radio frequency plasma reactor



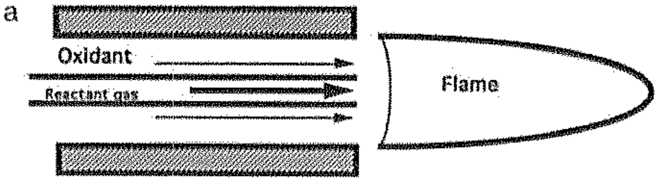
Direct current plasma reactor



Ring, Fundamentals of Ceramic Powder Processing and Synthesis, p. 258

Flame synthesis of ceramic powder

Flame reactor



A flame is the visible, gaseous part of a fire. The applied heat causes fuel molecules in the candle wax to vaporize. In this state they can then readily react with oxygen in the air, which gives off enough heat in subsequent exothermic reaction to vaporize yet more fuel, thus sustaining a consistent flame.

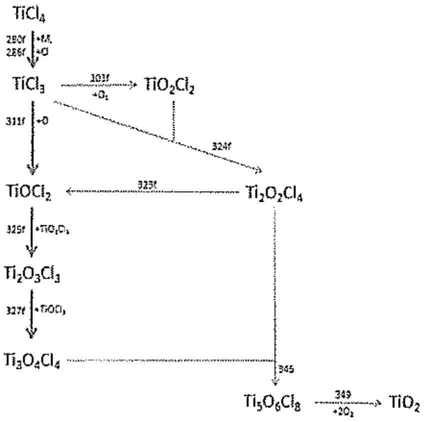
http://en.wikipedia.org/wiki/Flame

Examples:

Reaction of titanium tetrachloride with oxygen or steam to produce a submicron spherical pigment grade titania

$TiCl_4$ (g) + $2H_2O$ (g) → TiO_2 (s) + 4HCl (g)

Highly exothermic reaction

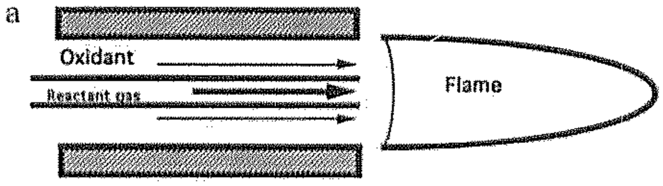


Singh Direct Numerical Simulation and Reaction Path Analysis of Titania Formation in Flame Synthesis

Ring, Fundamentals of Ceramic Powder Processing and Synthesis, p. 258

Flame synthesis of ceramic powder

Flame reactor



Examples:

- Reaction of silicon tetrachloride with oxygen to produce silica

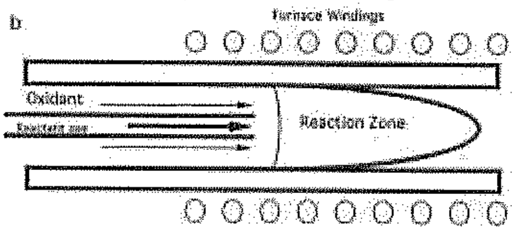
  $SiCl_4$ (g) + O_2 (g) → SiO_2 (s) + $2Cl_2$ (g)

- Production of Al_2O_3
  reactant: acetylacetone $Al(C_3H_7O)_3$
- Production of Fe_2O_3, Cr_2O_3, Al_2O_3, V_2O_3, TiO_2, SnO_2, SiO_2, ZrO_2
  reactant: metal chlorides
- Production of GeO_2, SiO_2, PO_5, B_2O_3
  reactant: $GeCl_4$, $SiCl_4$, $SiBr_4$, $POCl_3$, BCl_3

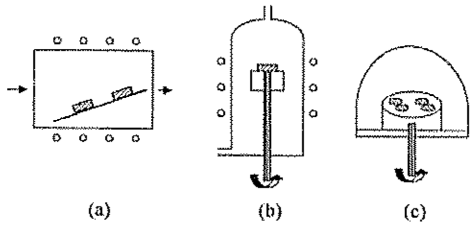
Singh Direct Numerical Simulation and Reaction Path Analysis of Titania Formation in Flame Synthesis
Ring, Fundamentals of Ceramic Powder Processing and Synthesis, p. 258

Chemical Vapor Deposition process

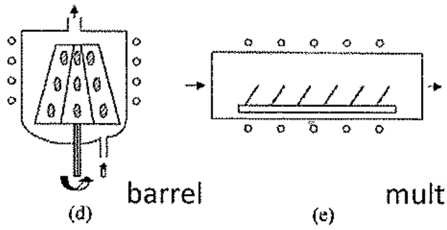
Furnace reactor



Various CVD reactor configurations for coating:



horizontal vertical semi-pancake



barrel multiple wafer

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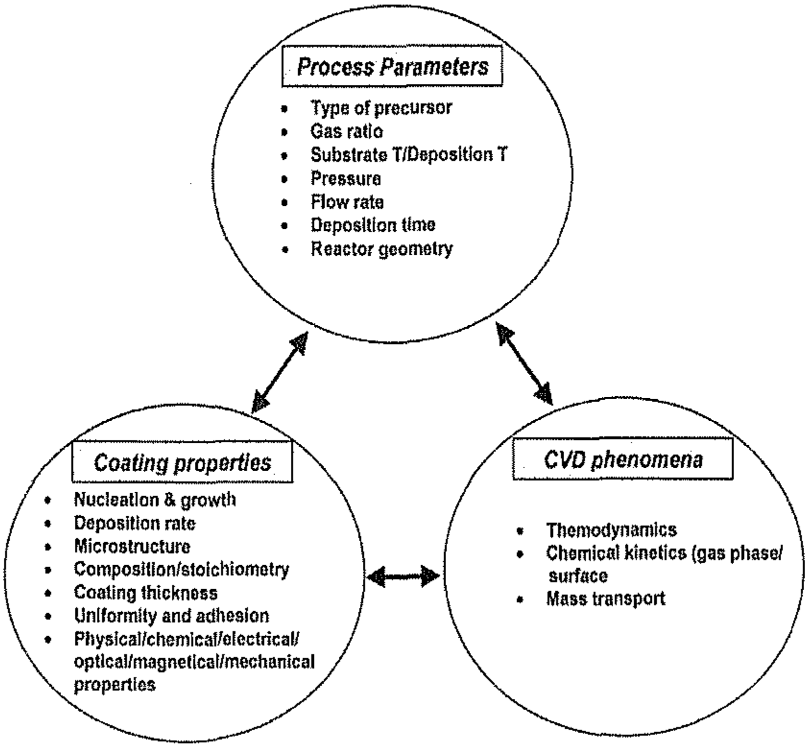
Relationship of process parameters, CVD phenomena and coating properties



Process Parameters

- Type of precursor
- Gas ratio
- Substrate T/Deposition T
- Pressure
- Flow rate
- Deposition time
- Reactor geometry

Coating properties

- Nucleation & growth
- Deposition rate
- Microstructure
- Composition/stoichiometry
- Coating thickness
- Uniformity and adhesion
- Physical/chemical/electrical/optical/magnetical/mechanical properties

CVD phenomena

- Themodynamics
- Chemical kinetics (gas phase/surface
- Mass transport

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Relationship of process parameters, CVD phenomena and coating properties

Temperature

- controls both the thermodynamics and the kinetics of the coating process
- deposition temperature must be achieved and maintained in order for the reaction to occur on the substrate and not in the gas phase
- temperature must be chosen to result in an appropriate microstructure of product (e.g. grain size and shape)
- the uniformity of the coating depends on temperature

Pressure

- Atmospheric pressure – growth processes are frequently transport controlled The structure and composition of the deposited films depend on the substrate temperature, gas flow rates, reactor geometry and gas viscosity
- Low pressure - growth processes are frequently controlled by chemical reaction

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Relationship of process parameters, CVD phenomena and coating properties

Coating uniformity

Reduction of reactants can result in a non-uniform coating thickness.

This can be overcome by

- rotating the substrate
- improve precursor mixing by stirring the reactants and/or reversing the gas flow direction periodically
- tilting the substrate (e.g. 45) to enhance the projection of down stream substrates into the boundary layer
- create a temperature gradient across the substrate

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Chemical Vapor Deposition process

Thermally activated chemical vapor deposition (TACVD)
- Atmospheric pressure APCVD
- Low pressure LPCVD (0.01–1.33 kPa)
- Ultrahigh vacuum UHVCVD (less than 10^{-4} kPa)

Plasma enhanced chemical vapor deposition (PECVD)
- Radio frequency plasma reactor
- Direct current plasma reactor

Photo-assisted chemical vapor deposition (PACVD)

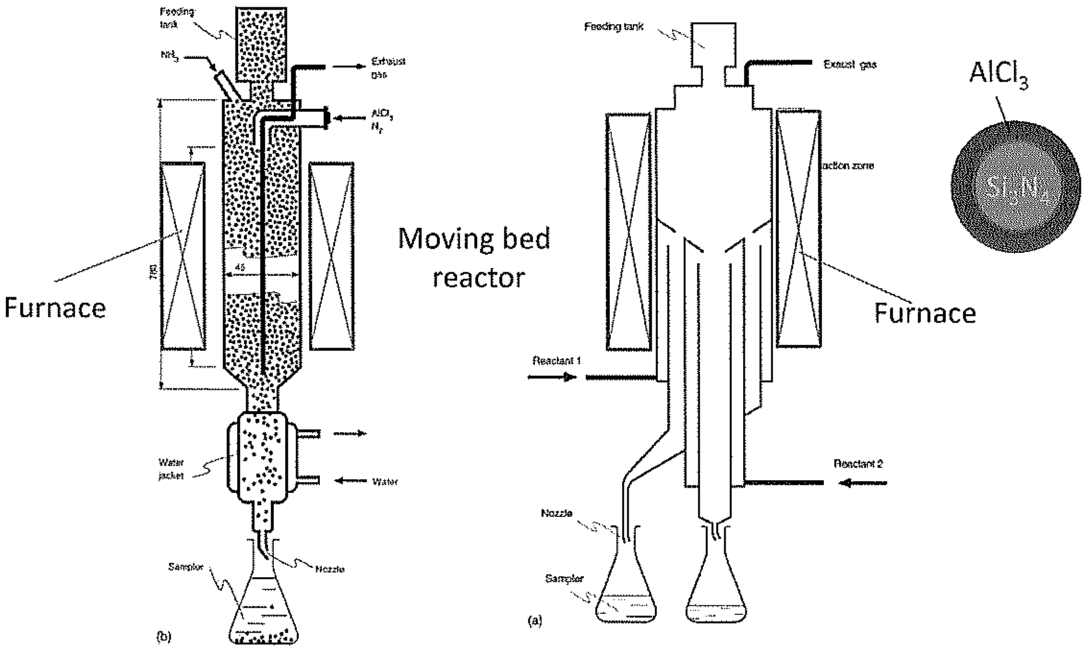
Metalorganic chemical vapor deposition (MOCVD)

Singh Direct Numerical Simulation and Reaction Path Analysis of Titania Formation in Flame Synthesis
Ring, Fundamentals of Ceramic Powder Processing and Synthesis, p. 258

Thermally activated chemical vapor deposition

Applications   Coating of ceramic powder

Coating of silicon nitride fine particles with aluminum nitride $AlCl_3 + NH_3 \rightarrow AlN + 3HCl$



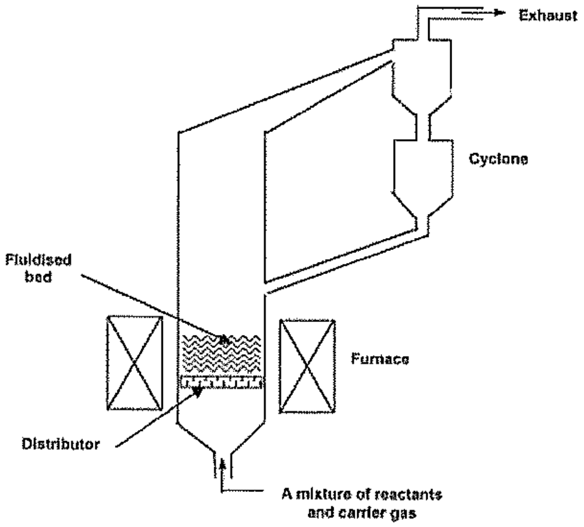
Boris Golman and Shinohara/Chem. Eng. Res. Des., 77 (A1), 39-46, 1999

Thermally activated chemical vapor deposition

Applications   Coating of ceramic powder

Coating of refractory materials TiC, TiB_2 and B_4C with carbon for nuclear applications

Carbon is deposited from the decomposition of a hydrocarbon precursor such as propylene (C_3H_6) at 1350 C.



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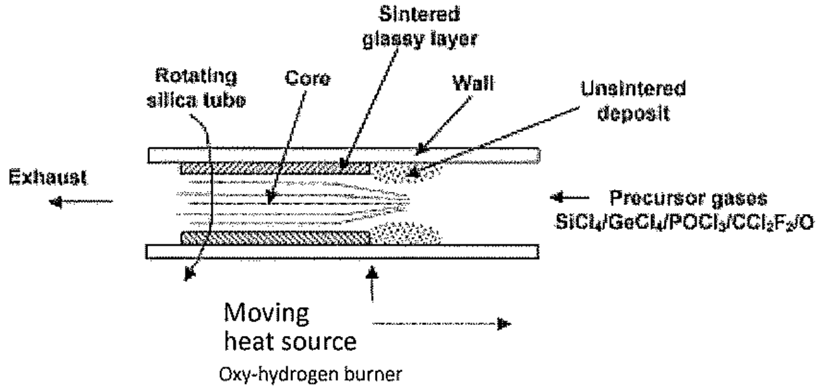
Thermally activated chemical vapor deposition

Applications Optical fibers



- SiO_2 particles are formed in gas phase via homogenous gas phase reaction $SiCl_4+O_2 \rightarrow SiO_2+ 2Cl_2$
- Particles are deposited in the form a porous mass ahead of the burner, initially onto the wall of the silica tube.
- The heat of the burner fuses the porous mass into a sintered glassy layer. The deposition process continues until the core material has been deposited.
- The tube is then heated at high temperature (e.g. 1800 C) to form a solid preform rod which is subsequently heated and drawn to 100 μm fibers.

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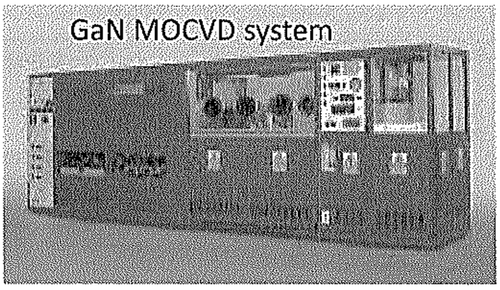
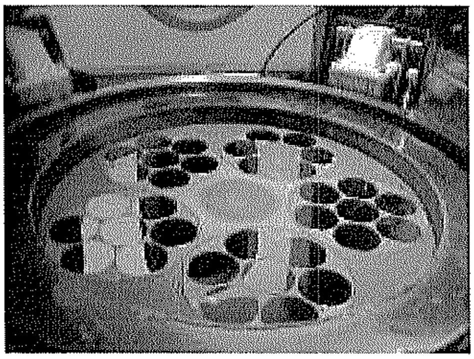
Metal-Organics Chemical Vapor Deposition (MOCVD)

Use metalorganics as precursor
Metalorganics : metal atom bonded to organic radicals, e.g. metal alkyls $Al(CH_3)_3$



Advantages

- Decompose at low temperature
- Decompose cleanly to give desired product
- Process can be performed at atmospheric pressure and low pressure
- Deposition is kinetically limited at low temperature or pressure → *Reproducible and uniform coating*



Limitations

- Metalorganic precursors are very expensive and they are not widely available commercially
- Precursors are normally very reactive and hence they are difficult to purify.
- Toxic

Metal-Organics Chemical Vapor Deposition (MOCVD)

Applications

- Growth of epitaxy of III-V semiconducting materials for opto-electronic applications (light-emiting diode, solar cells, photocathodes, advanced laser)

$$(CH_3)_3Ga(g) + NH_3(g) \xrightarrow[1040C]{H_2} GaN(s) + 3CH_4(g)$$

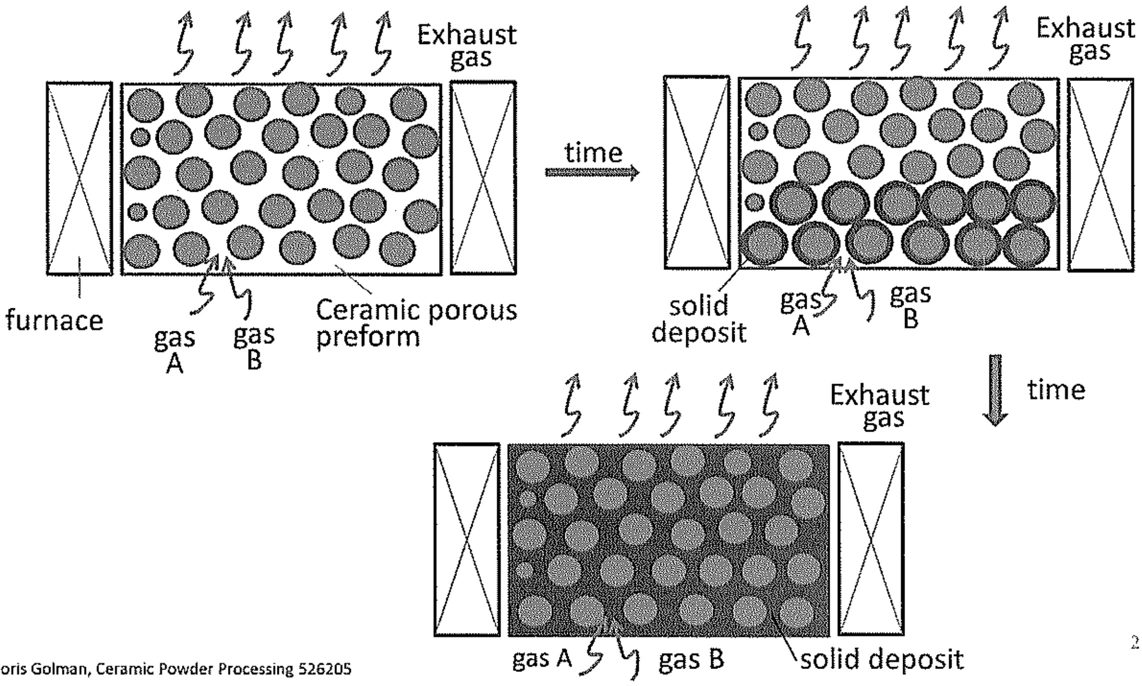
- Growth of ferroelectric (e.g. $PbTiO_3$, $PbZrTiO_3$, $BaTiO_3$), dielectric (e.g. ZnO) and superconducting (e.g. YBa_2Cu_3Ox) films.

Applications of Chemical Vapor Deposition Coating

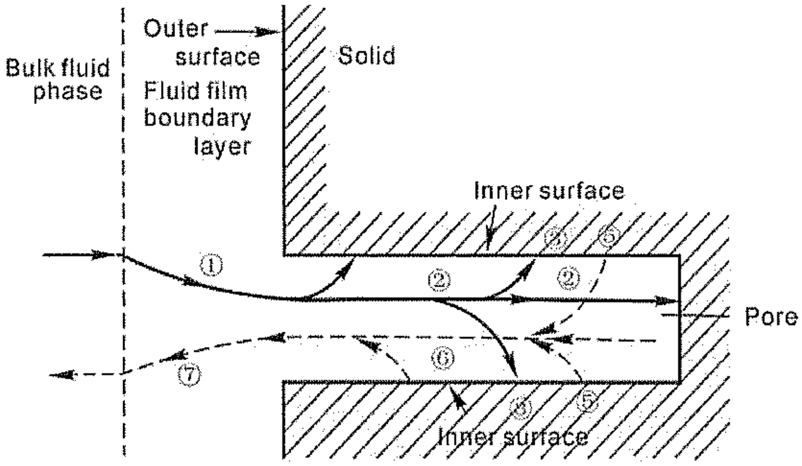
CVD Coatings	Substrates	Properties
Chromium	Solid solution alloys (i) with Iron, Nickel and Cobalt (ii) on Iron as carbides and nitrides	Corrosion / oxidation resistance Wear / corrosion resistance
Aluminium	As Aluminides with Iron, Cobalt and Nickel	High temperature oxidation resistance
Boron	As Borides with Iron, Cobalt and Nickel	Wear / erosion resistance
Silicon	As Silicides with Iron, Tungsten and Molybdenum	High temperature oxidation resistance
Titanium	As carbides, nitrides and carbonitride on ferrous and non-ferrous alloys	Wear resistance
Manganese	Solid solution alloys on carbon steels	Wear resistance

Chemical Vapor Infiltration (CVI) for manufacturing of ceramic matrix composites

Chemical Vapor Infiltration method of ceramic matrix composites fabrication is a process in which reactant gases diffuse into a porous preform and form a deposition. Deposited material is a result of chemical reaction occurring in porous space.



Mechanism of Chemical Vapor Infiltration (CVI)



1. gaseous precursors penetrate into the boundary layer from the bulk gas;
2. gaseous species are transported by diffusion into the pores within the fiber preform;
3. gaseous species are adsorbed onto the inner surface of the pore;
4. chemical reactions take place and coating forms on the fibre surface;
5. volatile by-products are desorbed from the surface;
6. gaseous by-products are transport outwards by diffusion; and
7. gaseous by-products return to the bulk gas through the boundary layer.

CVD – An Integrated Engineering Design Approach

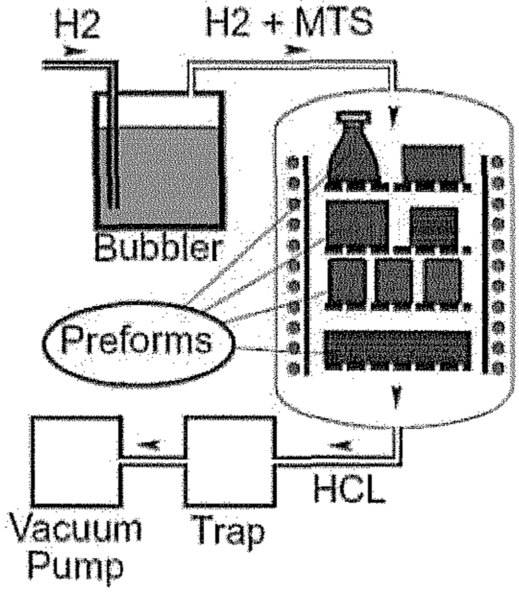
Chemical Vapor Infiltration (CVI) for manufacturing of ceramic matrix composites

Isothermal and isobaric CVI

Isothermal and isobaric CVI (I-CVI):
both temperature and pressure are kept constant during the infiltration process.

Advantages
- relatively easy
- good consistency of the finished product due to strict thermal and pressure parameter control
- a large number of complex preforms can be densified simultaneously

Disadvantages
- rapid deposition reactions result in significant density gradients from the external region to the interior region of the preform, which slows down the deposition rate.
- slow-deposition reaction results in a long densification time.



Applications of Chemical Vapor Infiltration

Preparation of carbon-fiber-reinforced silicon carbide composite to improve the oxidation resistance of C/C composites

Precursor: methyltrichlorosilane (MTS, CH_3SiCl_3)
Carrier gas: hydrogen
Conditions: temperature of 1000°C, H_2/MTS mol ratio of 10 with Ar as dilute gas, reduced pressure of 10 to 30 kPa
Traditional sintering method: 2000°C

Reduced pressures in I-CVI is used
(1) to increase gas-phase diffusivity → more uniform distributions of density and microstructure within the composites
(2) to reduce or eliminate undesirable gas nucleation and the formation of by-products, such as tar and soot in the case of carbon CVI.

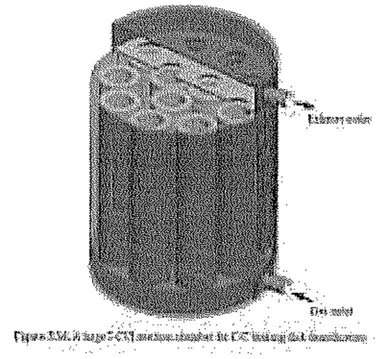
brittle ceramic fibres, such as Nicalon SiC and Al_2O_3 fibres, remain undamaged during the CVI process

ceramic matrix produced by CVI is much purer than that obtained with the hot pressing method, in which sintering additives are generally needed

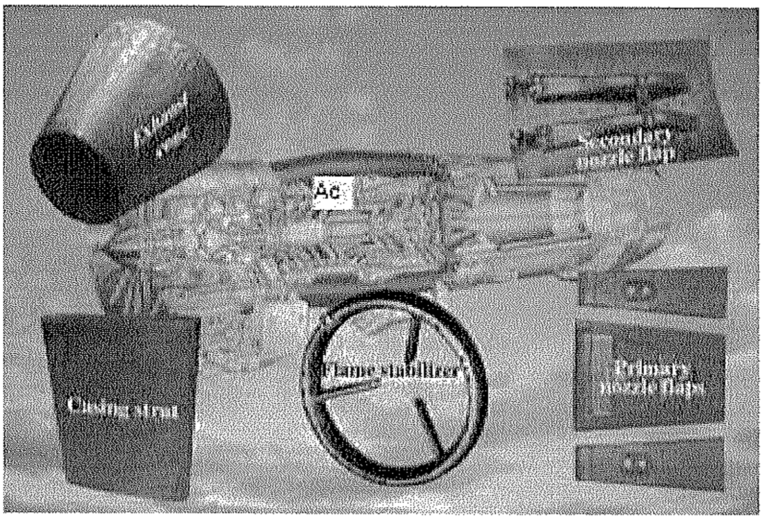
$CH_3SiCl_3(V)$ + excessive $H_2 = SiC(s) + 3HCl + H_2$

Applications of Chemical Vapor Infiltration

manufacture of carbon/carbon braking disks



Application SiC-matrix components in aero-engines

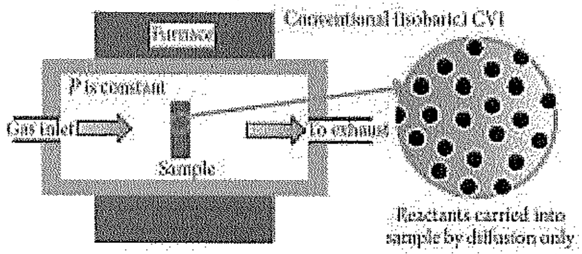


The potential applications are nozzle flaps, exhaust cone, flame stabilizer, combustion liners and turbines.

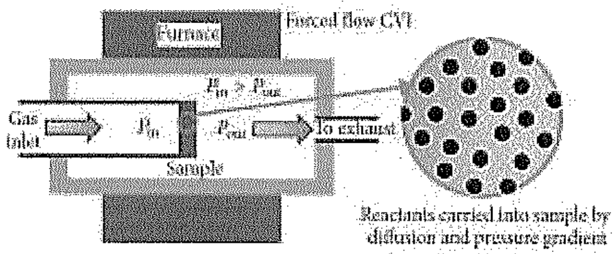
Chemical Vapor Infiltration (CVI) for manufacturing of ceramic matrix composites

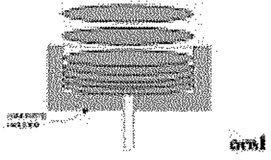
Thermal Gradient and Forced Flow CVI

Conventional (isobaric) CVI

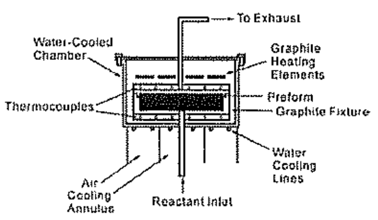


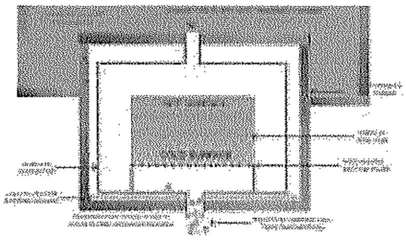
Forced flow CVI





Thermal gradient CVI





Advantages

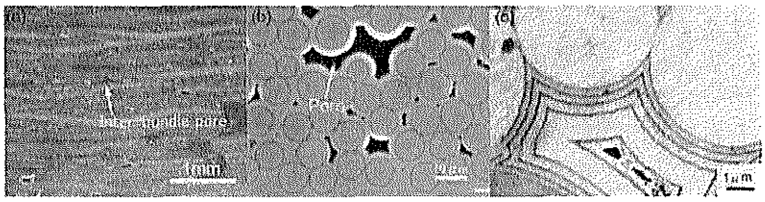
- reduced processing time
- improved infiltration efficiency

C.P. Deck, Modeling Forced Flow Chemical Vapor Infiltration Fabrication of SiC-SiC Composites for Advanced Nuclear Reactors, Science and Technology of Nuclear Installations Volume 2013, Article ID 127676

Chemical Vapor Infiltration (CVI) for manufacturing of ceramic matrix composites

Thermal Gradient and Forced Flow CVI

Cross-sections of FCVI-SiC/SiC



SiC fiber fabrics as preforms: 2D-plain weave of Tyranno SA.
Precursors: propylene for carbon deposition and the methyltrichlorosilane for SiC deposition and infiltration.
Process:
The carbon interphase was deposited on the fiber surface by decomposition of propylene with flow rate of 5×10^{-2} dm^3/min and 1 dm^3/min Ar at 5 Pa, **1100 °C**.
The SiC interphase was deposited by the decomposition of MTS with the flow rate of 0.15 g/min and 0.25 dm^3/min H_2 at 5 Pa, **1100 °C**.

Fracture surface of FCVI-SiC/SiC with multilayer SiC/C interphase

N. Igawa, Fabrication of SiC fiber reinforced SiC composite by chemical vapor infiltration for excellent mechanical properties, Journal of Physics and Chemistry of Solids, V 66, 2–4, February–April 2005, 551–554

Chemical Vapor Infiltration (CVI) for manufacturing of ceramic matrix composites

Advantages

- Low fiber damage due to relatively low infiltration temperatures
- Matrices of high purity may be fabricated
- Low infiltration temperatures produce low residual mechanical stresses
- Enhanced mechanical properties (strength, elongation, toughness)
- Good thermal shock resistance
- Increased creep and oxidation resistance
- Matrices of various compositions may be fabricated (SiC, C, Si_3N_4, BN, B_4C, ZrC, etc.)

Disadvantages

- Slow process rate (may continue up to several weeks)
- High residual porosity (10-15%)
- High capital and production costs

http://www.substech.com/dokuwiki/doku.php?id=fabrication_of_ceramic_matrix_composites_by_chemical_vapor_infiltration_cvi

Advantages and disadvantages of gas phase reaction processing

Advantages

- High purity product materials
- Dopants can be easily added
- Produces very fine particles with narrow size distribution
- Produces uniform coating films with good reproducibility
- Reactors can work continuously and can be controlled precisely
- Reasonable processing cost for the conventional CVD technique

Disadvantages

- Particles are difficult and expensive to separate from large volume of gas
- Chemical and safety hazards caused by the use of toxic, corrosive, flammable and/or explosive precursor gases.
- The use of more sophisticated reactor and/or vacuum system such as low pressure or ultrahigh vacuum CVD, plasma assisted CVD and photo-assisted CVD tends to increase the cost of fabrication