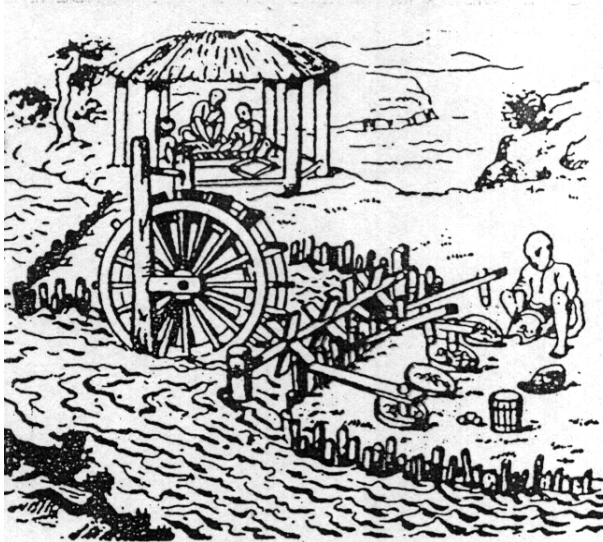


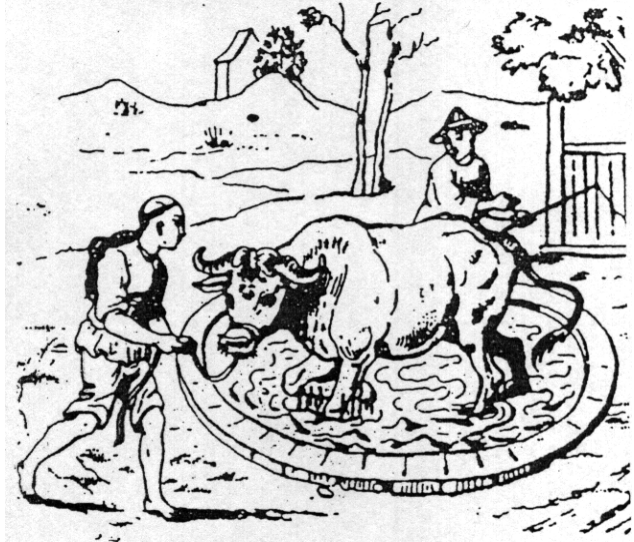
Theory and Practice of Ceramic Processes

Process – in turn appearing physicochemical changes of a matter

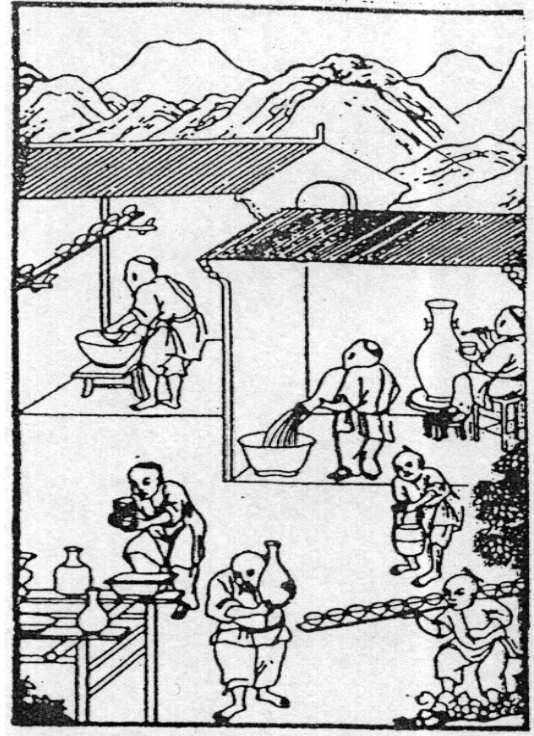
Ceramic process – process connected to the ceramic technology, a part of it, adjusted to raw material properties, and a type of the resultant product and product properties



Powder preparation



Powder processing



Forming → Drying → Firing (sintering) → Final treatment

Ceramics

A solid state material manufactured from inorganic and non metallic species and possessing high temperature stability

Traditional ceramics – made from naturally occurring raw materials – clay minerals=hydrated aluminosilicates which have layer structures, silica (SiO_2), feldspar, talc, wollastinite, sillimanite.

Advanced ceramics – made from refined minerals or synthesized powders = oxides (Al_2O_3 , ZrO_2 , ThO_2 , BeO , MgO , MgAl_2O_4), ferrites, nitrides, carbides, borides, BaTiO_2 (ferroelectric ceramics).

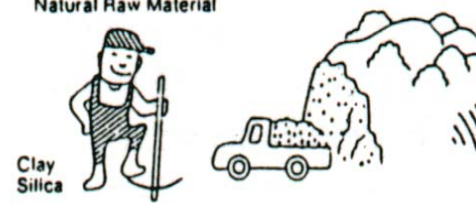

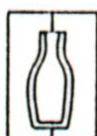
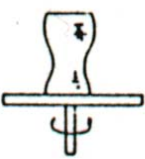


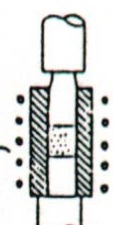
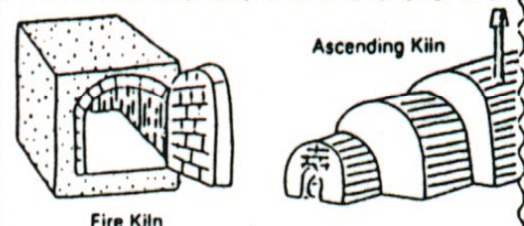


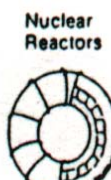





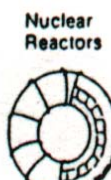


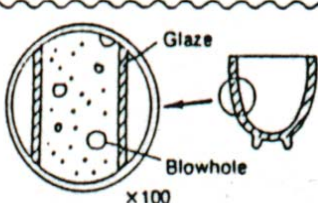




Traditional Ceramics

Whitewares	Dishes, plumbing, enamels, tiles
Heavy clay products	Sewer pipe, brick, pottery, sewage treatment, and water purification components
Refractories	Brick, castables, cements, crucibles, molds
Construction	Brick, block, plaster, concrete, tile, glass, fiberglass
Abrasive products	Grinding wheels, abrasives, milling media, sand-blast nozzles, sandpaper
Glass	Too numerous to list

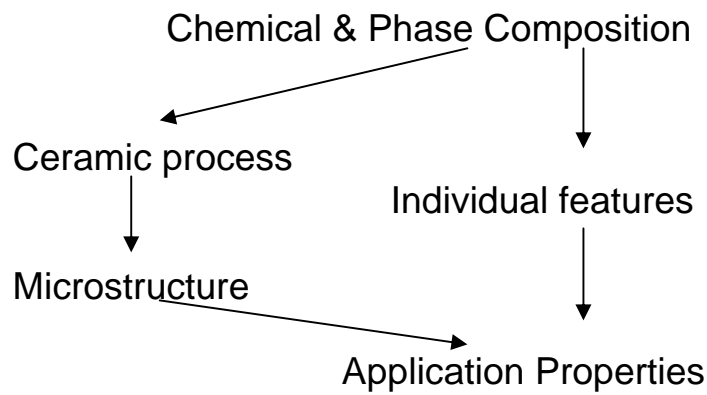
Modern Ceramics

Electronics	Heating elements, dielectrics, substrates, semi-conductors, insulators, transducers, lasers, hermetic seals, igniters
Aerospace and automotive	Reentry, radomes, turbine components, heat exchangers, emission control
Medical	Prosthetics, controls
High-temperature structural	Kiln furniture, braze fixtures, advanced refractories
Nuclear	Fuels, controls
Technical	Laboratory ware
Miscellaneous	Cutting tools, wear-resistant components, armor, magnets, glass-ceramics, single crystals, fiber optics

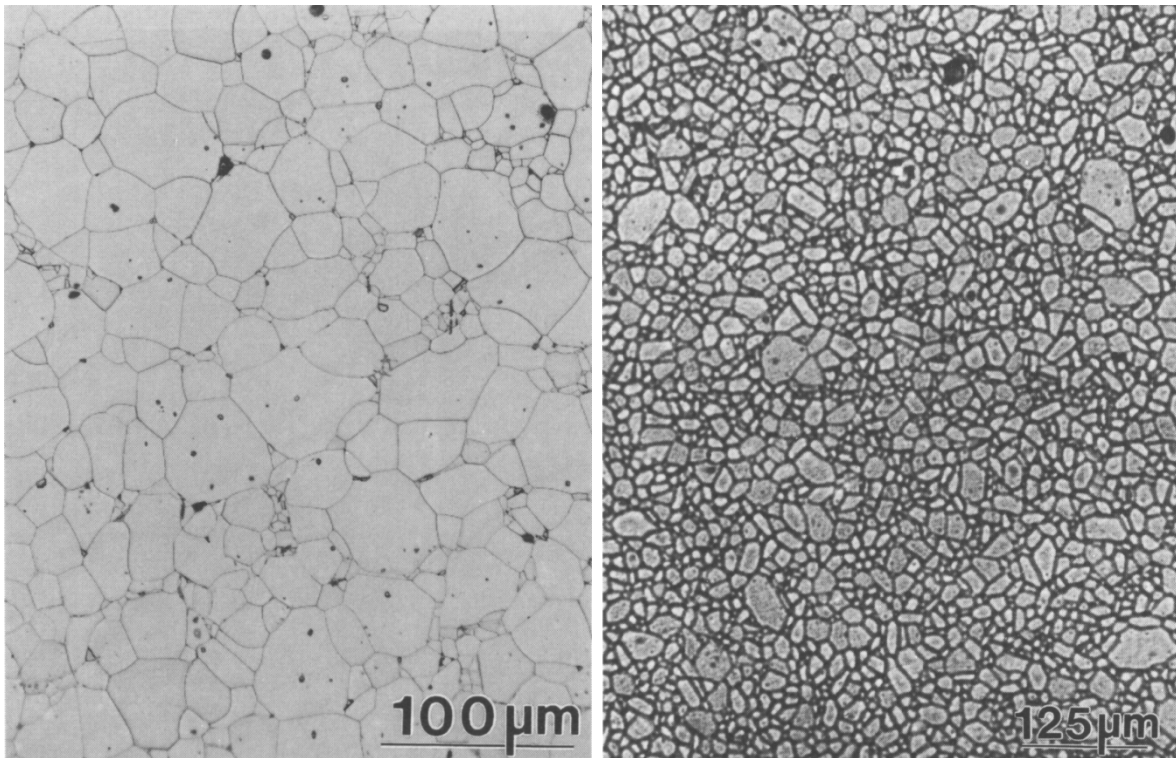
Differences between traditional and advanced ceramics

	TRADITIONAL CERAMICS	FINE CERAMICS
Raw Material	<p style="text-align: center;">Natural Raw Material</p> <p>Clay Silica</p> 	<p style="text-align: center;">Artificial Raw Material</p> <p>$Al_2O_3, SiC, ZrO_2, Si_3N_4, etc.$</p> 
Forming	<p>Slip Casting</p>  <p>Potter's Wheel</p> 	<p style="text-align: center;">Hot Isostatic Press</p>    <p style="text-align: center;">Rubber Press</p> <p style="text-align: center;">Hot Press</p>
Sintering	<p style="text-align: center;">Ascending Kiln</p>  <p style="text-align: center;">Fire Kiln</p>	<p style="text-align: center;">Rockets</p>   <p style="text-align: center;">Nuclear Reactors</p>  <p style="text-align: center;">Automobile Engine Parts</p> 
Products	<p style="text-align: center;">Pottery</p>  <p style="text-align: center;">Brick</p> 	  <p style="text-align: center;">Nuclear Reactors</p>  <p style="text-align: center;">Automobile Engine Parts</p> 
Structure	 <p style="text-align: center;">Optical Microscope</p>  <p style="text-align: center;">Glaze</p> <p style="text-align: center;">Blowhole</p> <p style="text-align: center;">x 100</p> <p style="text-align: center;">Microphotograph</p>	<p style="text-align: center;">Electron Microscope</p>   <p style="text-align: center;">x 50,000</p> <p style="text-align: center;">Electron Microphotograph</p>  <p style="text-align: center;">Mechanical Parts</p>  <p style="text-align: center;">Artificial Bones</p>

Factors affecting application properties of ceramic materials



Influence of the process on microstructure and properties



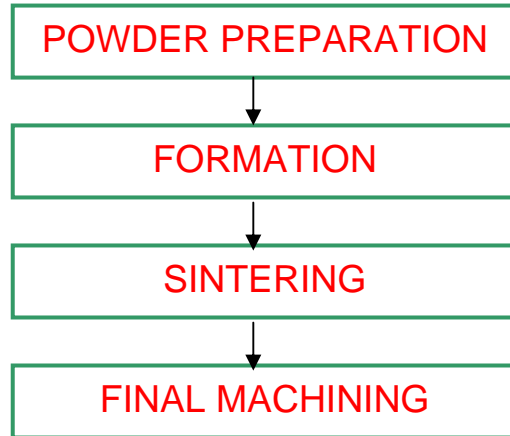
a)

b)

a) Coarse-grained, transparent Al₂O₃(>99,9%) added with MgO, sintered with no liquid phase at 1700-1800°C in H₂.

b) 99% Al₂O₃ with small amount of a glassy phase sintered at 1700-1750°C.

Typical scheme of the technology of polycrystalline ceramics

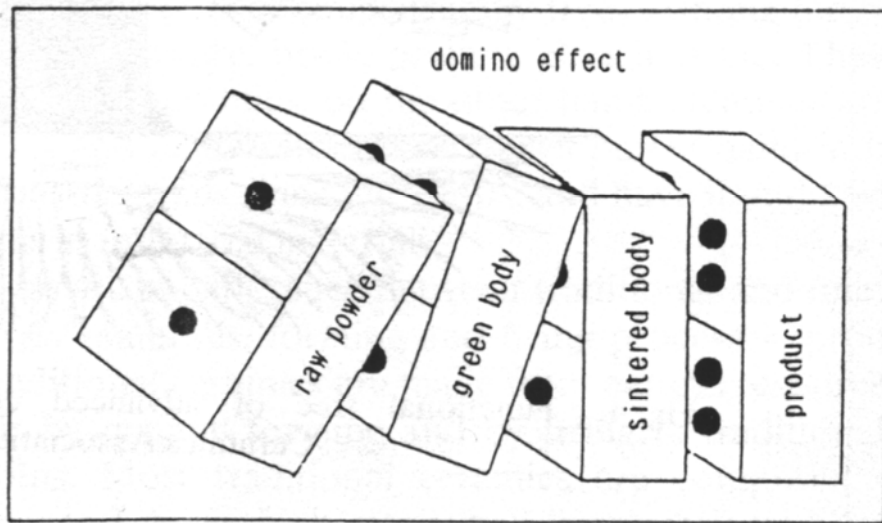


Glass technology, Glass-crystalline materials, Coatings require different production processes

The properties of ceramics are largely dependent on the quality of the starting raw material powders.

“domino effect”

The performance of advanced ceramics is determined by the combination of raw material powder and processing. High performance will not be achieved unless raw material powders are properly processed. However, the raw material powder comes first, as powder compacts, and hence sintered bodies, inherit the properties of raw material powders, so that even careful forming and precise firing would not lead to the desired performance of the final products if inadequate raw material powders were used.



Domino effect in ceramic processing: the starting point is raw powder.

Selection criteria for ceramic starting powders

- ❖ polymorphic form
- ❖ purity
- ❖ particle size distribution
- ❖ reactivity (sinterability)

Selection criteria are dependent on the properties required in the finished component

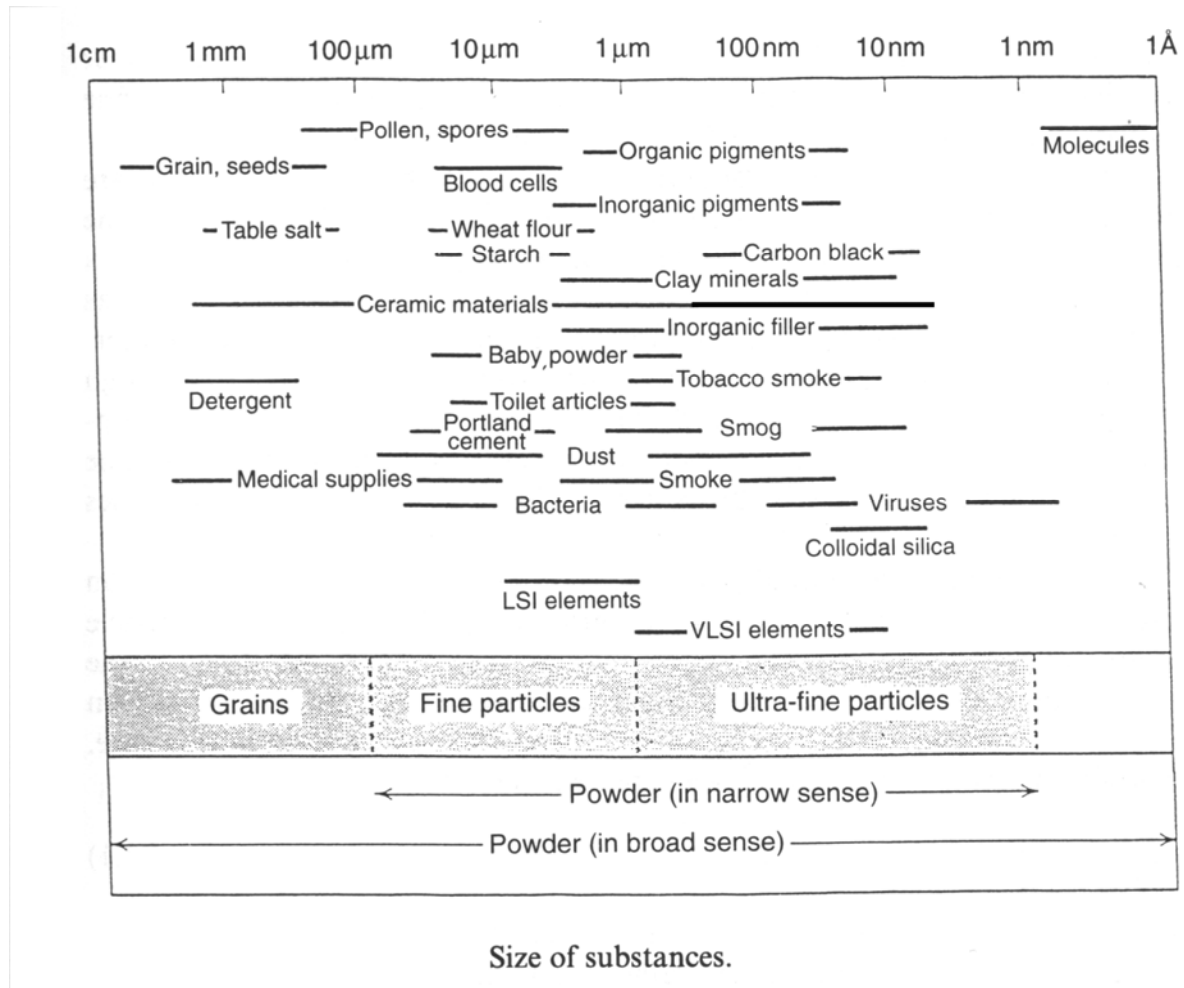
Purity strongly influences high-temperature properties such as strength, stress rupture life and oxidation resistance, also electrical, magnetic and optical properties

Particle size distribution – should provide maximum particle packing and uniformity during consolidation or shaping, this is required to achieve maximum, reproducible strength. Small particle size is important if high strength is the primary objective. Refractories are an example of the bodies which contain either large particles or high porosity as an important constituent in achieving the desired properties.

Reactivity (sinterability) – very small particles with high surface area have high surface free energy and thus have a strong thermodynamic drive to decrease their surface area by bonding together.

Powder fundamentals

A powder is an assembly of fine solid particles that interact moderately with each other. The fine solid particles must be only slightly aggregated with each other, and when in the unconstrained assembled state they must be capable of a certain amount of movement.

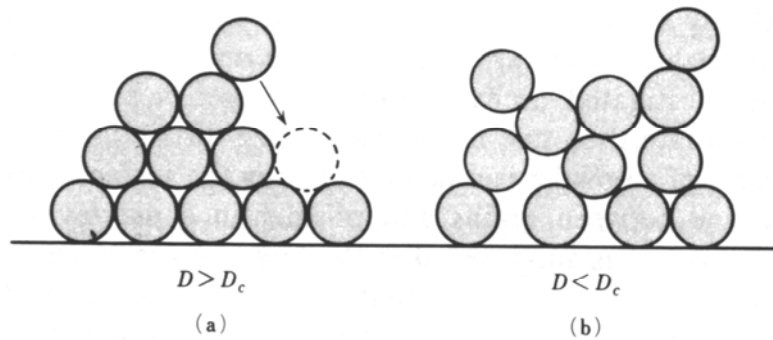


Grains – particles large than $50\mu\text{m}$

Fine particles - those ranging from $1\mu\text{m}$ to $50\mu\text{m}$ (“fine powders”)

Ultra-fine particles – those ranging from 10nm to $1\mu\text{m}$ (“ultra-fine powders”)

Ceramic powder agglomeration



Packing model of particles.

D – particle size, D_c – critical particle size at which cohesive and gravitational forces acting on a particle are in balance.

If the gravitational force on each particle is greater than the adhesive or cohesive forces between particles, then all the particles roll down to the kinetically most stable position independently of particle size (a), and always make a fixed close-packed structure in this case. The packing structure is greatly influenced by the shape and size distribution of the particles and by the pressure on the particles.

With decreasing size and weight, most of the particles remain fixed in the positions in which they first made contact with each other, owing to the interactions between them, This results in a bulky packing structure (b). A porous structure is easily formed by smaller and lighter particles. In this case, the adhesive force may be due to water (surface tension force) or to electrostatic, van der Waals or macro-frictional forces depending on the geometrical structure of the surface.

Terminology

Primary particles – a discrete, low-porosity unit. It may be a single crystal (crystallite), a monophasic polycrystal, a multiphase polycrystal, a glass.

Crystallite – a smallest unit of powder structure which coherently disperses X-radiation

Agglomerate – an assemblage of numerous primary particles having a network of interconnective pores. The particles are bonded together by surface forces and/or solid bridges. The surface forces may be electrostatic or van der Waals attractions between particles or liquid capillary forces due to the presence of liquid within the agglomerate. Solid bridges are a result of sintering, fusion, chemical reaction, or setting of a binder.

Solid agglomerates are defined as agglomerates with solid bridges.

Weak agglomerates are agglomerates with surface forces as bonds.

Agglomeration driving force - Most ceramic powders are composed of small primary particles. Because of this they have a very high surface area and usually a high surface free energy. To reduce this surface free energy the particles tend to agglomerate.

The agglomerate can have a very dominant influence on the properties of a powder.

Aggregate – a mono- or multiphase assemblage of a few crystallites which is free of pores. A kind of solid agglomerate.

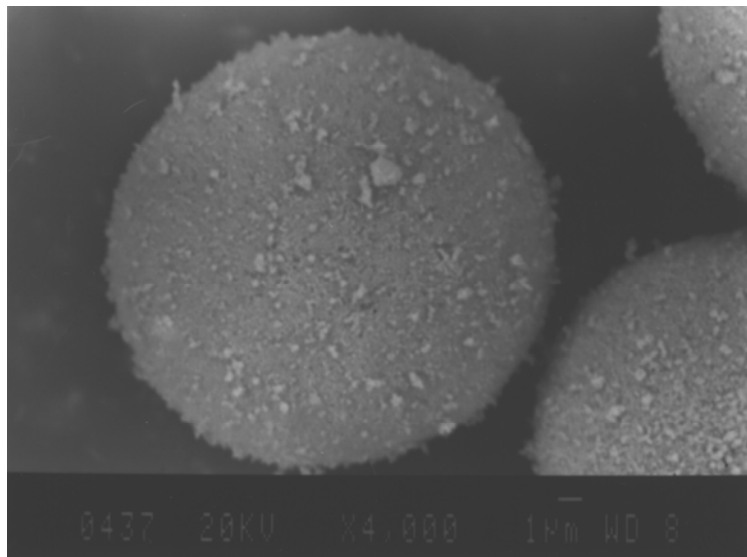
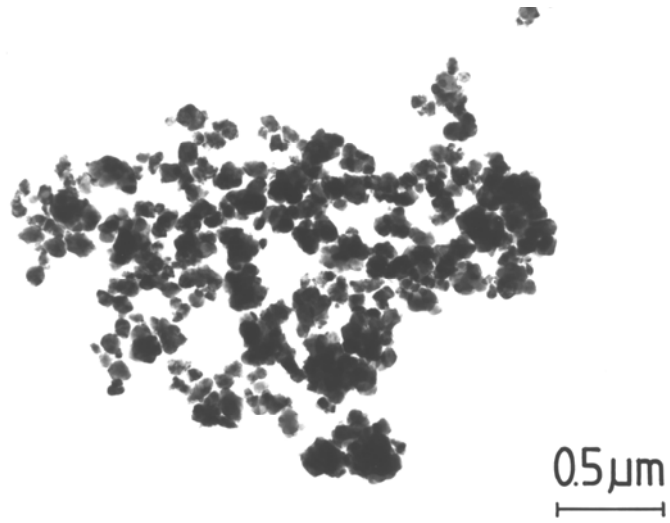
Particle – a single primary particle or a solid agglomerate. As such, it is a small mass that is free to move as an entity when the powder is dispersed by the breaking of the surface bonds. Most particle-size measuring techniques operate on such particles.

Granules – agglomerates that are intentionally formed by the addition of a granulating agent to promote the formation of large agglomerates. An example of a granule is the product from a spray dryer.

Flocks – a cluster of particles that form in a liquid suspension. The flock can be dispersed by appropriate modification of the interfacial forces through alteration of the solution chemistry. The particles of a flock are held together by short-range interfacial forces or by inorganic flocculating agents.

Colloids – particles that, when dispersed in fluid, are fine enough so that Brownian motion maintains them in the suspension without settling. In general, colloids are particles of submicron size (<500 nm).

Examples of the ceramic powder morphology



2.85 mol % Y_2O_3 – 97.15 mol % ZrO_2 ultra-fine powders as-milled and granulated in a spray-dryer

The properties which are important in evaluating raw material powders for forming and firing processes.

Characteristics of Ceramic Starting Powders	
<i>Physical characteristics</i>	<i>Chemical characteristics</i>
Grains (primary particles)	Bulk composition
Size	Major elements (1-100%)
Shape	Minor elements (10 ppm-1%)
Agglomerates (secondary particles)	Trace elements (< 10 ppm)
Size	Crystal structure
Shape	Crystallinity
Porosity	Crystal type
Amount (see density)	Lattice constant
Size	Defects
Shape	
Particle contact	Phases
Coordination	
Strength	Surface composition
Density	Major elements
Specific surface area	Minor elements
Permeability	Trace elements
Compactibility	Inorganic species
Flowability	Organic species
	Water
	Phases

PARTICLE SIZE, SHAPE, AND DISTRIBUTION

Affect behaviour of raw materials when they are physically mixed together and when the mixture is reacted at high temperature to form desired compound

particle size determines an effective surface area

AGGLOMERATE SHAPE AND SIZE

Affects packing behaviour of the powder during formation processes.

AGGLOMERATE STRENGTH

The presence of strong agglomerates that cannot be broken down during piece part formation by pressing, extrusion, etc. can have a strong, negative influence on the density of the green part and sintered part.

Theories of agglomerate strength

An early theory for agglomerate strength based on well known equation for the van der Waals' attractive force F_{att} between two spheres of diameter D , separated by a distance L , in terms of the Hamaker constant A (10^{-9} J) was developed by Rumpf. By assuming these forces for a particle assembly of volume fraction ϕ he obtained the strength σ of the agglomerate as

$$\sigma = \frac{1.1\phi}{(1-\phi)} \frac{F_{att}}{D^2} = \frac{1.1\phi}{(1-\phi)} \frac{A}{24L^2D}$$

The equation shows the important part played by the particle packing; poor packing which means the large porosity produces poor strength of the agglomerate. The importance of very fine particle sizes is anticipated by this equation, because of the inverse dependence on particle diameter D .

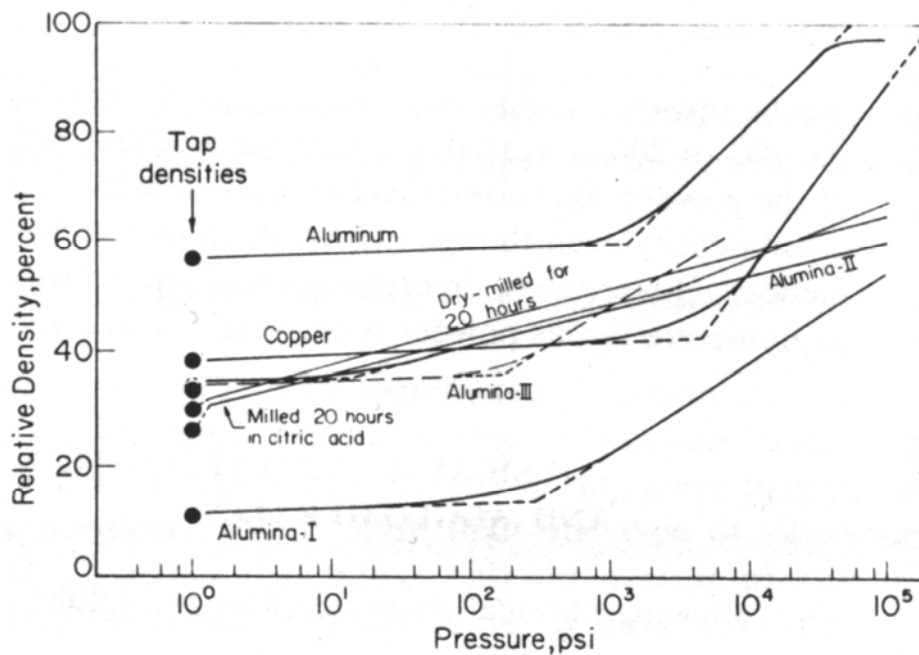
A new theory based on fracture mechanics analysis has been done by Kendall who derived the following equation for the agglomerate strength σ^* :

$$\sigma^* = \frac{15.6\phi^4 \Gamma_c^{5/6} \Gamma^{1/6}}{(Dc)^{1/2}}$$

where σ^* is the bending strength of a beam containing a through edge notch of the length c , Γ_c is the fracture energy and D is the diameter of clean, smooth spheres from which the beam is composed. This equation shows stronger influence of packing fraction ϕ , the weaker dependence on particle diameter D and includes the effect of flaw size c .

Determination of relative strength of agglomerates

The strength of agglomerates in a powder can be determined from powder-compaction data. By this technique the relative strength of the agglomerates in a powder is related to a break in the compaction curve when the logarithm of pressure is plotted against percentage of theoretical density.



Compaction data for several powders.

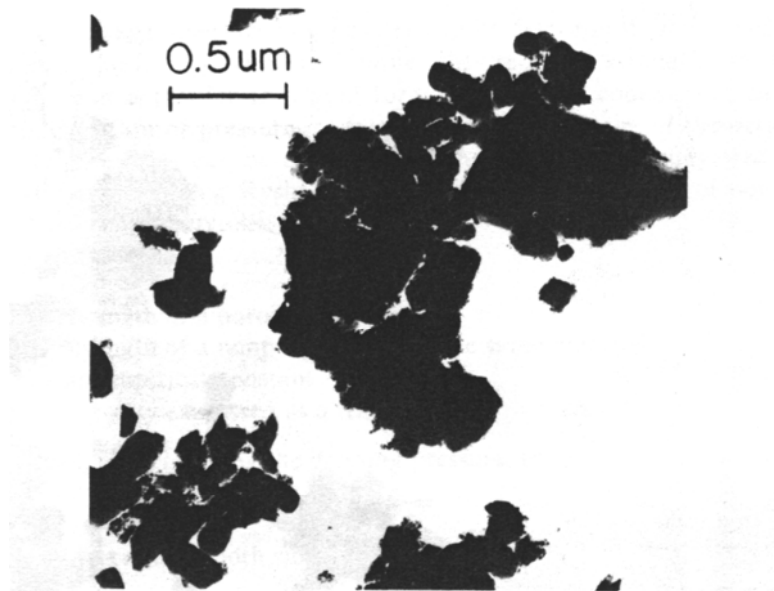
The breaks in the curves for aluminium and copper indicate the pressure at which plastic deformation of the powder particles at their contact points begins to control the compaction behaviour.

The break in the curve for alumina I at 300 psi (an unmilled, calcined powder containing two distinct types of agglomerates) indicates the pressure at which crushing and deformation of the contact points of the porous agglomerates begins.

A slight break in the curve for alumina II (dry-milled reactive powder) indicates the relative strength of the agglomerates bonded by the milling aid.



Electron micrograph of alumina I agglomerates.



Electron micrograph of alumina I powder after water milling for 20 hours with citric acid.

PARTICLE AND AGGLOMERATE HARDNESS

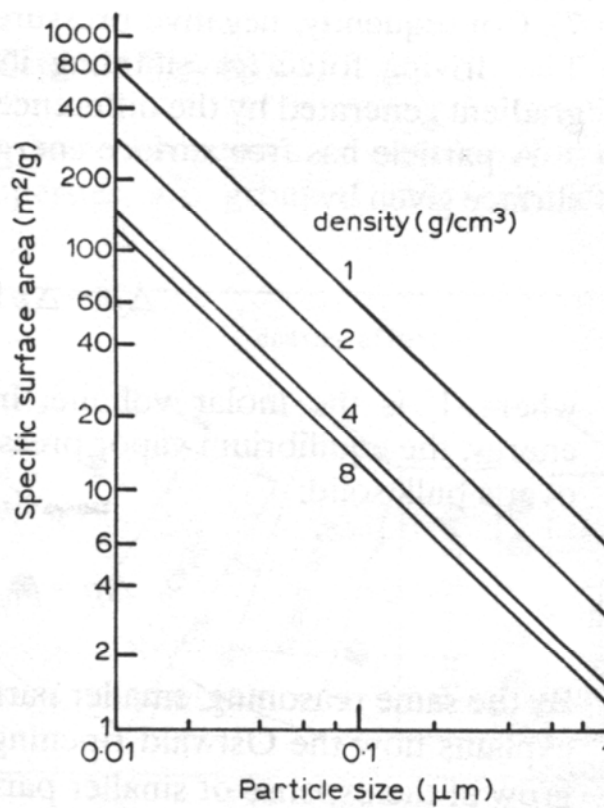
Affects the ability to comminute the particles and homogenize the powder

Causes contamination of the powder during ball-milling

SPECIFIC SURFACE AREA

Specific surface area is a surface area per unit weight.

This characteristic offers information on the combined effects of particle size, shape, size distribution, surface texture and open porosity of an agglomerate



Relationships between particle size and specific surface area.