CERAMIC MATERIALS I

Asst. Prof. Dr. Ayşe KALEMTAŞ

akalemtas@mu.edu.tr, akalemtas@gmail.com, Phone: 211 19 17
Metallurgical and Materials Engineering Department

Application Base Classification

Ceramic Materials

Advanced Ceramics		Traditional Ceramics
Structural Ceramics	**Functional Ceramics**	Whitewares
Bioceramics	Electronic substrate, package ceramics	Cement
Ceramics used in automotive industry	Capasitor dielectric, piezoelectric ceramics	Abrasives
Nuclear ceramics	Magnetic ceramics	Refractories
Wear resistant ceramics (tribological)	Optical ceramics	Brick and tile
	Conductive ceramics	Structural clay products

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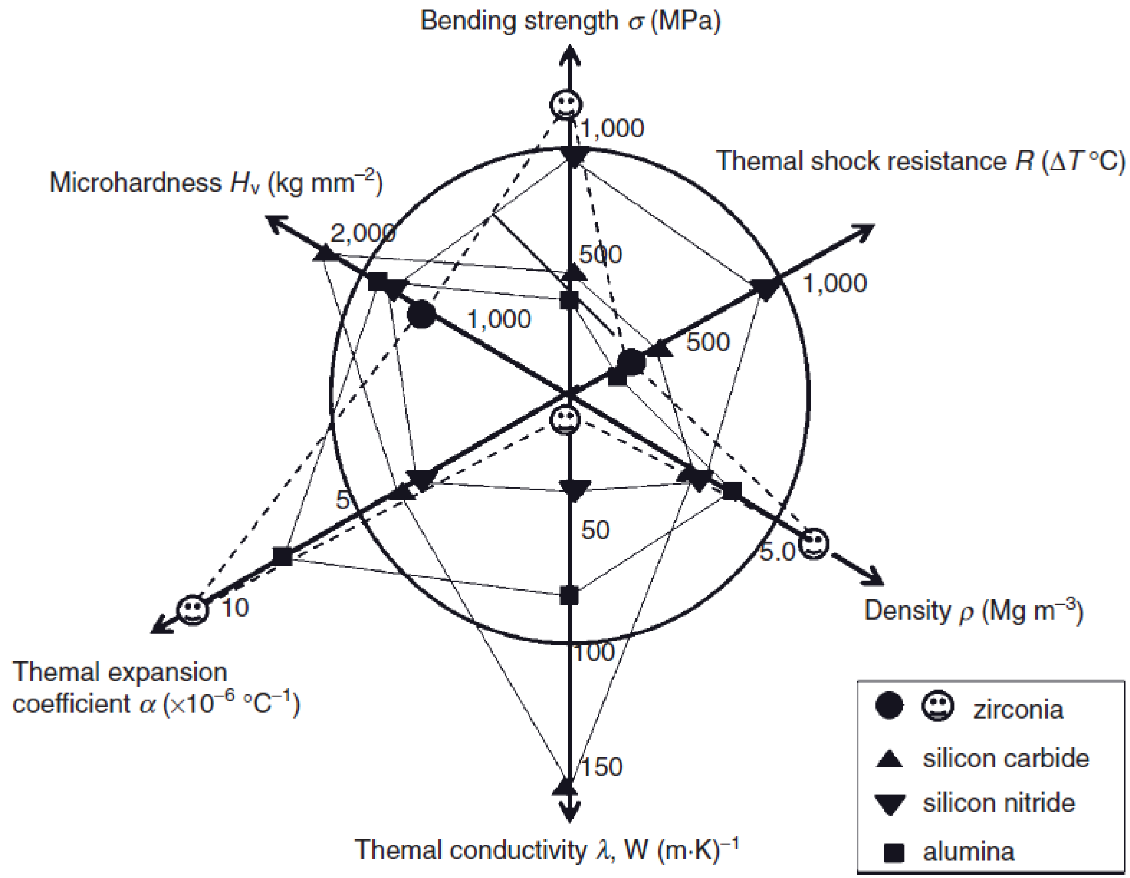
STRUCTURAL CERAMICS

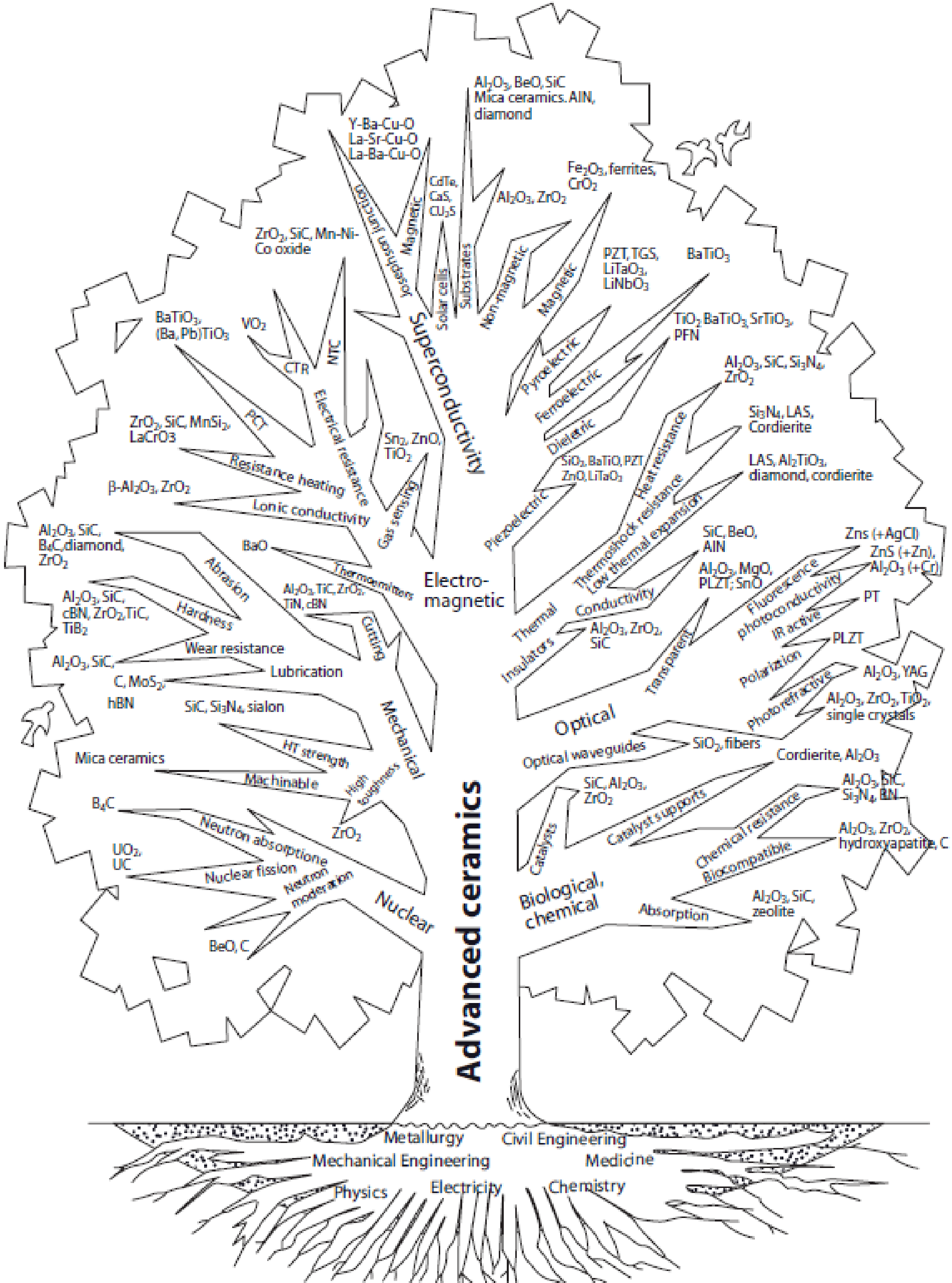
These are used for applications where a component of an engineering system is subjected to high mechanical, Tribological, thermal, or chemical loads. Typical structural ceramics are alumina, partially and fully stabilized zirconia, cordierite, mullite, spinel, silicon nitride and SiAlONs, silicon carbide, boron nitride, titanium nitride, and titanium boride.



Performance–application diagram of four typical advanced structural ceramics: zirconia; silicon carbide; silicon nitride; and alumina. Owing to the dependency of the properties on processing conditions, the values given are only tentative. Zirconia ceramics are characterized by a combination of useful properties unmatched by other oxide and nonoxide ceramics.

Classic and Advanced Ceramics: From Fundamentals to Applications. Robert B. Heimann 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, ISBN: 978-3-527-32517-7

FUNCTIONAL CERAMICS



Functional ceramics, in contrast to structural ceramics, utilize microstructural effects localized within the volume, at grain boundaries or at the surfaces of conducting or nonconducting ceramics. Such effects encompass semiconducting, varistor, piezoelectric, pyroelectric, ferroelectric and superconducting properties. Novel ceramic technologies for the automotive industry include knock and oxygen sensors, exhaust gas catalysts and fuel cells, as well as future ceramic gas turbines and adiabatic turbo - compound diesel engines.

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Preparation of Advanced Ceramic Powders

Ceramic powder characteristics are important because the purity of the powder sets the maximum purity level of the final processed ceramic part, and the particle size and size distribution play major roles in defining the microstructure and properties of the final parts.

Both the purity and the microstructure of sintered ceramics influence the properties of ceramic materials, including mechanical, thermal, electrical, and magnetic properties and chemical corrosion resistance.

Preparation of Advanced Ceramic Powders

Properties of final ceramic products are significantly affected by the properties of the starting raw material powders, on which several requirements are imposed:

- high purity
- fine particle size (< 1 μm)
- narrow particle size distribution
- free of agglomerates
- controlled particle shape
- homogenous chemical and phase composition

Powder Preparation Methods

There are various ceramic powder preparation methods. One is a ***“break-down”*** process, in which coarse particles are ground and divided into finer ones, and the other is referred to as a ***“build-up”*** process, in which particles are produced by special techniques.

Ceramic Powder Preparation Methods

- Mechanical
- Chemical

Powder Preparation Methods

Breaking-down process: Comminution and classification – powders by grinding and milling of row materials that are either natural in origin or a natural mineral after thermal decomposition or materials synthesised in "building-up" process.

Common Mechanical Powder Preparation Methods for Ceramics

Method	Advantages	Disadvantage
Comminution	Inexpensive Wide applicability	Limited purity Limited homogeneity Coarse particle size
Mechanochemical synthesis	Fine particle size Good for non-oxides Low temperature route	Limited purity Limited homogeneity

Powder Preparation Methods

Common Chemical Powder Preparation Methods for Ceramics

Method	Advantages	Disadvantage
Solid-state reaction ▪ Decomposition, reaction between solids	Simple apparatus Inexpensive	Agglomerated powder Limited homogeneity for multicomponent powders
Liquid solutions ▪ Precipitation or coprecipitation; solvent vaporization (spray drying, spray pyrolysis, freeze drying); gel routes (sol-gel, Pechini, citrate gel, glycine nitrate) ▪ Non-aqueous liquid reaction	▪ High purity, fine particle size, composition control, chemical homogeneity ▪ High purity, fine particle size	▪ Expensive, poor for non-oxides, powder agglomeration commonly a problem ▪ Limited to non-oxides
Vapour phase reaction ▪ Gas-solid reaction ▪ Gas-liquid reaction ▪ Reaction between gases	▪ Commonly inexpensive for coarse particle size ▪ High purity, fine particle size ▪ High purity, fine particle size, inexpensive for oxides	▪ Commonly low purity, expensive for fine powders ▪ Expensive, limited applicability ▪ Expensive for non-oxides, agglomeration commonly a problem

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Solid-Phase Synthesis

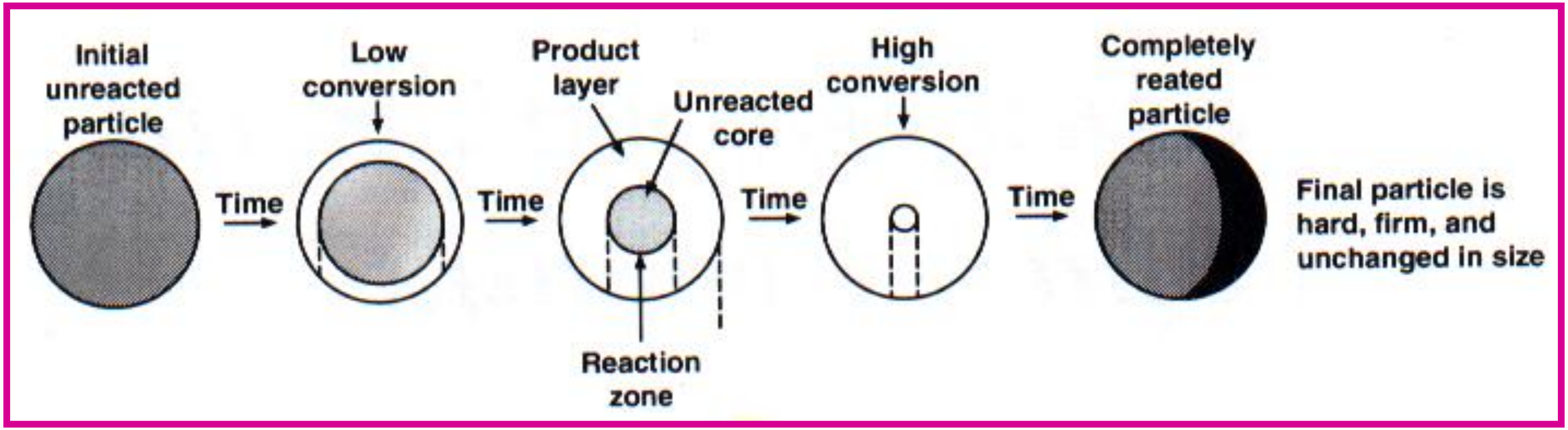
A solid is a reactant in two general types of powder synthesis reactions. One-type is a fluid-solid reaction, where the fluid is either a liquid or a gas. The other type is a solid-solid reaction.

Fluid-solid reactions can be represented by

A (fluid) + *b* B (solid) $\rightarrow$ *d* D (solid)
A (fluid) + *b* B (solid) $\rightarrow$ *d* D (solid) + *e* E (fluid)
b B (solid) $\rightarrow$ *d* D (solid) + *e* E (fluid)

In some cases, the solid product (D) forms a shell on the outside of particle B, giving a diffusion barrier for further reaction. This type of reaction is modeled as a ***"shrinking core"*** model.

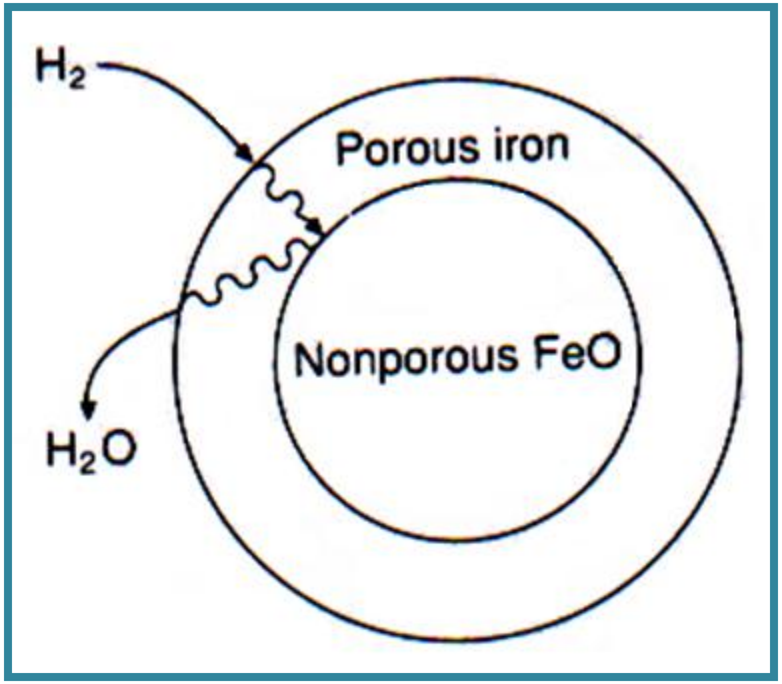
Solid-Phase Synthesis



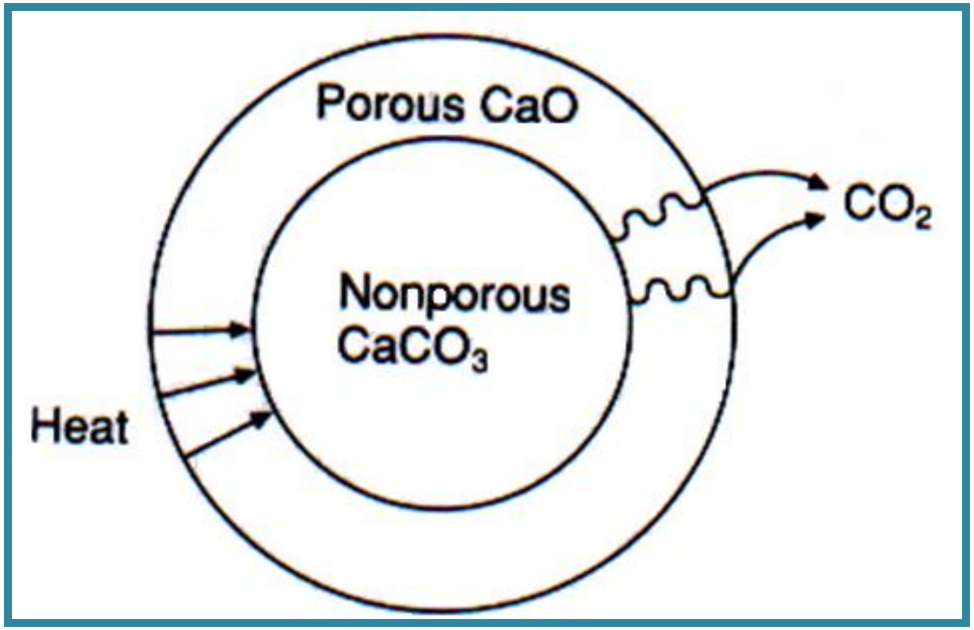
Shrinking core model

Solid-Phase Synthesis

Examples of Shrinking Core Reactions



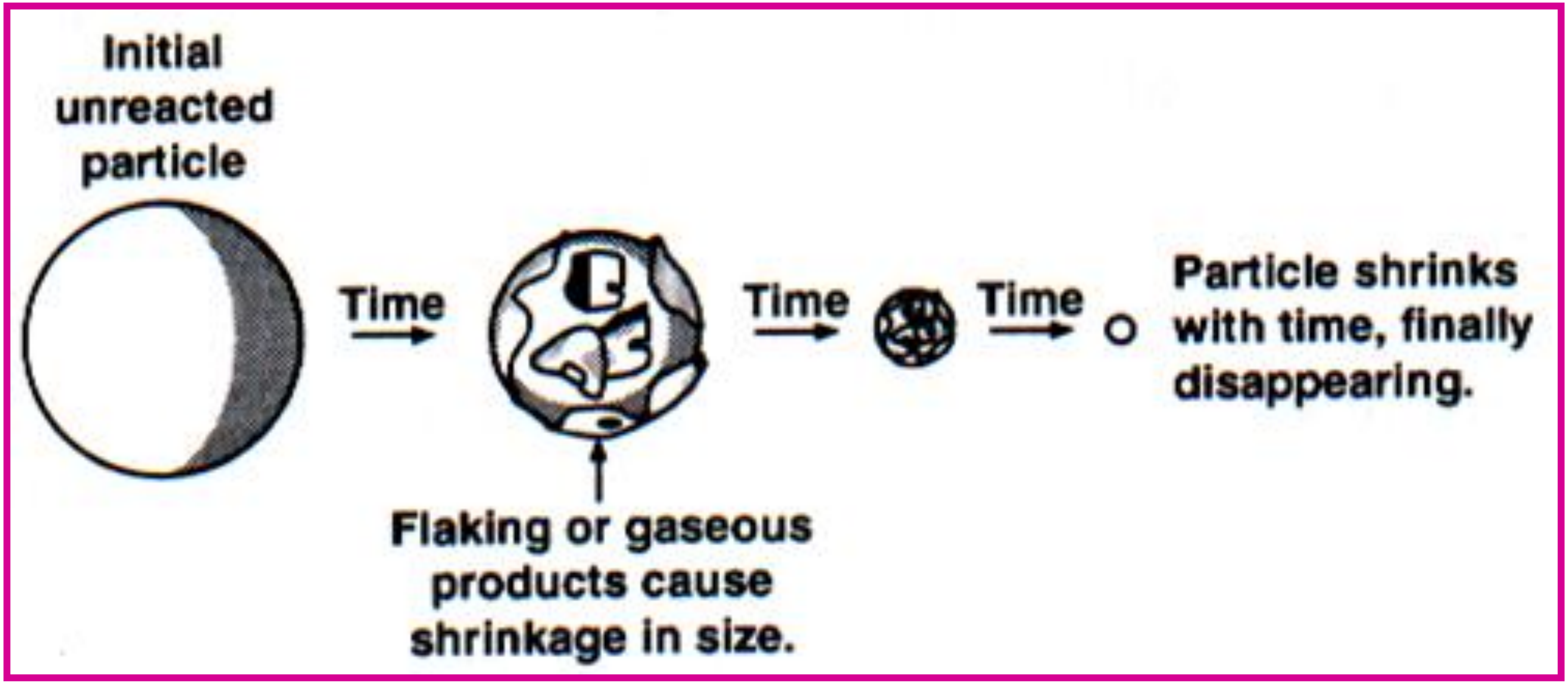
$FeO + H_2 \rightarrow Fe + H_2O$



$CaCO_3 + heat \rightarrow CaO + CO_2$

Solid-Phase Synthesis

In other cases, the product D flakes off the surface of particle B, because there is a large differences in the molar volume reactant B and product D. This type of reaction is modeled as a ***"shrinking sphere" model.***



Shrinking sphere model

Solid-Phase Synthesis

Before the reaction kinetics can be discussed, the thermodynamics must be discussed to see if the reactions are either spontaneous or at equlibrium.

- When Gibbs free energy of reaction is negative, the reaction is spontaneous.
- When Gibbs free energy of reaction is positive, the reaction is non-spontaneous.
- When Gibbs free energy of reaction is zero, the reaction is at equlibrium.

Solid-Phase Synthesis

Oxidation reactions

- Oxidation of metals and
- oxidation of sulfides are of interest in ceramic powder production.

The oxidation of sulfides is a common extractive metallurgical process, generating an oxide ceramic powder. The oxide product is usually an intermediate product on the way to metal production but if sufficiently pure it can be used directly as a ceramic powder.

These reactions are strongly exothermic, which is typical of these types of oxidation reactions.

The oxidation of metal powders is a method to produce relatively pure oxides.

Solid-Phase Synthesis

Oxidation reactions

- Oxidation of metals

$O_{2(g)}$ + 4/3 Al → 2/3 Al_2O_3 ΔH = - 268.4 kcal/mole

- Oxidation of sulfides

$O_{2(g)}$ + 2/3 $ZnS_{(s)}$ → 2/3 $ZnO_{(s)}$ + 2/3 $SO_{2(g)}$ ΔH = -166.9 kcal/mole

11/2$O_{2(g)}$ + 2 $FeS_{2(s)}$ → $Fe_2O_{3(s)}$ + 4 $SO_{2(g)}$ ΔH = - 592.0 kcal/mole

Solid-Phase Synthesis

Reduction reactions

- Reduction reactions are frequently used to produce metal powders and are not often used for the production of ceramic powders.

- These reduction reaction can, however, be the first step in a sequence of steps to produce carbide and nitride powders.

$Fe_3O_{4(s)} + 4\,H_{2(g)} \rightarrow 3\,Fe_{(s)} + 4\,H_2O_{(g)}$ $\Delta H = +\,36.6$ kcal/mole

$CuO_{(s)} + H_{2(g)} \rightarrow Cu_{(s)} + H_2O_{(g)}$ $\Delta H = -\,20.2$ kcal/mole

$SiO_{2(s)} + 2\,H_{2(g)} \rightarrow Si_{(s)} + 2\,H_2O_{(g)}$

Solid-Phase Synthesis

Nitridation reactions

- Direct nitridation of metal powders is commonly used to produce Si_3N_4, AlN, BN and other nitrides.

- These reactions are strongly endothermic, requiring energy to continue.

$$N_{2(g)} + 3/2\ Si_{(s)} \rightarrow \frac{1}{2}\ Si_3N_{4(s)} \qquad \Delta H = +\ 89.5\ kcal/mole$$

$$N_{2(g)} + 2\ Al_{(s)} \rightarrow 2AlN_{(s)} \qquad \Delta H = +\ 152.8\ kcal/mole$$

$$N_{2(g)} + 2\ B_{(s)} \rightarrow BN_{(s)} \qquad \Delta H = +\ 120.4\ kcal/mole$$

Solid-Phase Synthesis

Liquid-solid reactions

- These reactions take place at ambient temperature and follow shrinking core kinetics similar to the solid-gas reactions.

- These reactions have reasonably fast reaction kinetics at low temperatures because the liquid has a very high concentration of reactant compared to the gas phase.

$Ba(OH)_2$ (1, solution) + $TiO_{2(s)} \rightarrow BaTiO_{3(s)}$ + H_2O (1)

3 H_2O (1) + $2AlN_{(s)} \rightarrow Al_2O_{3(s)}$ + 2 NH_3 (1, solution)

Solid-Phase Synthesis

Solid-solid reactions

- These reactions are frequently used to produce multicomponent ceramic powders.

$NiO_{(s)} + Al_2O_{3(s)} \rightarrow NiAl_2O_{4(s)}$
$NiO_{(s)} + Cr_2O_{3(s)} \rightarrow NiCr_2O_{4(s)}$
$MgO_{(s)} + Fe_2O_{3(s)} \rightarrow MgFe_2O_{4(s)}$
$ZnO_{(s)} + Al_2O_{3(s)} \rightarrow ZnAl_2O_{4(s)}$
$BaCO_{3(s)} + SiO_{2(s)} \rightarrow BaSiO_{3(s)} + CO_{2(g)}$
$4B_{(s)} + C_{(s)} \rightarrow B_4C_{(s)}$
$SiO_{2(s)} + C_{(s)} \rightarrow SiC_{(s)} + CO_{2(g)}$
$WO_{2(s)} + C_{(s)} \rightarrow WC_{(s)} + CO_{2(g)}$

Solid-Phase Synthesis

Solid-solid reactions

- Silicon carbide SiC is produced in large tonnages using the ***"Acheson process"*** by reacting a batch consisting principally of high-purity sand and low-sulfur coke at 2200-2500°C in an electric arc furnace.

- High purity Si sources must be used to give high purity SiC.
- Homogenous mixing is desired.

$$SiO_2 + 3C \rightarrow SiC + 2CO_{(g)}$$

- Acheson process: SiO_2 sand + C (coke) → electric arc furnace (> 2000°C) → coarse SiC → grinding, purification; *major method*, impurity include: unreacted Si, Fe, O etc.

THE END

Thanks for your kind attention

Any Questions