Shape Forming Processes

There are a couple main shape forming processes such as *pressing*, *casting*, *plastic forming* and *green machining*.

PRESSING

Premixed powders are pressed under (i) uniaxial or (ii) isostatic pressures. Before pressing; milling/grinding, screening, drying, binder and lubricant mixing processes are essential.

Binders provides necessary plasticity during pressing. They may be organic or inorganic. Typical organic binders are Polyvinyl alcohol (PVA), polyethylene glycol (PEG), ethylene glycol, waxes, celluloses, thermoplastic or thermoset resins, chlorinated hydrocarbons, starches, gelatins, acrylics … etc. Typical inorganic binders are; clays, bentonites, Mg-Al silicates, soluble silicates, colloidal silica, colloidal alumina.

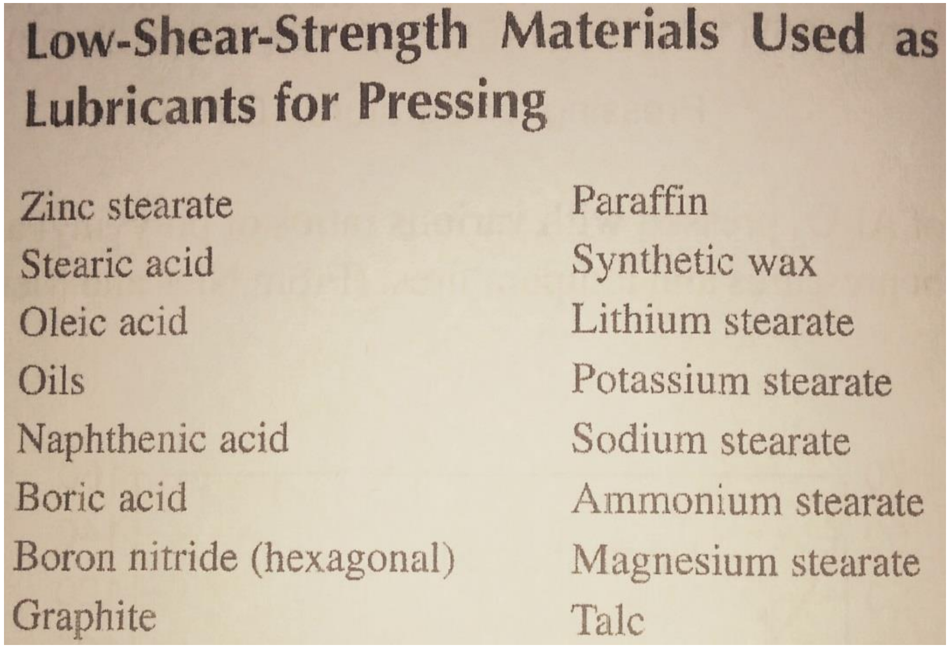
The amount of organic binder is quite low, i.e. 0.3 – 5 wt% depending to the final physical property requirements.

Shape Forming Processes

PRESSING

Lubricants are used to reduce friction between particles and the wall of the pressing die during pressing to increase uniformity of the pressed part.

Lubricants are basically low-shear strength materials. Below, some examples of organic and inorganic lubricants are listed.



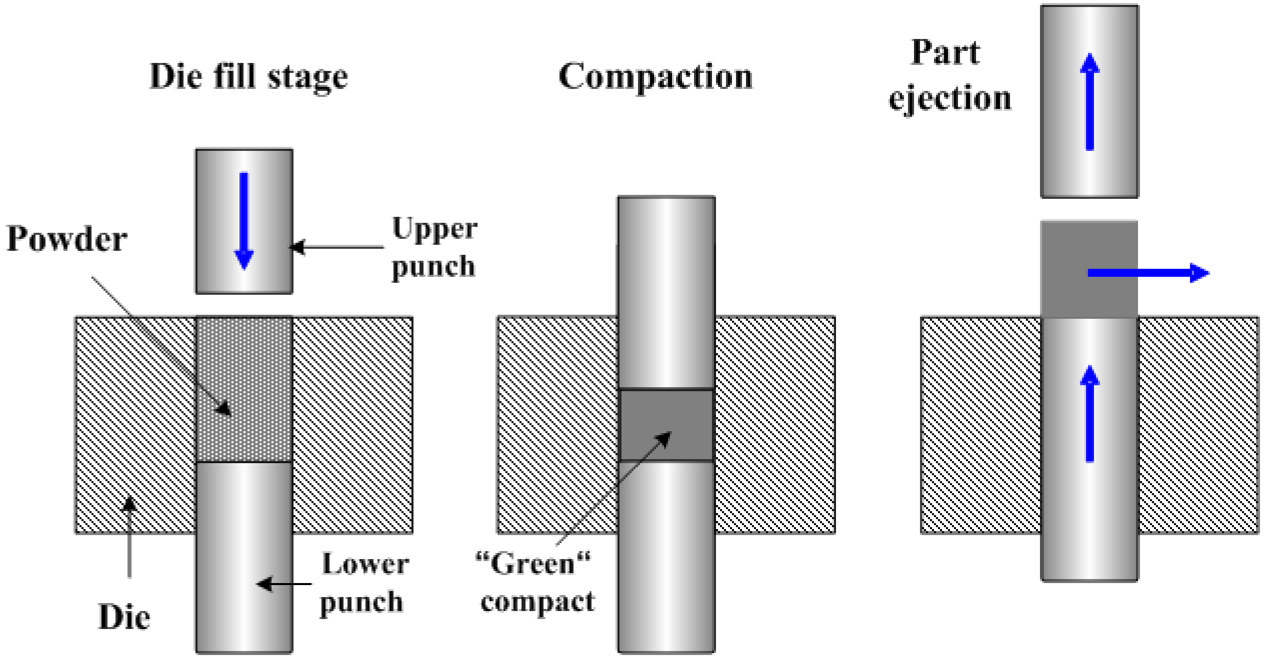
Low-Shear-Strength Materials Used as Lubricants for Pressing

Zinc stearate
Stearic acid
Oleic acid
Oils
Naphthenic acid
Boric acid
Boron nitride (hexagonal)
Graphite

Paraffin
Synthetic wax
Lithium stearate
Potassium stearate
Sodium stearate
Ammonium stearate
Magnesium stearate
Talc

Shape Forming Processes

UNIAXIAL PRESSING



Powder amount must be calculated properly. If you need 100 unit volume after firing with no porosity, your green powder compact must be around 120 unit volume. (The difference is porosity/air)

Shape Forming Processes

UNIAXIAL PRESSING

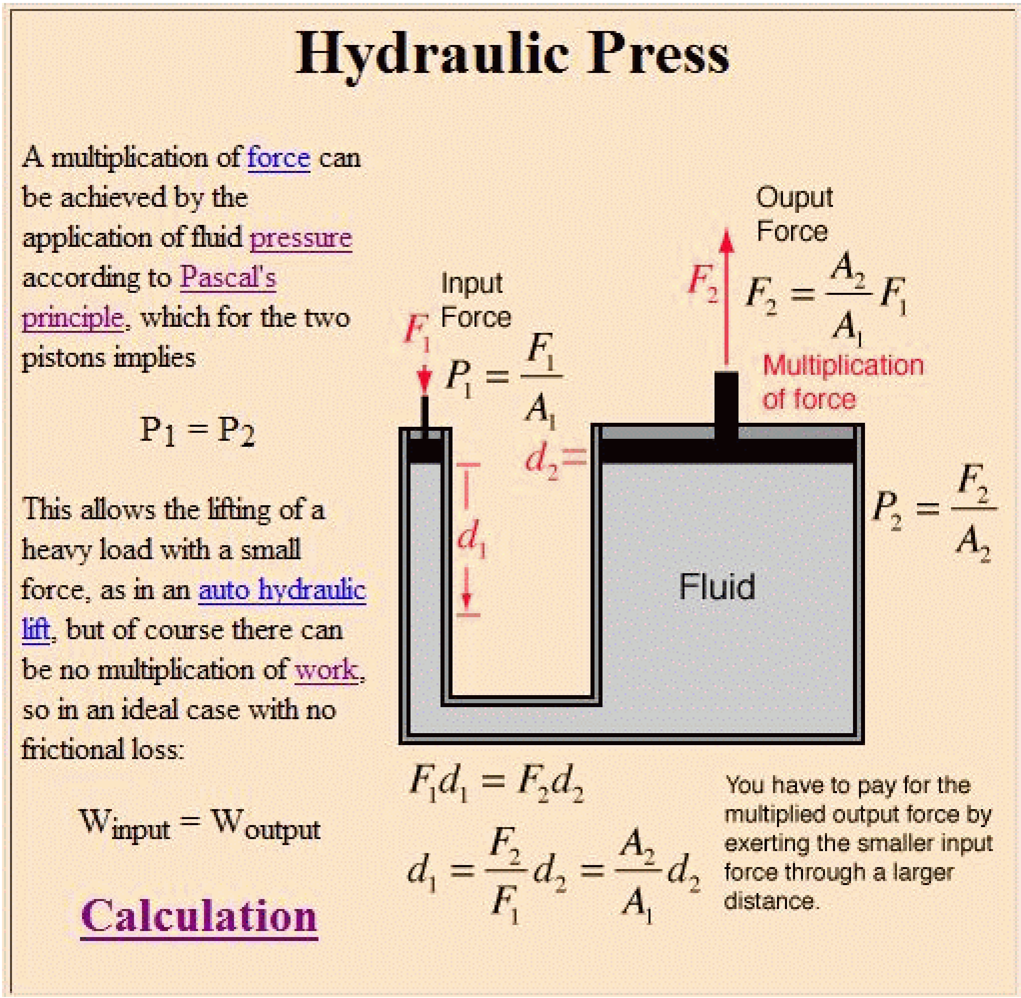
Problems of uniaxial pressing are;

- Die wear – possible solution is to use proper lubricant
- Cracking – possible solutions: increase green strength by proper binder selection, use of lubricant to decrease wall friction

For ceramics; exceeding 100 Mpa in uniaxial pressing may result in lamination. To be able to apply higher pressures, forces must act from every point to the sample, wchich can be in a fluid, which will be discussed soon.

Shape Forming Processes

UNIAXIAL PRESSING



Hydraulic Press

A multiplication of force can be achieved by the application of fluid pressure according to Pascal's principle, which for the two pistons implies

$$P_1 = P_2$$

This allows the lifting of a heavy load with a small force, as in an auto hydraulic lift, but of course there can be no multiplication of work, so in an ideal case with no frictional loss:

$$W_{input} = W_{output}$$

Calculation

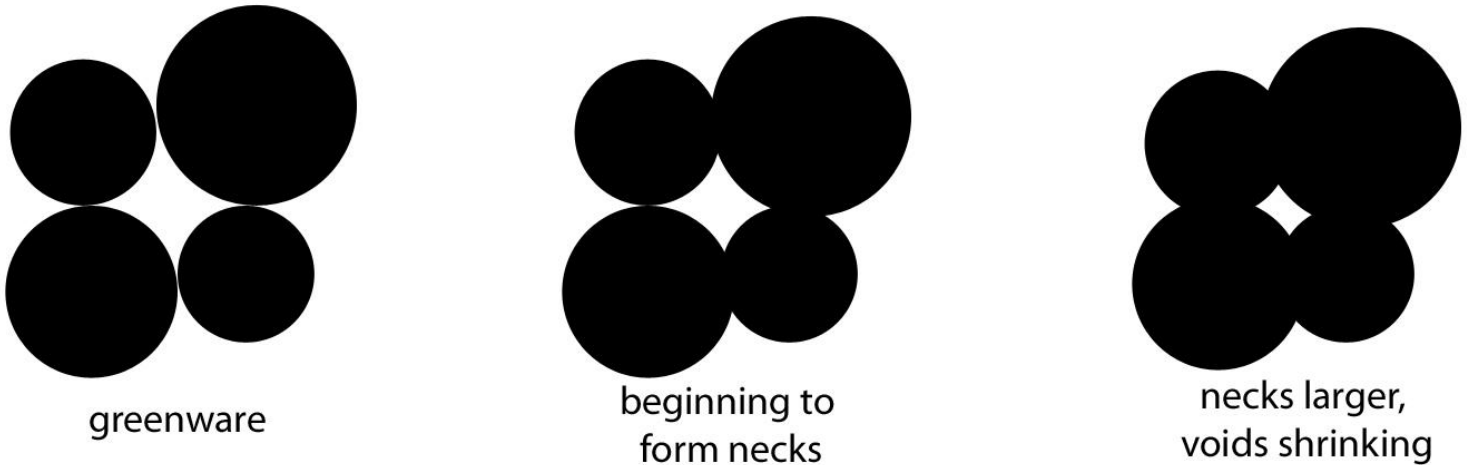
$$F_1 d_1 = F_2 d_2$$

$$d_1 = \frac{F_2}{F_1} d_2 = \frac{A_2}{A_1} d_2$$

You have to pay for the multiplied output force by exerting the smaller input force through a larger distance.

Shape Forming Processes

SINTERING

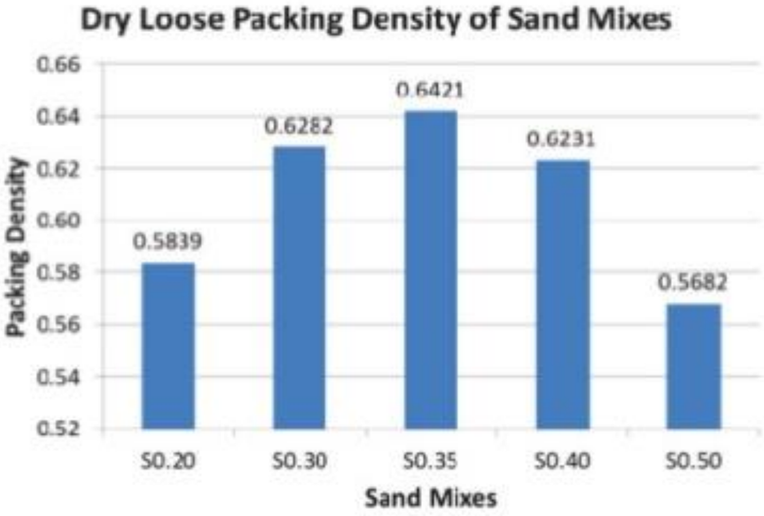


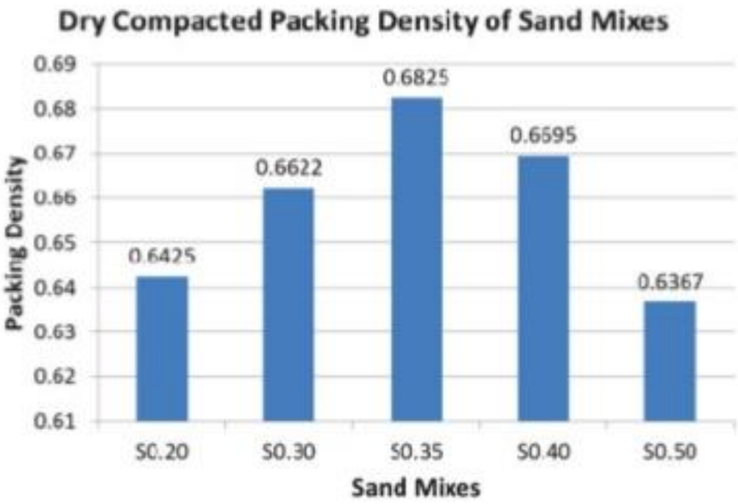
The phenomena in the figure is called, sintering. Sintering is essential in powder metallurgy and ceramic processing. Fusion, neck formation and pore elimination/densification are basic steps of sintering.

Shape Forming Processes

SINTERING

The effect of compaction to the final density of the ceramic product is limited. The theoretical density difference between loose and compacted mixtures is only around 4%. Please check the packing density numbers, and compare with BCC and FCC atomic volume density.





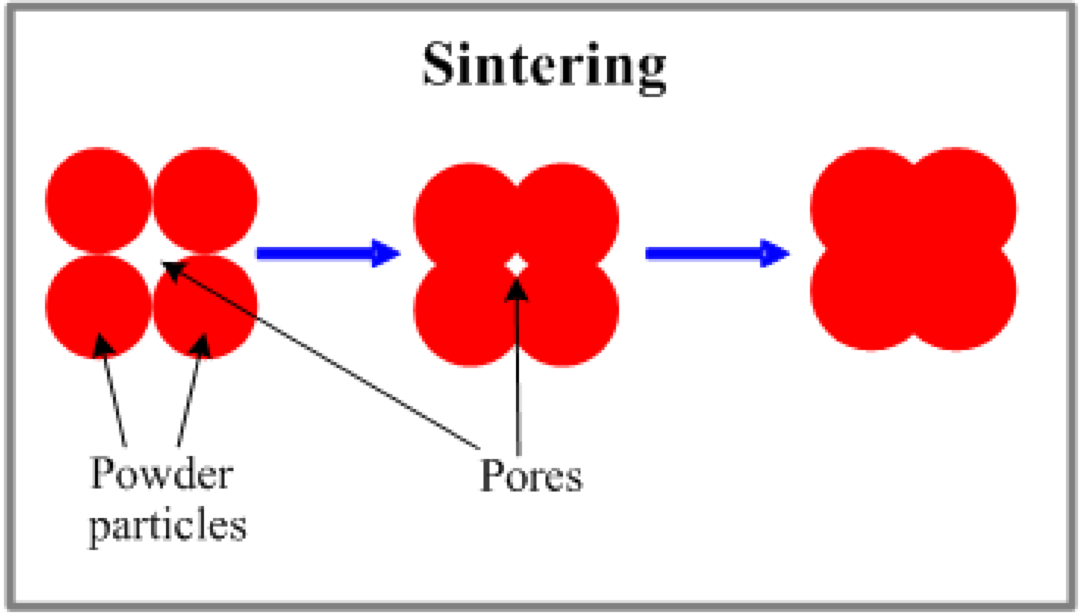
Shape Forming Processes

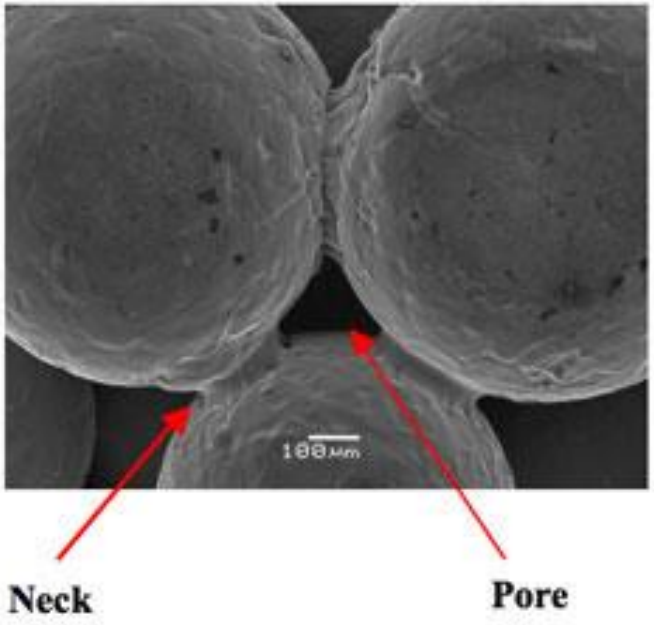
SINTERING

For sintering, following criteria must be met:

- A mechanism for material transport, and
- A source of energy to activate and sustain this material transport must be present

The primary mechanism for transport are diffusion and viscous flow. Heat is the primary source of energy in conjunction with the surface tension.

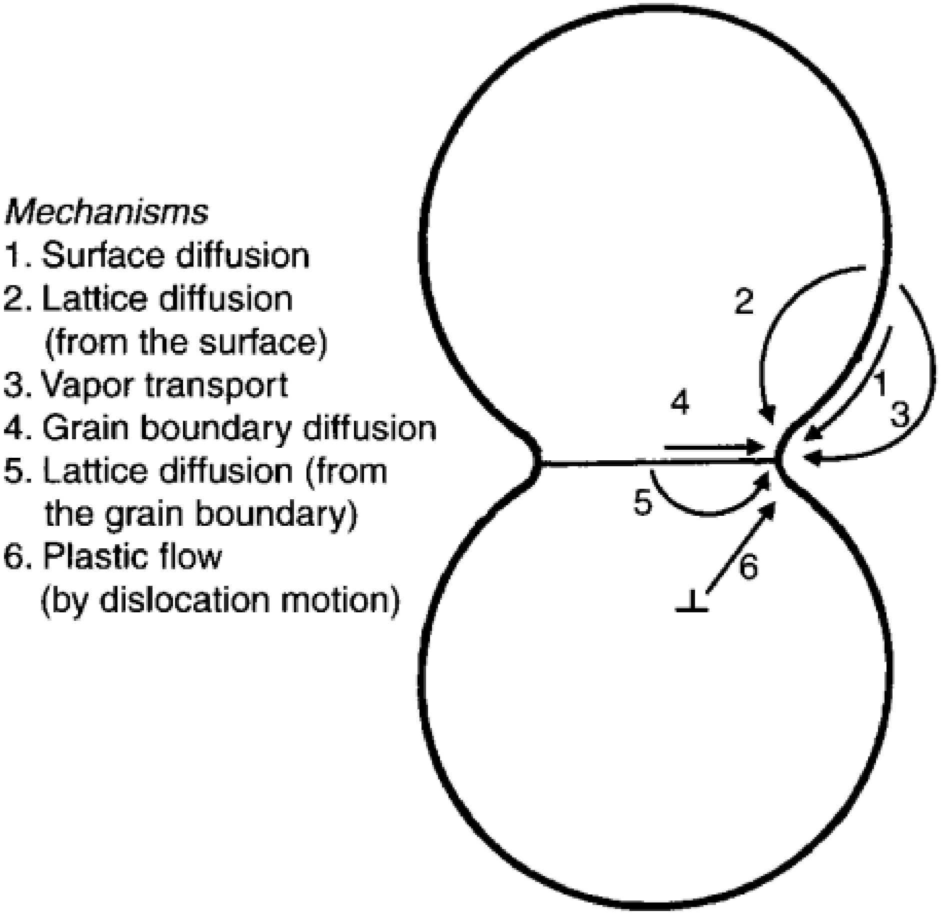




Shape Forming Processes

SINTERING MECHANISMS

- Vapor Phase – evaporation-condensation – Driving force is differences in vapor pressure
- Solid State– diffusion of atoms – Driving force is differences in free energy or chemical potential btw the free surfaces of particles
- Liquid Phase – viscous flow, diffusion – Capillary pressure, surface tension



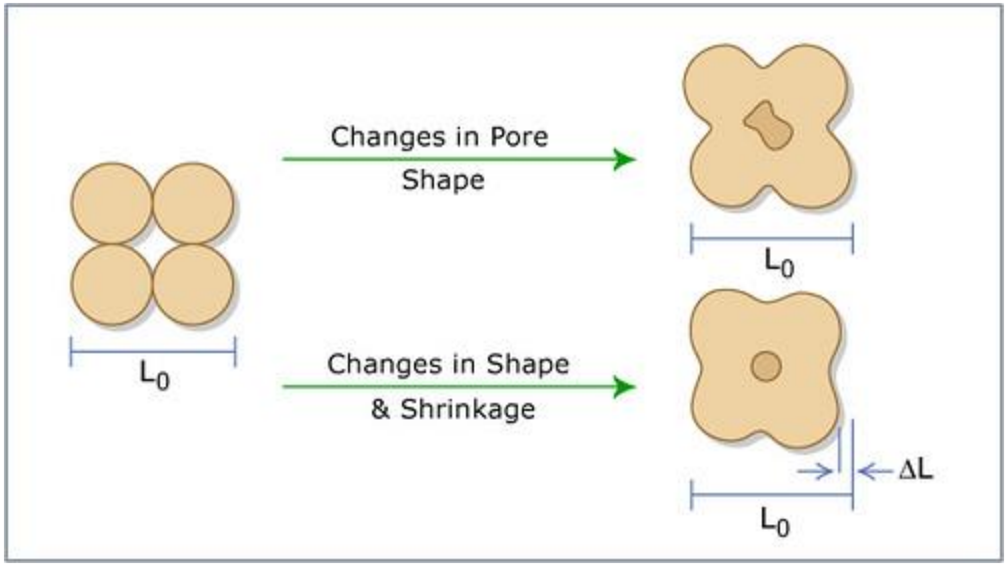
Mechanisms
1. Surface diffusion
2. Lattice diffusion (from the surface)
3. Vapor transport
4. Grain boundary diffusion
5. Lattice diffusion (from the grain boundary)
6. Plastic flow (by dislocation motion)

Free energy of the system is decreased, because surface area is decreased. Energy of solid/gas inerface is larger than energy of solid/solid interface

Shape Forming Processes

SINTERING MECHANISMS

Green ceramic – relative density is around 50%-60%
In pore elimination, particle centers approach eachother.



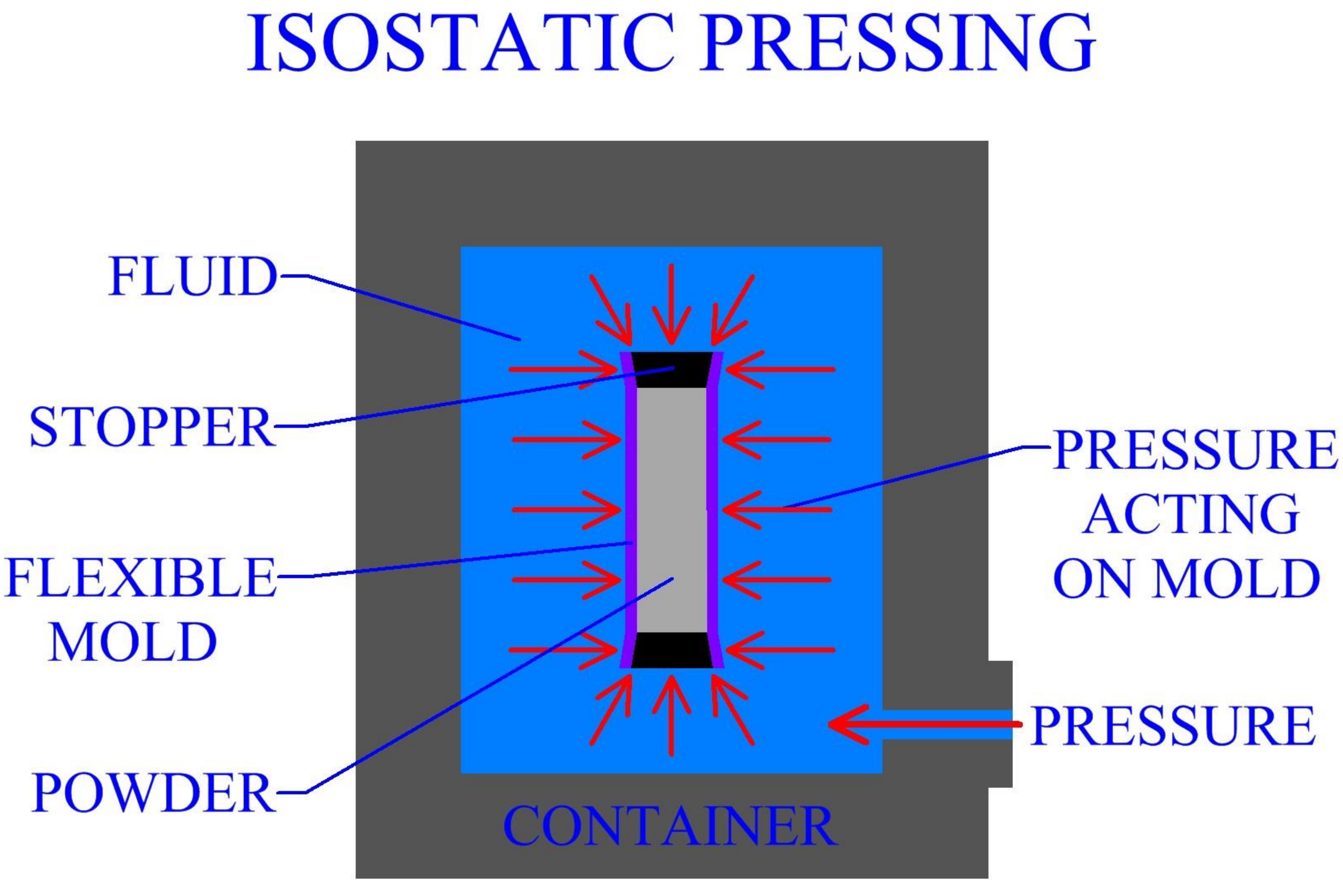
After neck formation and pore elimination it is possible to reach → 90-99%
For fully sintered parts, sample shrinks about 20% . Densification occurs during and after pore elimination.

But to be able to achieve >90% th. density, uniaxial pressing + heat treatment will not be enough. Isostatic Pressing is needed.

Shape Forming Processes

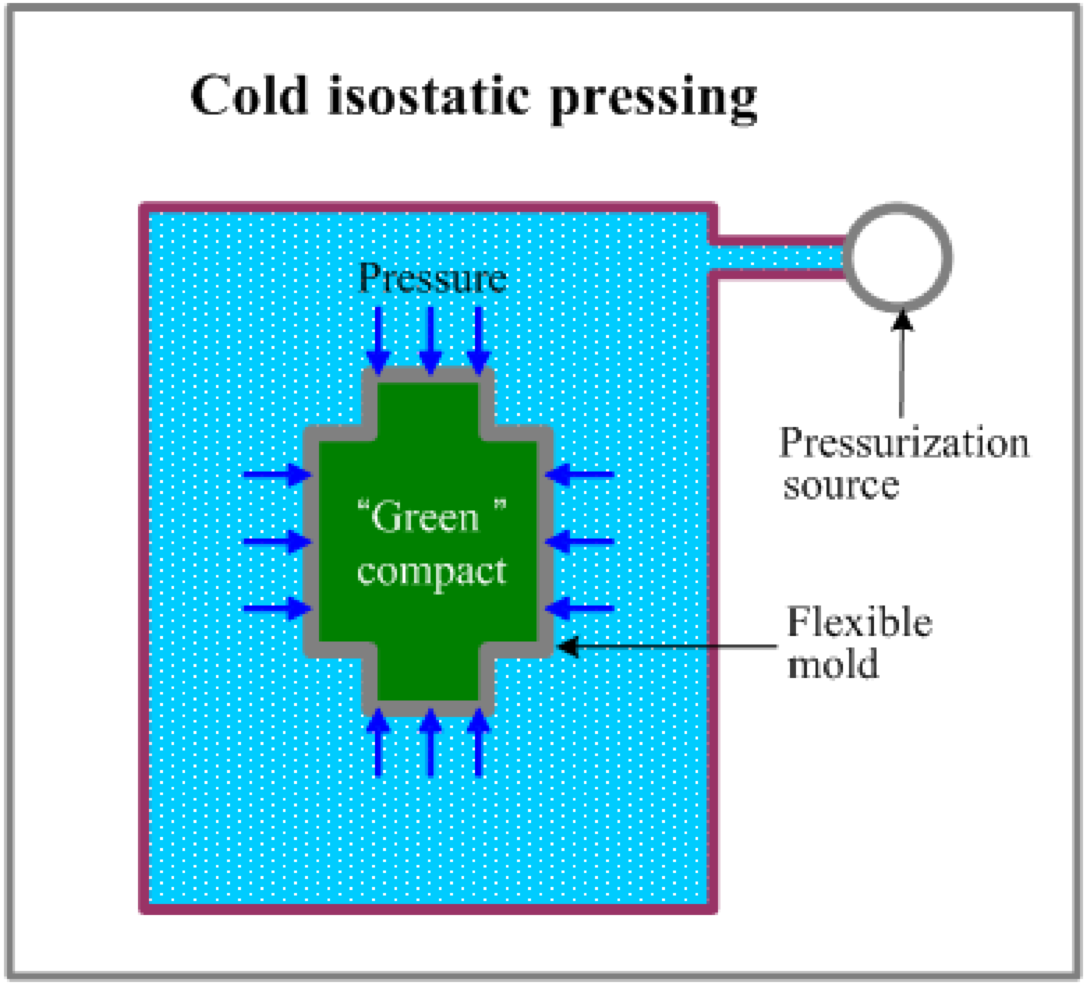
ISOSTATIC PRESSING

Isostatic pressure can overcome some of the limiations of uniaxial pressing . If the pressure can be applied from all directions to the sample, instead or 1 or 2 directins, this pressure is called Isostatic Pressing.



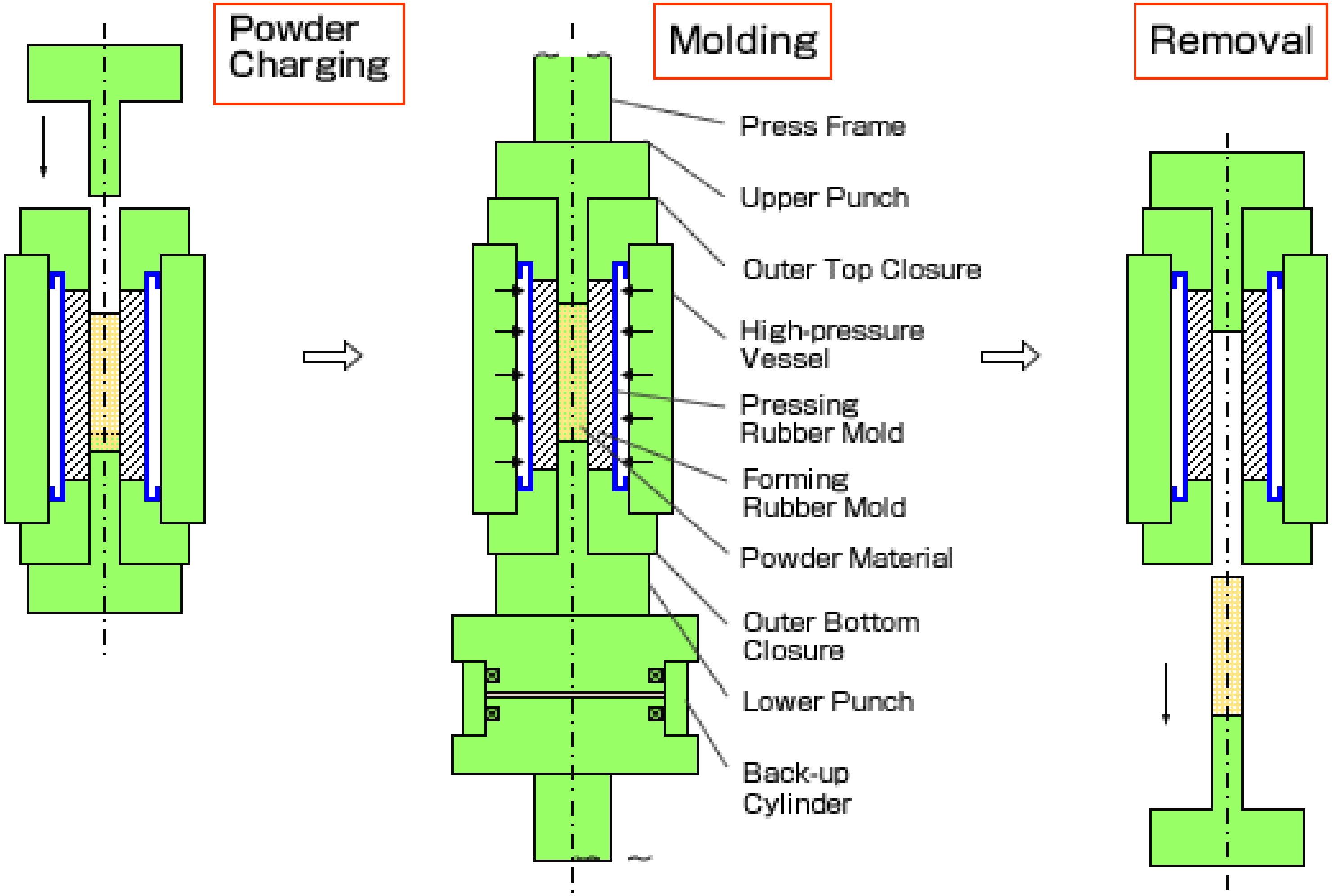
Shape Forming Processes

WET BAG ISOSTATIC PRESSING



Shape Forming Processes

DRY BAG ISOSTATIC PRESSING



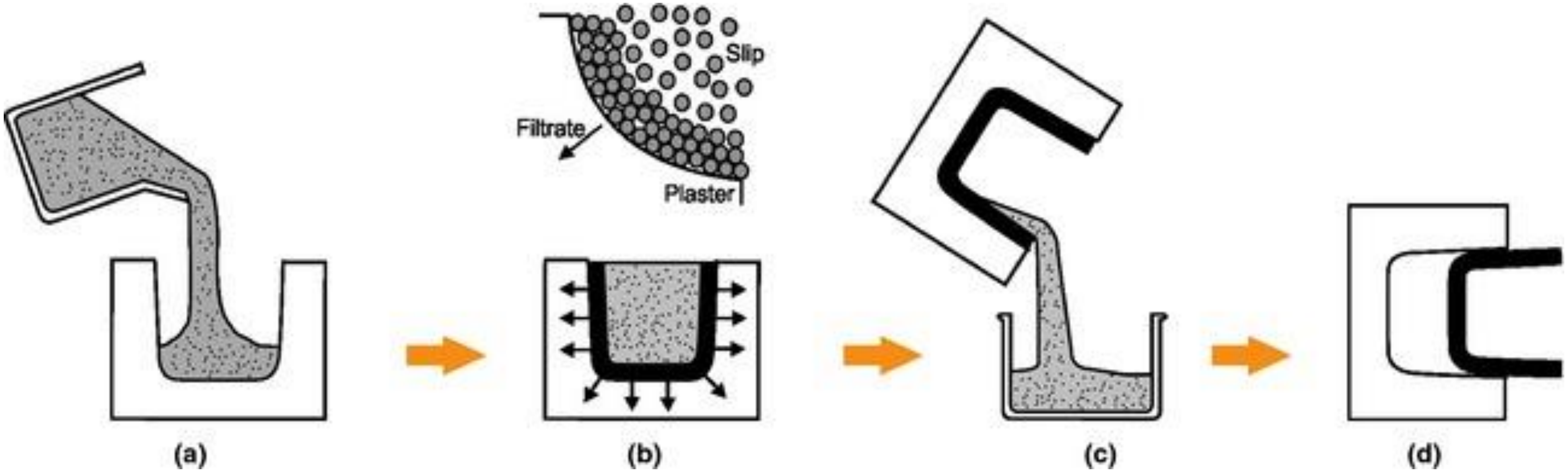
Shape Forming Processes

DRY BAG ISOSTATIC PRESSING

Shape Forming Processes

CASTING

Ceramics, since they have very high melting points, they cannot be melted & casted. They are produced from powders. *Slip Casting* is a method to produce ceramics. Ceramic particles suspended in a liquid are cast into a porous mold that removes the liquid and leaves a particulate compact in the mold.

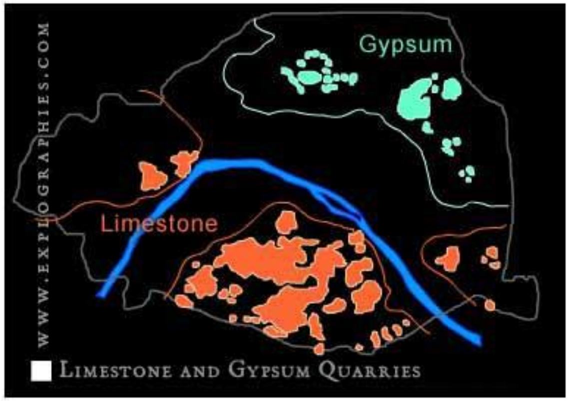


Shape Forming Processes

SLIP CASTING

Molds are generally Gypsum (Plaster of Paris)

$$CaSO_4 \cdot 2H_2O + \textit{heat} \rightarrow CaSO_4 \cdot 0.5H_2O + 1.5H_2O$$



«dry» Calcium sulfate hemihydrate absorbs water and become calcium sulfate dihydrate. Pororsity of the mold is essential, otherwise water cannot penetrate inside of the mold.

Shape Forming Processes

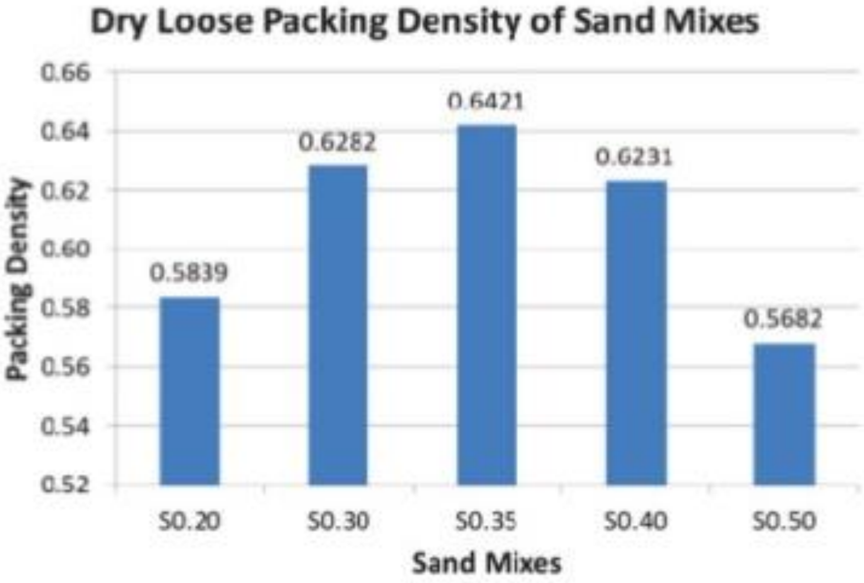
SLIP CASTING

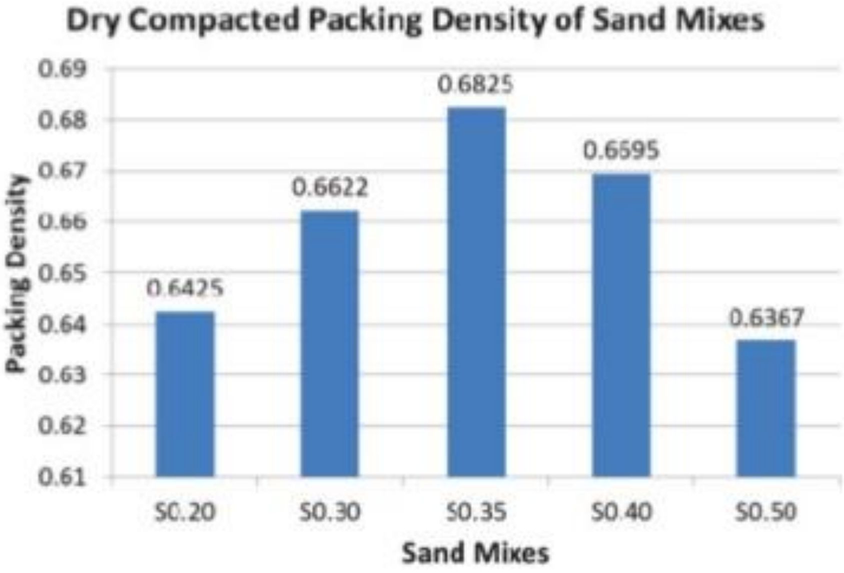
To some extent, complex shaped ceramics can be produced.

Shape Forming Processes

SLIP CASTING

The effect of compaction to the final density of the ceramic product is limited. Please check the theoretical density difference between loose and compacted mixtures. And please check the packing density amounts, and compare with BCC and FCC atomic volume density.



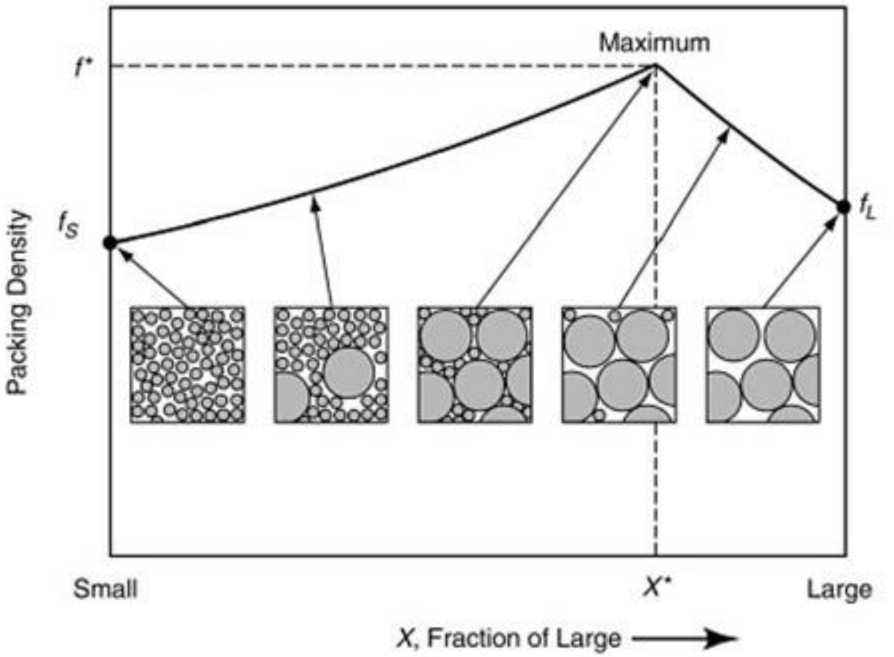


Shape Forming Processes

SLIP CASTING

Slip Preparation is critically essential. Final product quality depends on mainly slip preperation.

- Typical starting powder size is around 325 mesh (44μm). For high strength required applications, submicron particle size is needed. To achieve maximum packing density, particle sizing and required size distribution is needed.



Please calculate the optimum powder distribution and packing density to fill your container of 10cmx10cmx10cm cube. You can have minimum 1-μm diameter powders. Assume your powders are all spherical.

← This is your hint.

Shape Forming Processes

SLIP CASTING

The most common slip preparation method is wet ball milling or mixing.
Ingredients (powder, binders, sintering aids, dispersing agents) are added to the mill with proper proportions of the selected casting liquid.
By checking the viscosity, characteristics of the slip can be categorized.

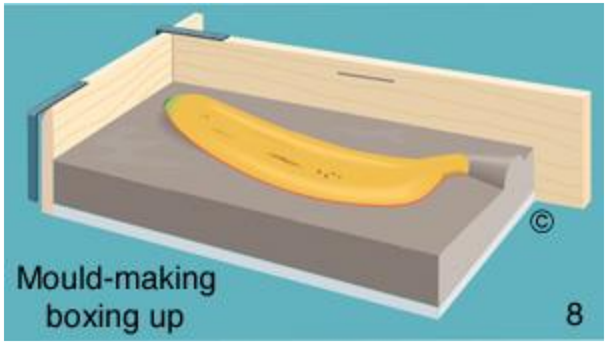
The mold for slip casting must have a controlled porosity. Traditional mold materials is gypsum, so called Plaster of Paris. The amount of porosity can be adjusted by changing gypsum-water ratio. Generally Plaster:Water ratio is around 70:100 by weight. After mixing gypsum and water, the gypsum-slip is casted into a container. The shape of the desired final product must be inside of the mold with a slip filling gap. (see Figures)

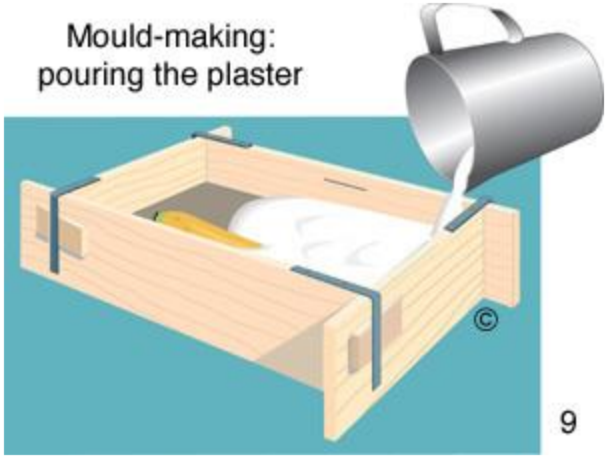
$$CaSO_4 \cdot 2H_2O + \mathit{180^0C} \rightarrow CaSO_4 \cdot 0.5H_2O + 1.5H_2O$$

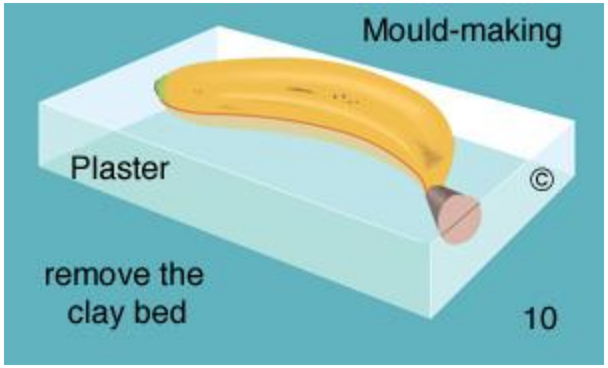
After heating at around 180^0C, the mold is dried, became gypsum hemihydrate and ready to absorb water from the slip to be poured into it.

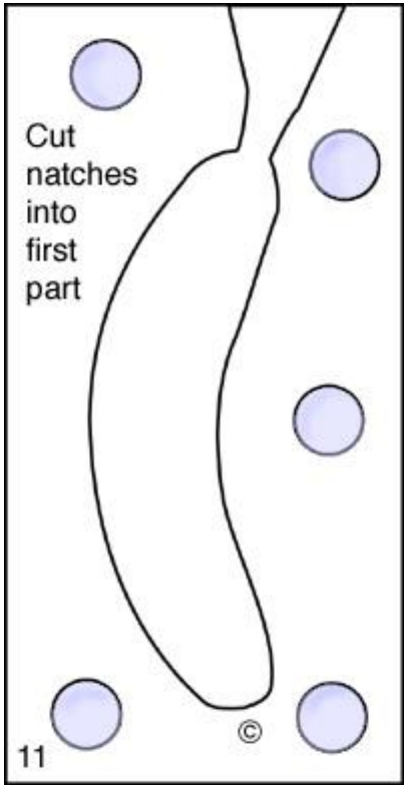
Shape Forming Processes

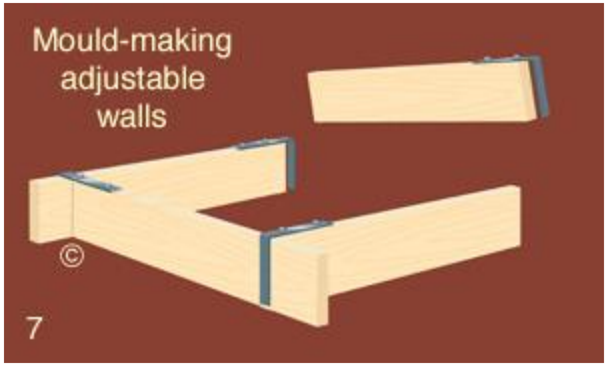
SLIP CASTING

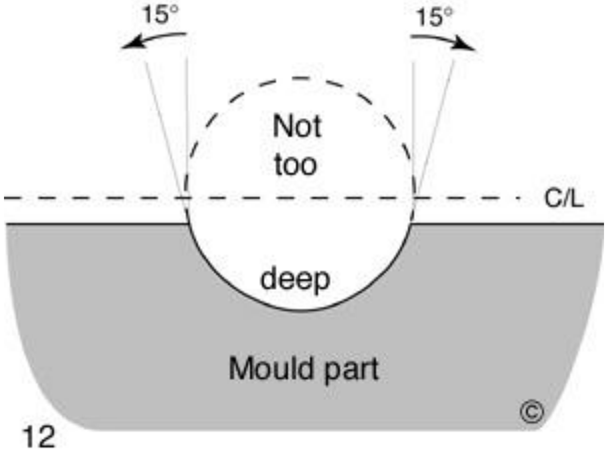








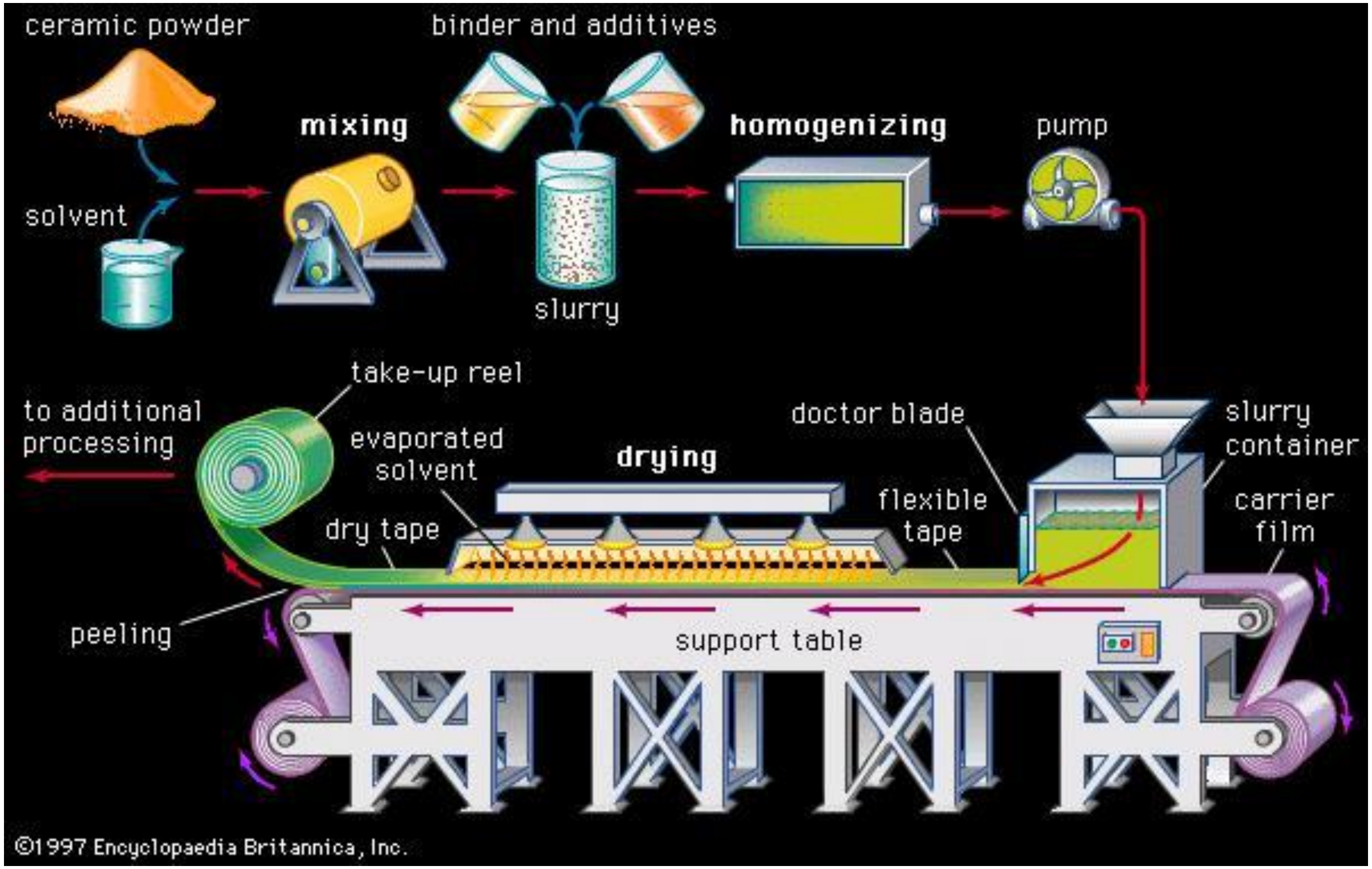




Shape Forming Processes

TAPE CASTING

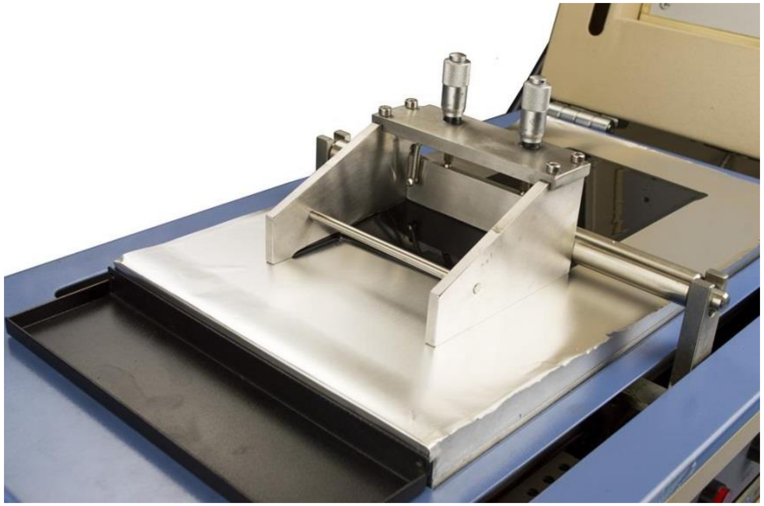
In some applications, thin sheets of ceramics are needed, for example electronics, dielectrics for capacitors. Tape casting is suitable to produce thin films of large quantity and low cost.



©1997 Encyclopaedia Britannica, Inc.

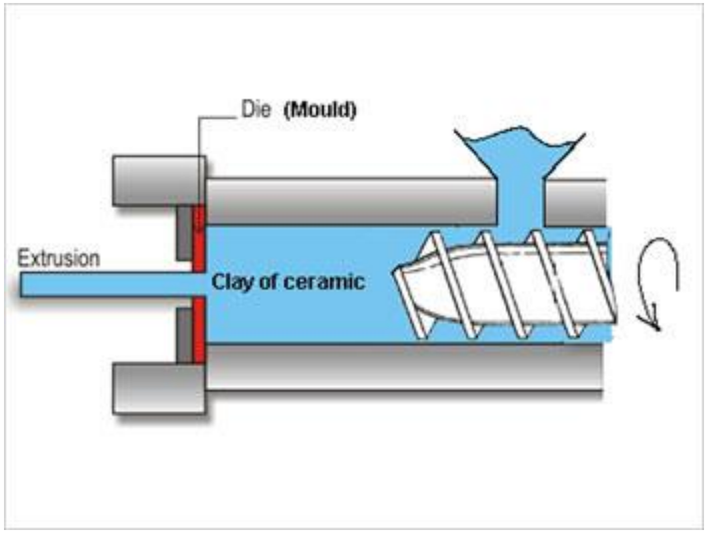
Shape Forming Processes

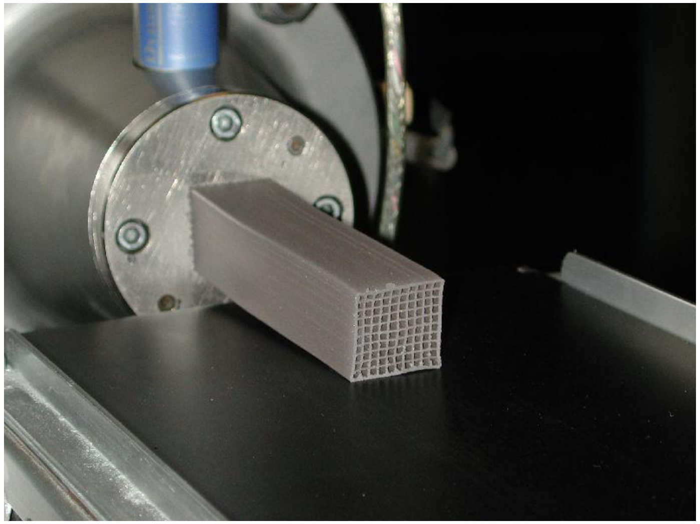
TAPE CASTING



Shape Forming Processes

EXTRUSION





Shape Forming Processes

EXTRUSION

Extrusion process consists of forcing a highly viscous, doughlike plastic mixture of ceramic powder + additives through a shaped die.

There are mainly 2 types of extruders, one is screw-type, the other is piston-type. In piston-type there is less contamination, but advantages of screw type are;

- It is possible to make continuous production,
- High-shearing is possible in twin screw extruders, which provides proper mixing in the exturder

Extrusion is a low-cost metod of forming large quantities of product. Bricks, furnace tubes, kiln furniture, thermocouple protection tubes, electronic substrates, refractories, whiteware etc.

Shape Forming Processes

EXTRUSION

Additives to a ceramic powder are required to achieve a mixture that has characteristics suaitable for extrusion. Following key characteristics must be considered:

- The mixture must be plastic enough to flow under pressure, yet rigid enough to resist deformation
- The mixture must not stick to the die, must yield smooth surfaces
- Fluid and ceramic should not seperated under pressure in the extruder
- Shrinkage during firing must be predictable (reproducible, homogenous porosity)
- Organics must be low-ash content to leave minimum residual during firing.

Flow characteristics (rheology) is the dominant factor.

- Compositions that contain clay, can be pasticized by just adding water. No organics needed.
- Compositions that does not contain clay needs organic plasticizers, additionally.

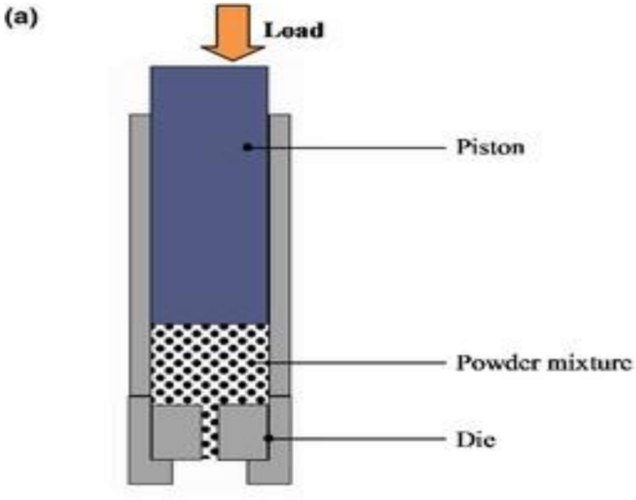
Shape Forming Processes

EXTRUSION

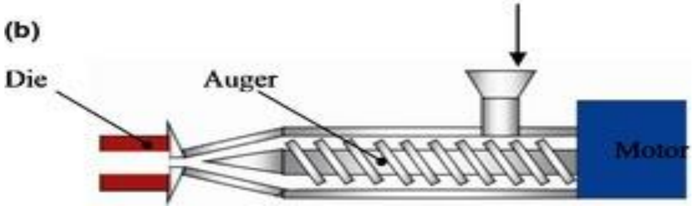
Extrusion process consists of forcing a highly viscous, doughlike plastic mixture of ceramic powder + additives through a shaped die.

There are mainly 2 types of extruders, one is screw-type, the other is piston-type. In piston-type there is less contamination, but advantages of screw type are;

- It is possible to make continuous production,
- High-shearing is possible in twin screw extruders, which provides proper mixing in the exturder



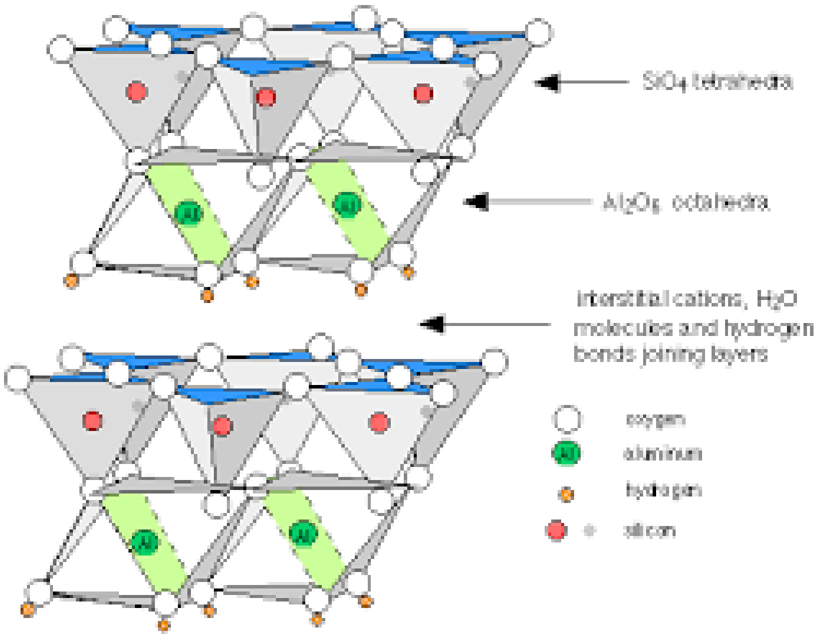
Extrusion is a low-cost metod of forming large quantities of product. Bricks, furnace tubes, kiln furniture, thermocouple protection tubes, electronic substrates, refractories, whiteware etc.



Shape Forming Processes

EXTRUSION

- Clay can absorb water between its sheets (remember clay microstructure) and this brings plasticity to itself.

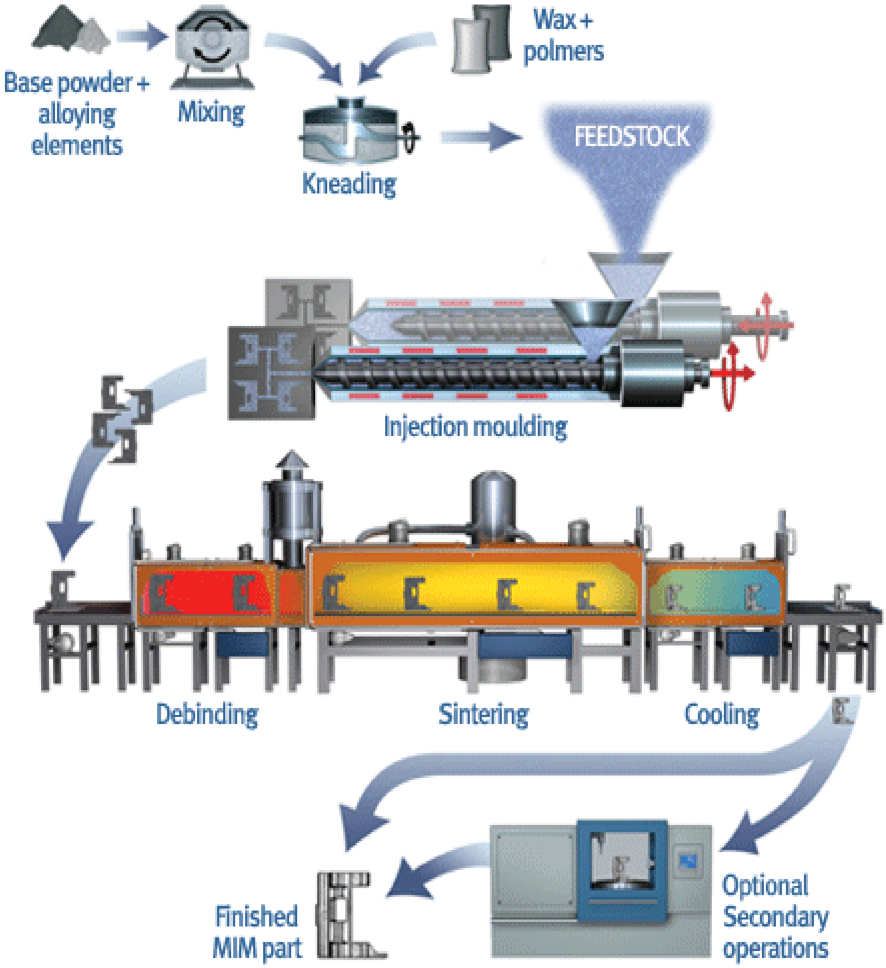


Shape Forming Processes

INJECTION MOULDING

Ceramic injection molding is ideal for high-volume production of complex, tight-tolerance components, ceramic injection molding offers significant advantages over conventional forming methods:

- Cost-effective technique for complex designs
- Ability to produce net or near-net shape parts
- Very tight tolerance control
- Low-cost, high-volume manufacturing runs



Shape Forming Processes

INJECTION MOULDING

For injection molding of ceramics, a thermoplastic polymer is required to the extent of 40 vol%, called binder.

For example, to injection mold silicon carbide (SiC), ethyl cellulose is such a binder used. During binder removal, which is firing of the molded product, 15-20 vol% shrinkage expected.

Injection molding is low cost, high capacity production method, but initial investment is high.

Operation temperature is just above the melting temperature of binder (answer of why thermoplastic polymers are used, not thermosets)

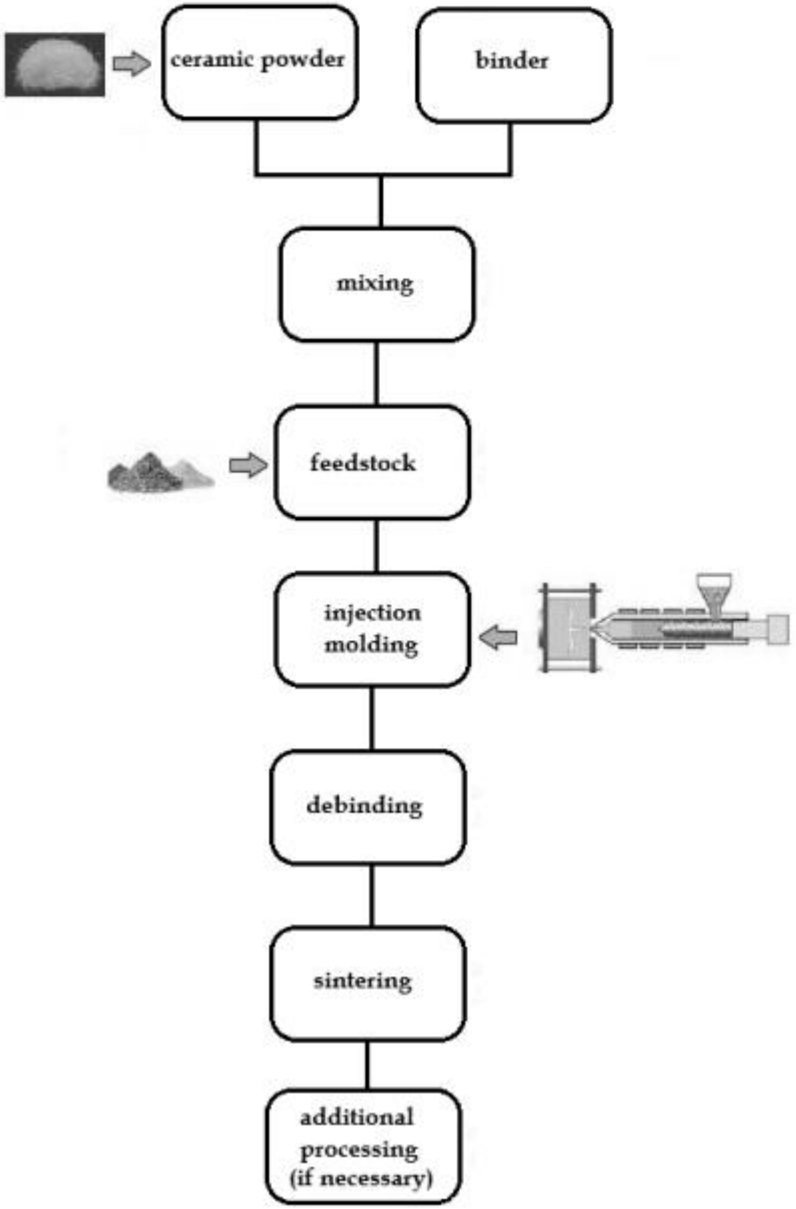
Shape Forming Processes

INJECTION MOULDING

The ceramic injection molding (CIM) process consists of four basic steps: feedstock preparation, injection molding, debinding process and sintering

Specific surface area, particle size, size distribution, particle shape and purity of the powder influence properties of the feedstock. Typical particle sizes in CIM are 1-2µm, but also much finer particles down to submicron or nano region are being used in advanced CIM.

CIM uses a feedstock of composite granulate. A high concentration of ceramic powder is mixed with a thermoplastic binder system to form moderate viscosity feedstock - homogenous powder-binder mix that is free of agglomerates, has optimum ceramic/binder content and still maintains sufficient fluidity



Shape Forming Processes

INJECTION MOULDING

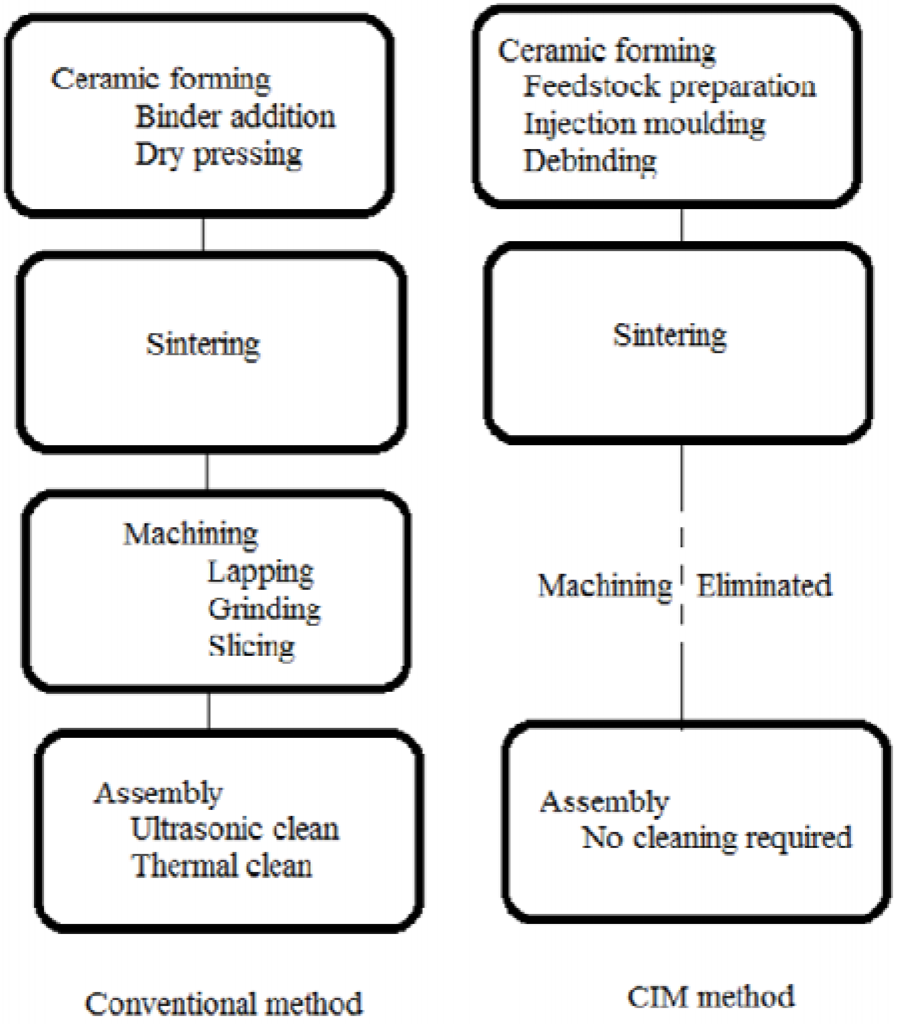
Example; Piezoelectric ceramics for CIM

Piezoelectric ceramics is one of the functional materials which have unique electrical properties with broadening range of applications. Lead zirconate titanate $Pb(Zr,Ti)O_3$ and barium titanate $BaTiO_3$ are ceramic materials that have found widespread use – especially lead zirconate titanate that is being widely used in sensors, transducers, microactuators, multilayer capacitors and micro-electromechanical systems (MEMS).

These materials are known for their superior piezoelectric and ferroelectric properties. When a mechanical force is applied, piezoelectric materials generate electrical voltage. Conversely, when an electric field is applied, these materials induce mechanical stress or strains. These effects are known as direct piezoelectric effect and converse piezoelectric effect, respectively.

Shape Forming Processes

INJECTION MOULDING



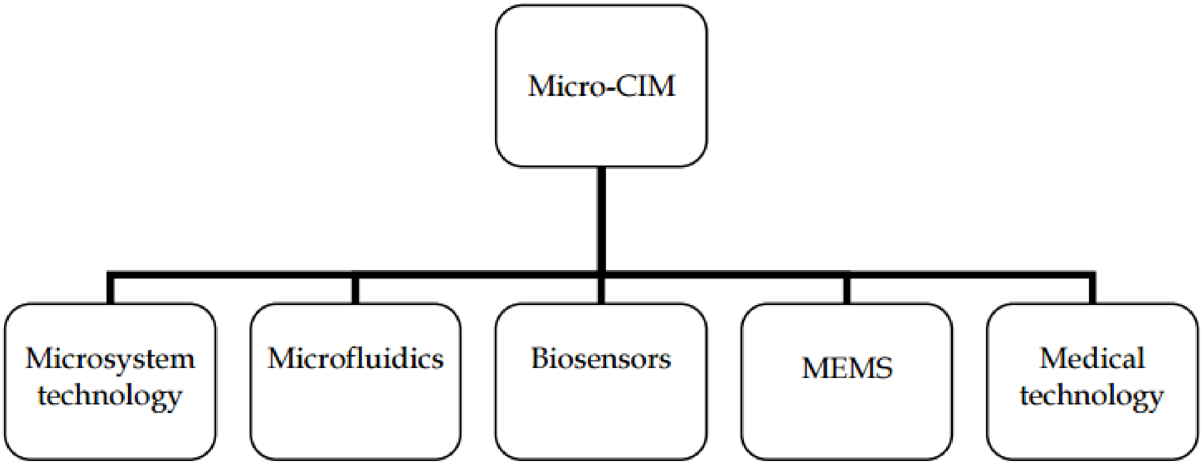
Piezoelectric ceramics production: conventional powder metallurgy method vs. CIM method (I. Stanimirović & Z. Stanimirović, 2010).

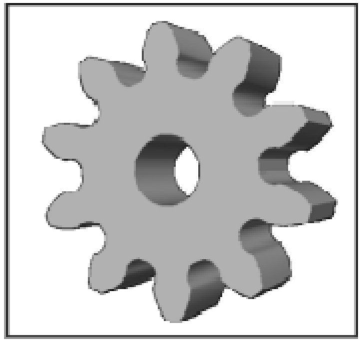
Shape Forming Processes

INJECTION MOULDING

Advanced CIM technologies

Mass produced micro-parts are mainly being produced from ceramic materials which are readily available in submicron sizes because fine ceramic powders are easier to handle in comparison with metallic materials which are often pyrophoric in submicron sizes and for that reason difficult to handle. Micro-CIM, as an expanding technology for mass-production of micro-parts, emerged as a combination of plastic micro-injection molding technology and ceramic injection molding technology.





Schematic of a ZrO_2 micro gearwheel (outer diameter 1200 µm).

Shape Forming Processes

GREEN MACHINING

The final shape and tolerances cannot always be achieved by pressing, casting or plastic forming. In many cases final dimensions are achieved by surface grinding or other finishing operations.

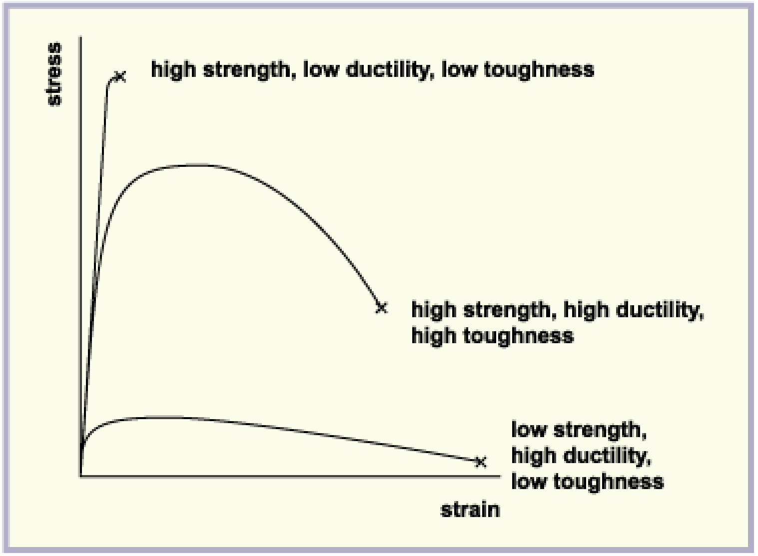
This requires diamond tooling → expensive
Therefore, final machining can be done before sintering/densification. This is called *Green Machining*.

Unfired ceramic → fragile

Properties of Ceramics

Mechanical Properties

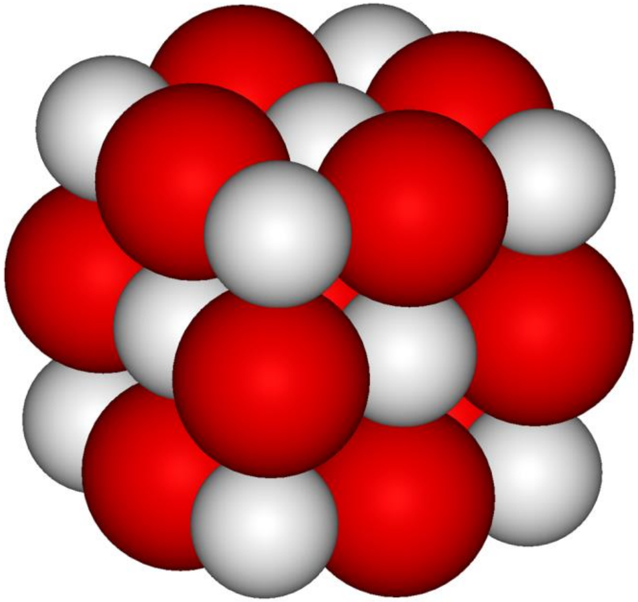
Ceramics work better in compression, rather than in tension. Why?

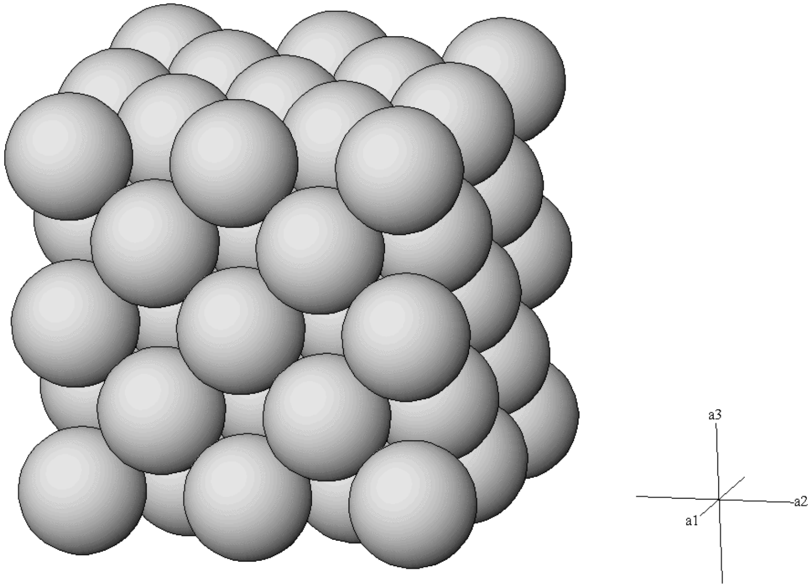


Properties of Ceramics

Mechanical Properties

Surface defect, negligible plastic deformation (because dislocations cannot move easily. Why in ceramics dislocations cannot move easily?) cause britleness in tensile loading.





Properties of Ceramics

Mechanical Properties

High performance structural ceramics possess high temperature capabilities + ability to carry some amount of tensile stress.

Ideally, ceramics are suitable for load-bearing applications. In these applications, compressive strength is important.

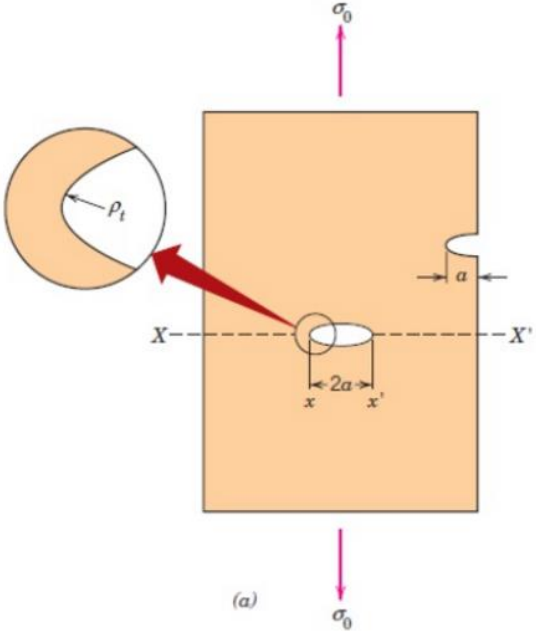
Fracture of ceramic samples under tensile loading takes place generally from the cracks nucleated by the surface flaws. Since ceramics fail after about 0.1% strain, they are tested in bending instead of tension.

Properties of Ceramics

Mechanical Properties

Surface or inner defects, negligible plastic deformation (because dislocations cannot move easily. Why in ceramics dislocations cannot move easily?) cause britleness in tensile loading.

Griffith Theory



If the crack is similar to an elliptical hole through plate, and is oriented perpendicular to applied stress, the maximum stress, at crack tip

$$\sigma_m = 2\sigma_o \left(\frac{a}{\rho_t} \right)^{1/2}$$

where

ρ_t = radius of curvature

σ_o = applied stress

σ_m = stress at crack tip

a = length of surface crack or ½ length of internal crack

Properties of Ceramics

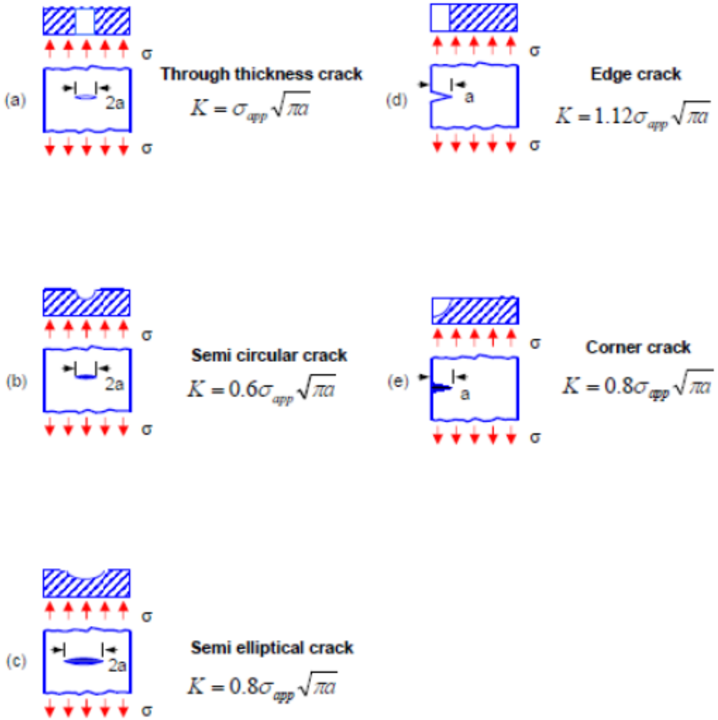
Fracture Toughness

Stress intensity factor K_{IC} can be described as Fracture Toughness of materials (material resistance to crack propagation) under conditions of:

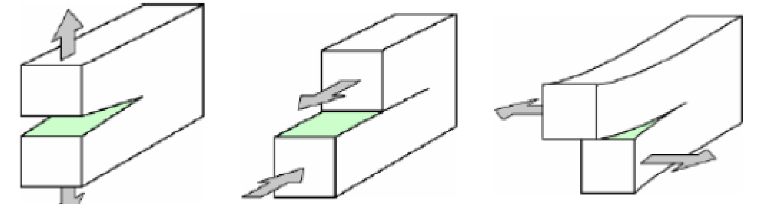
1) Brittle fracture
2) In the presence of a sharp crack
3) Under critical tensile loading

$$K_{IC} = \alpha \sigma_{app} \sqrt{\pi a_c}$$

where K_{IC} is the critical stress intensity factor for «mode I» failure, a_c is the critical crack length, σ_{app} is the applied stress, α is a parameter depend on specimen and crack geometry



Fracture Modes



Mode I: tension, opening

Mode II: In plane shear, sliding

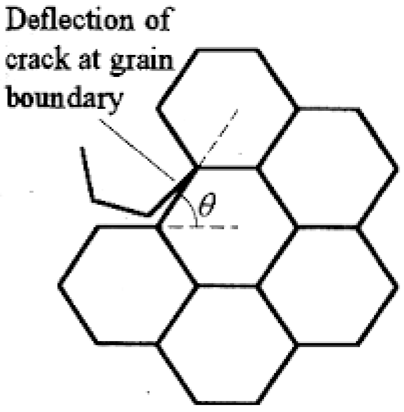
Mode III: Out of plane shear, tearing

Properties of Ceramics

Toughening Mechanisms

Crack Deflection

Polycrystalline ceramics are found to be tougher than single crystalline ones. For example Poly x-tal alumina has KIC of 4 MPa √m, and single x-tal aluminma has only 2.2 MPa√m.
The major reason of this is crack deflection, which is an energy absorbing mechanism because the path length of the crack is increased.



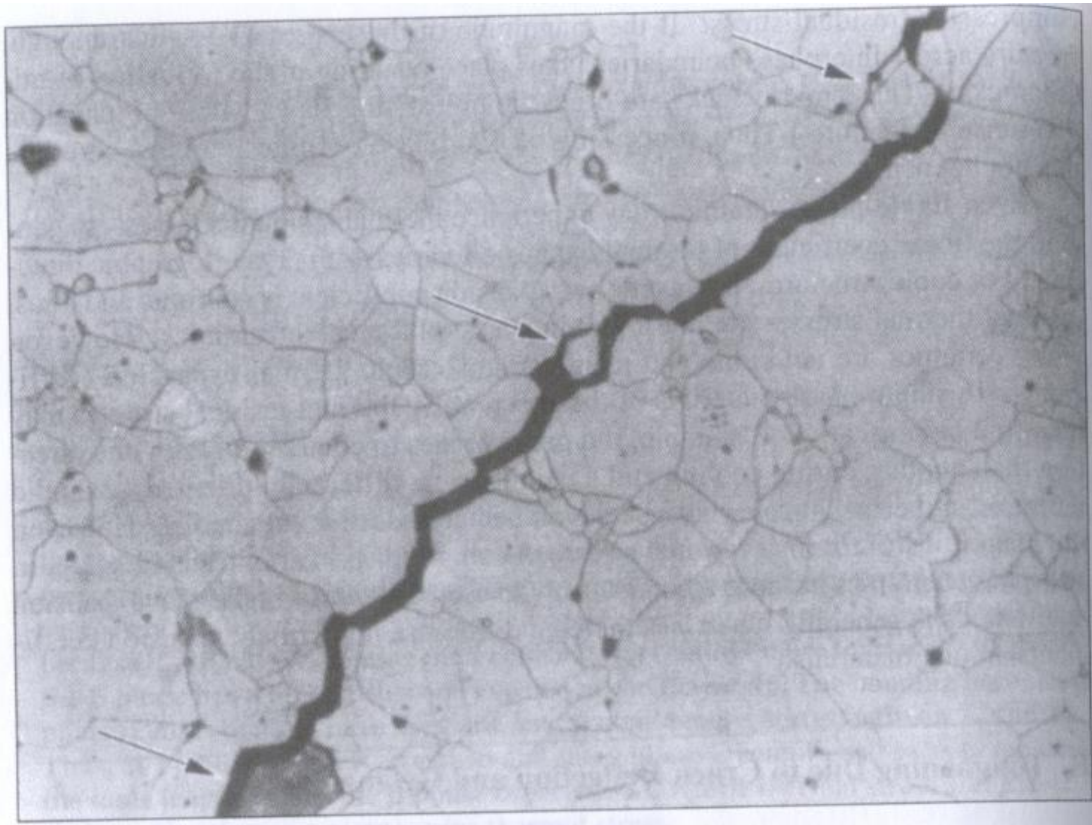


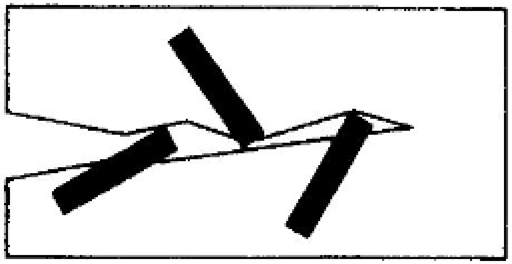
Figure 10.7
A crack in polycrystalline alumina with a mean grain size of 25 μm. The fracture is along grain boundaries and, as a result, the actual fracture surface area is greater than the nominal one which does not take into account such crack path diversions. The diversions add to the fracture work. (*From P. L. Swanson, C. J. Fairbanks, B. R. Lawn, Y-W. Mai, and B. J. Hockey, J. Amer. Cer. Soc., 70, 279, 1987.*)

Properties of Ceramics

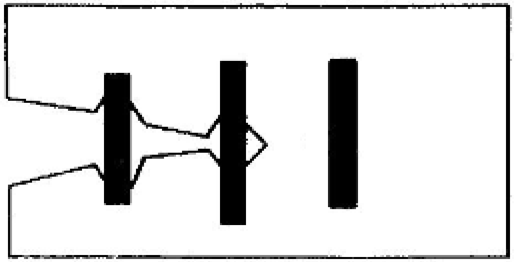
Toughening Mechanisms

Crack Bridging

Crack bridging occurs when a crack encounters with a reinforcing phase such as whiskers, continuous fibers or elongated particles.

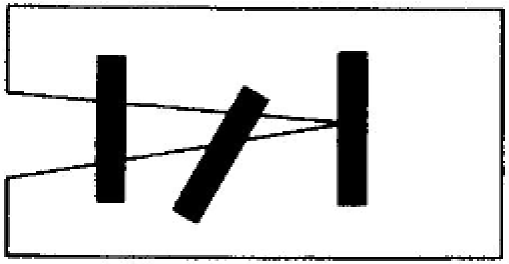


Crack Deflection



Interface Debonding
+
Crack Deflection

Crack bridging is another energy absorbing mechanism, which decreases the energy of crack. Therefore it helps the ceramic composite to be tougher.

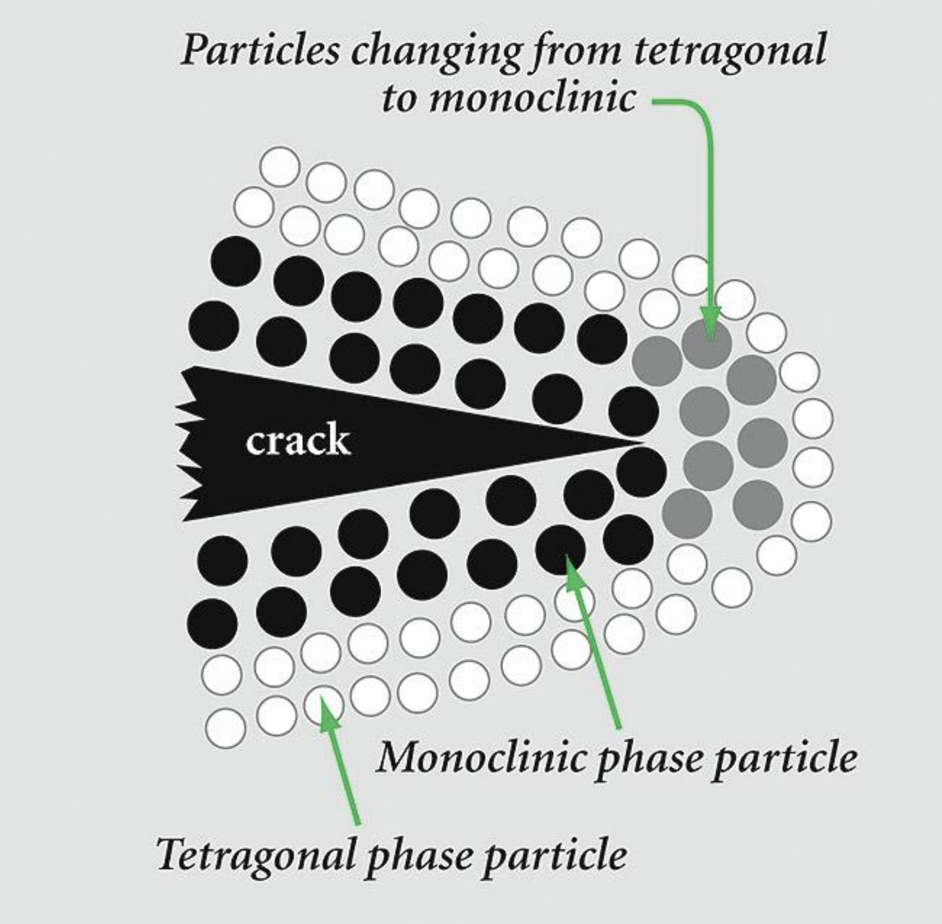


Fiber Bridging

Properties of Ceramics

Transformation Toughening

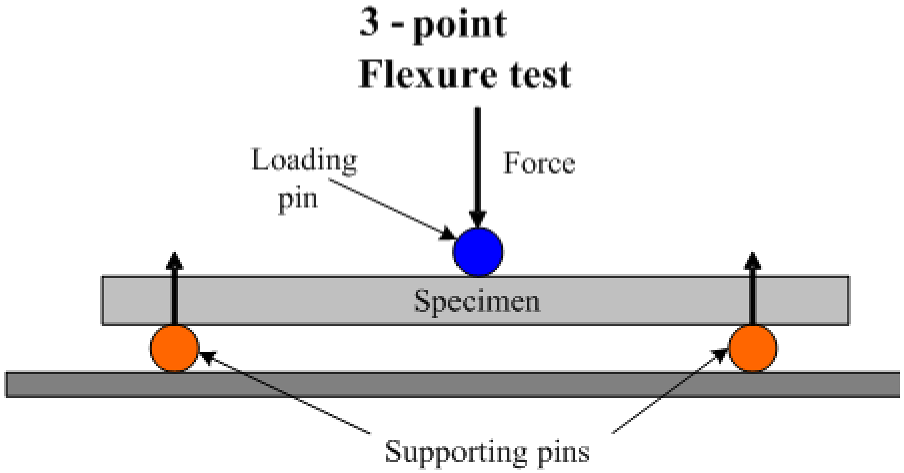
Zirconia- volume change under stress, if it is metastable tetragonal phase, it transforms under stress to monoclinic phase.

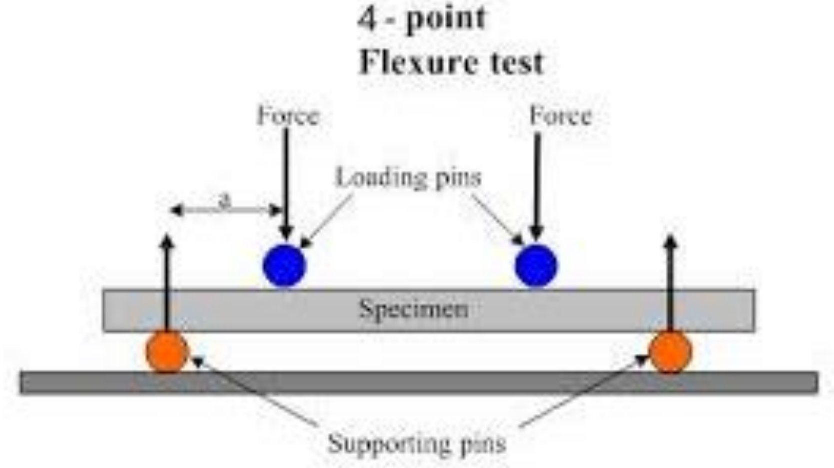


Properties of Ceramics

Mechanical Properties

Testing in Bending



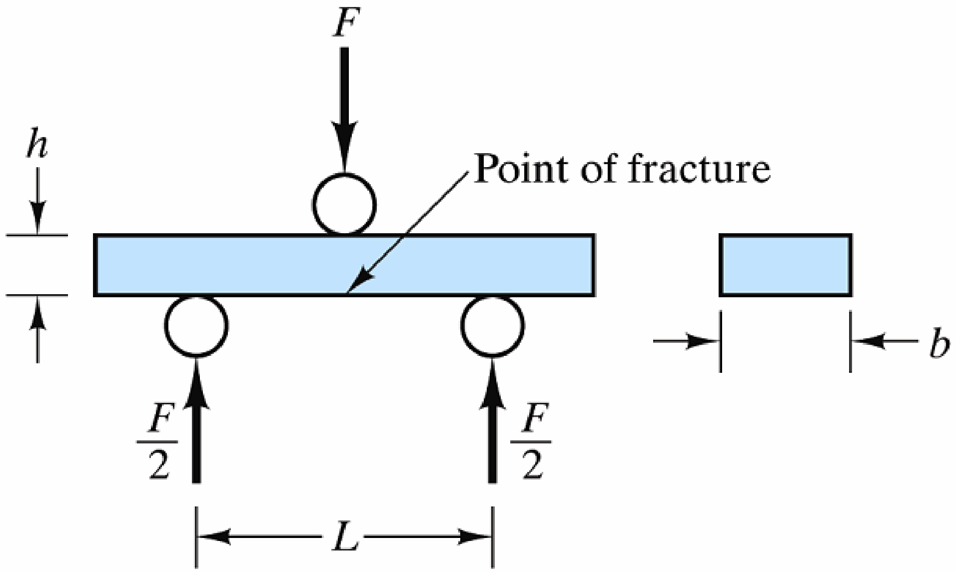


Lower cost testing system.
Sample geometry is simple (rectangular or cylindrical)
3-point or 4-point bending
A bend test determines Modulus of Rupture (MOR)

Properties of Ceramics

Mechanical Properties

Testing in Bending



Modulus of rupture = MOR

$$= 3FL/(2bh^2)$$

The bending test that generates a modulus of rupture.
This strength parameter is similar in magnitude to a tensile strength.
Fracture occurs along the outermost sample edge, which is under a tensile load.

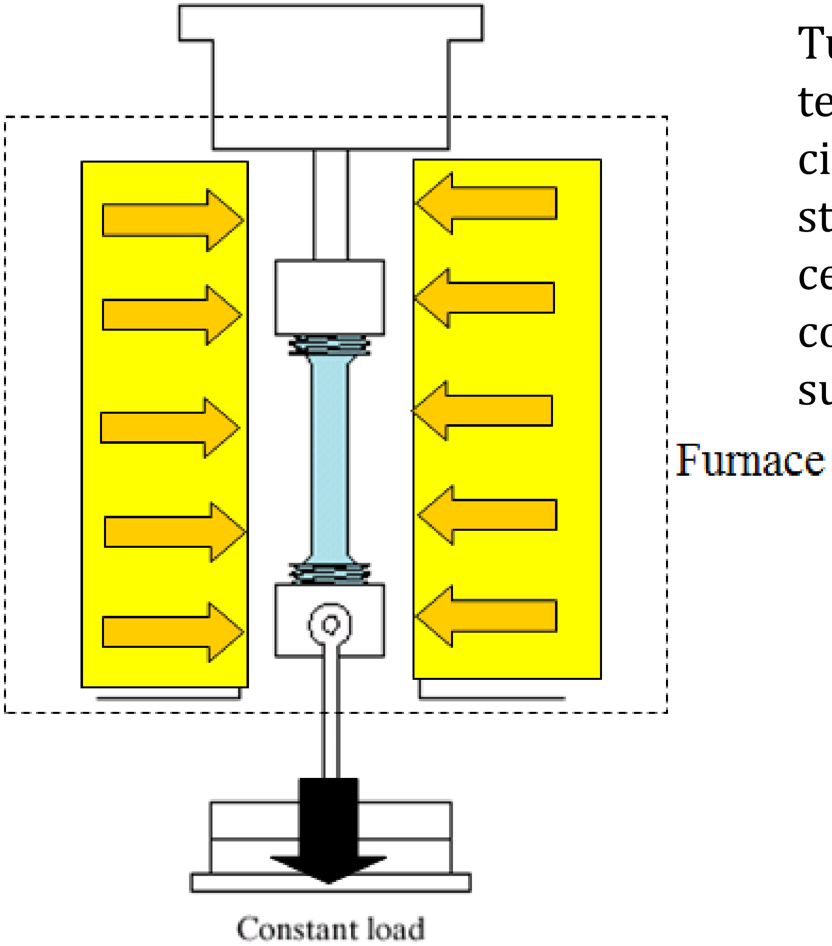
Properties of Ceramics

CREEP

Time-dependent deformation due to constant load at high temperature (> 0.5 T_m)

Examples: turbine blades, steam generators.

Creep test:



Turbine blade creep due to the inhospitable temperatures of a jet engine is an often cited example. High pressure boilers and steam lines, nuclear reactor fuel cladding, ceramic refractory brick in furnaces are components and systems that are also susceptible to creep effects.

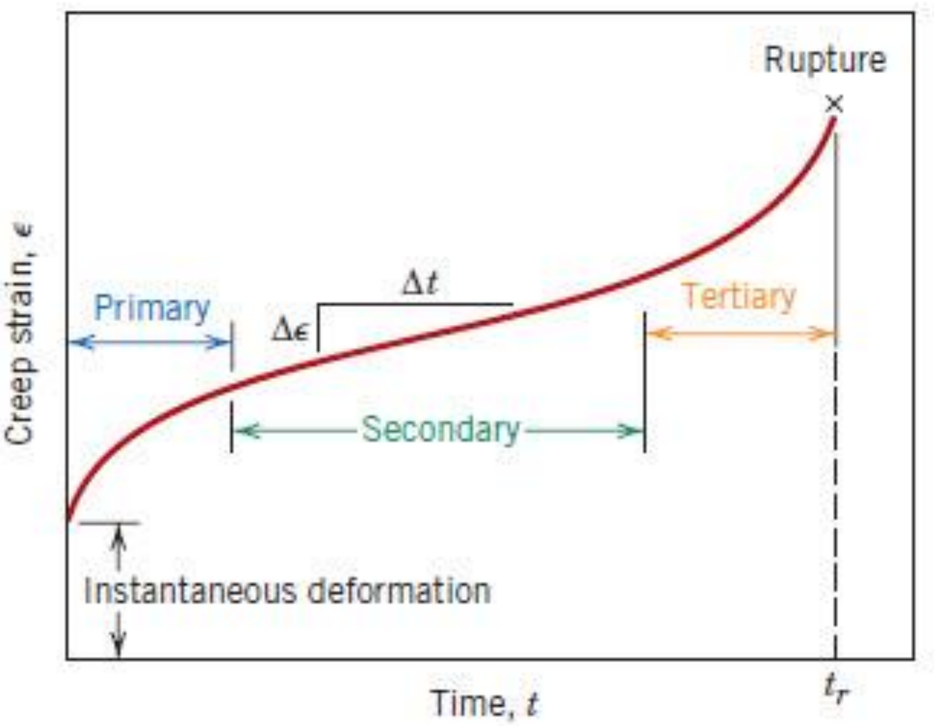
Properties of Ceramics

Mechanical Properties

CREEP

The term creep is deformation at constant stress as a function of time and temperature. A typical creep curve has four distinct regions:

The secondary creep region (steady-state creep) is the most useful for predicting the life of the ceramic.



$$\boxed{\dot{\varepsilon}_{ss} = A\sigma^{n} e^{-(Q/\bar{R}T)}}$$

$\dot{\varepsilon}_{ss}$ – *steady state creep rate*

A – *creep constant*

n – *creep exponent*

Q – *activation energy for creep* ($\mathrm{J}mol^{-1}$)

$\bar{R}$ – *universal gas constant* ($mol^{-1}K^{-1}$)

Properties of Ceramics

Mechanical Properties

CREEP

Engineers perform two types of tests. The first aims to determine the steady state creep rate over a suitable matrix of stress and temperature. These tests are performed at the <u>same stress</u> but at different temperatures, as well as at the <u>same temperature</u> but different stresses, as shown in Fig.

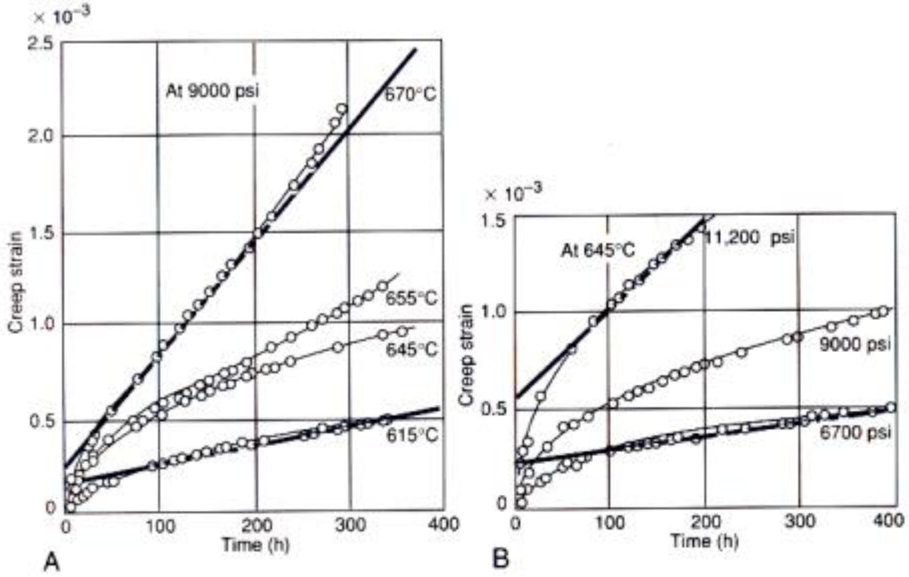


Figure 6. 15. Creep strain versus time in a 0.5 wt% o, 0.23 wt% steel. (A) Constant stress, variable temperature. (B) Constant temperature, variable stress. From A.J. Kennedy, *Processes of Creep and Fatigue in Metals*. Wiley, New York (1963)

Properties of Ceramics

Mechanical Properties

CREEP

Primary Creep or Transient Creep

This is the first stage of the creep which represents a region of decreasing creep rate. In this region the rate at which the material deforms decreases with time until it reaches a constant value.

In general, creep behavior of ceramics is similar to metals, however in ceramics creep happens at high temperatures ($>0.5\ T_m$)

In some ceramics, primary creep is the only creep region (SiC fibers)

$\varepsilon = \beta T^{m}$, where β is constant, m is a number btw 0.03 and 1.0 depending on the material, stress and temperature.

Properties of Ceramics

Mechanical Properties

CREEP

Steady-State or Secondary Creep

Strain increases linerly with time, the creep rate is constant, and deformation may continue for long time. This is the most important regime in creep. The equation is:

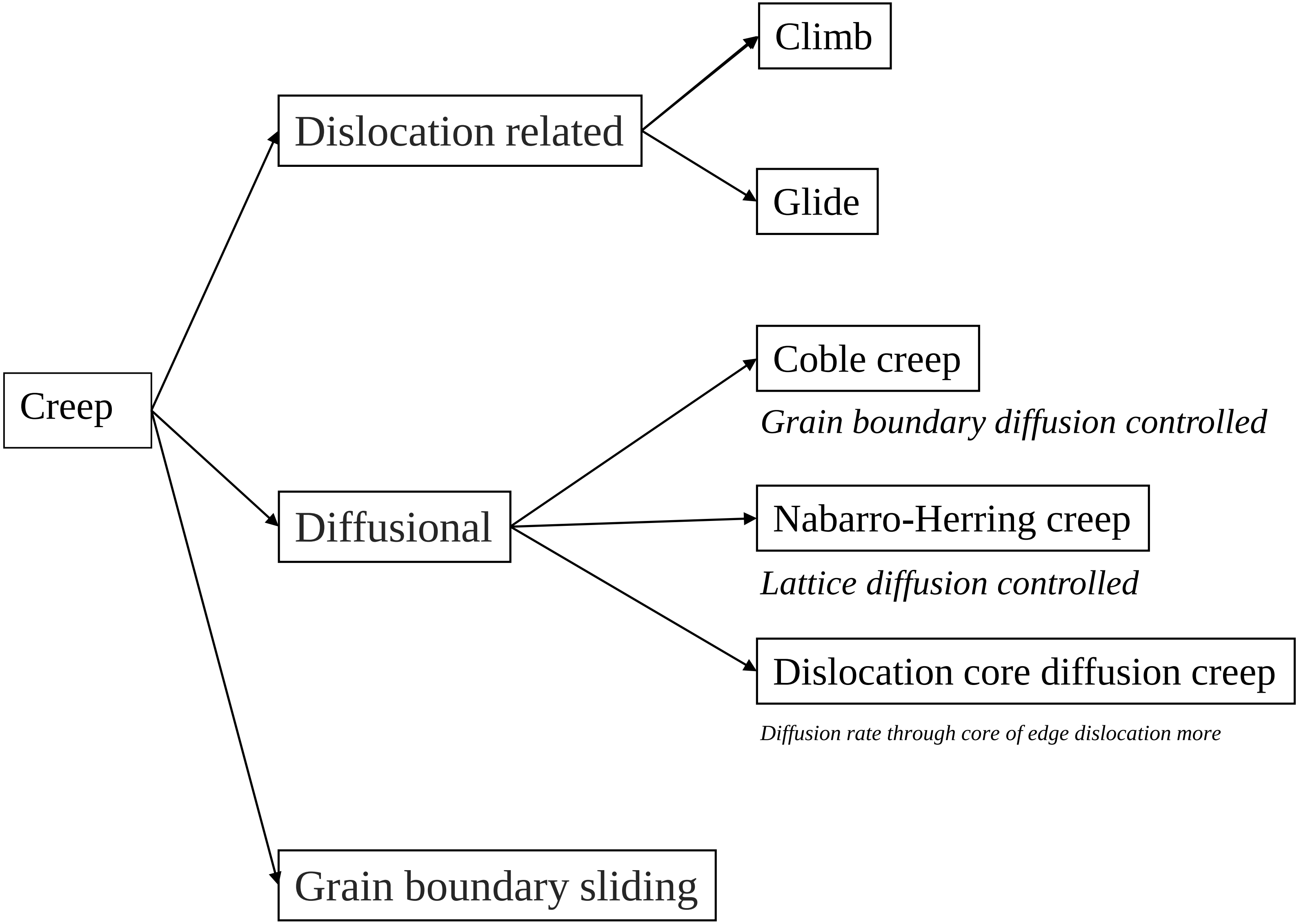
$$\varepsilon = Kt$$

where K is constant that depends on stress and temperature.

Tertiary Creep

A rapid increase in creep rate, just before failure. In ceramics, this stage is often missing.

Creep Mechanisms *of Ceramic Materials*



Creep

Dislocation related

Climb

Glide

Diffusional

Coble creep

Grain boundary diffusion controlled

Nabarro-Herring creep

Lattice diffusion controlled

Dislocation core diffusion creep

Diffusion rate through core of edge dislocation more

Grain boundary sliding

Properties of Ceramics

Mechanical Properties

CREEP

Dislocation Creep

Dislocation creep occurs by dislocation motion (climb, glide). For the climb controlled process, the creep rate can be expressed as:

$$\dot{\varepsilon} = \frac{\alpha D_L \mu b}{kT} \left(\frac{\sigma}{\mu}\right)^n$$

D_L is lattice diffusivity, μ is shear modulus, b is Burger's vector, α is dimensionless constat. The eqn can be simplify by taking all the «constants» into a temperture-dependent constant Γ;

$$\dot{\varepsilon} = \Gamma\, \sigma^n$$

For climb, n is in the range of 4-5, for glide, n=3.

Properties of Ceramics

Mechanical Properties

CREEP

Diffusion Controlled Creep

Diffusion controlled creep is due to the atomic diffusion. There is no dislocation motion. There is a counterflow of atoms. The creep rate is given by:

$$\dot{\varepsilon} = \frac{\alpha D_L \sigma \Omega}{d^2\, kT} \qquad \text{Nabarro-Herring}$$

which can be simplify by taking all the «constants» into a temperture-dependent constant Γ;

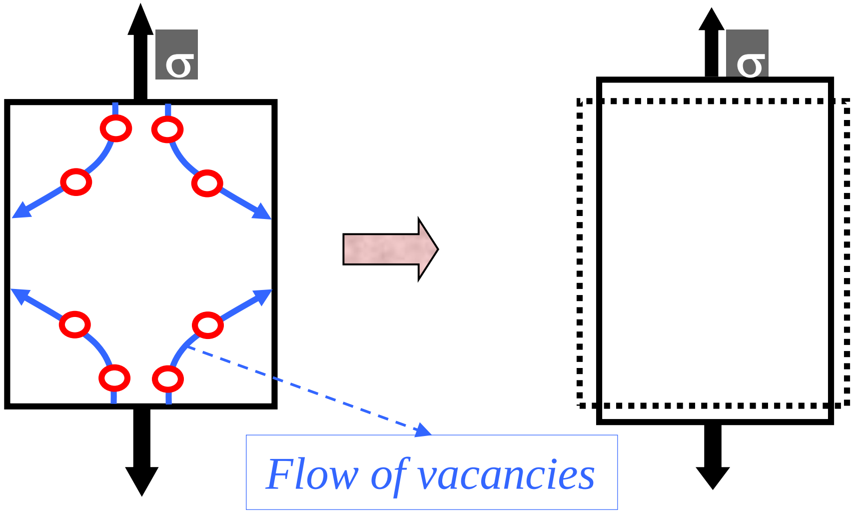
$$\dot{\varepsilon} = \Gamma\, \sigma^n$$

where α depends on the extent of grain boundary sliding (Herring)

Properties of Ceramics

Mechanical Properties

CREEP



Nabarro-Herring Creep

For simple tension measurements under steady state conditions α is 13.3.

It is assumed that;

- The main source and sink for vacancies are grain boundaries.
- We have equilibrium.
- There is no cavitation.

Properties of Ceramics

Mechanical Properties

CREEP

In response to the applied stress vacancies preferentially move from surfaces/interfaces (GB) of specimen transverse to the stress axis to surfaces/interfaces parallel to the stress axis→ thus causing elongation.

Diffusion of vacancies in one direction can be thought of as flow of matter in the opposite direction.

This process like dislocation creep (involving climb) is controlled by the diffusion of vacancies (but diffusional creep does not require dislocations to operate).

The diffusion could occur predominantly via the lattice (at high temperatures) or via grain boundaries (at low temperatures). The former is known as Nabarro-Herring creep, while the later is known as Coble creep.

Diffusion through edge dislocation cores (pipe diffusion) could play an important role in creep

Properties of Ceramics

Mechanical Properties

CREEP

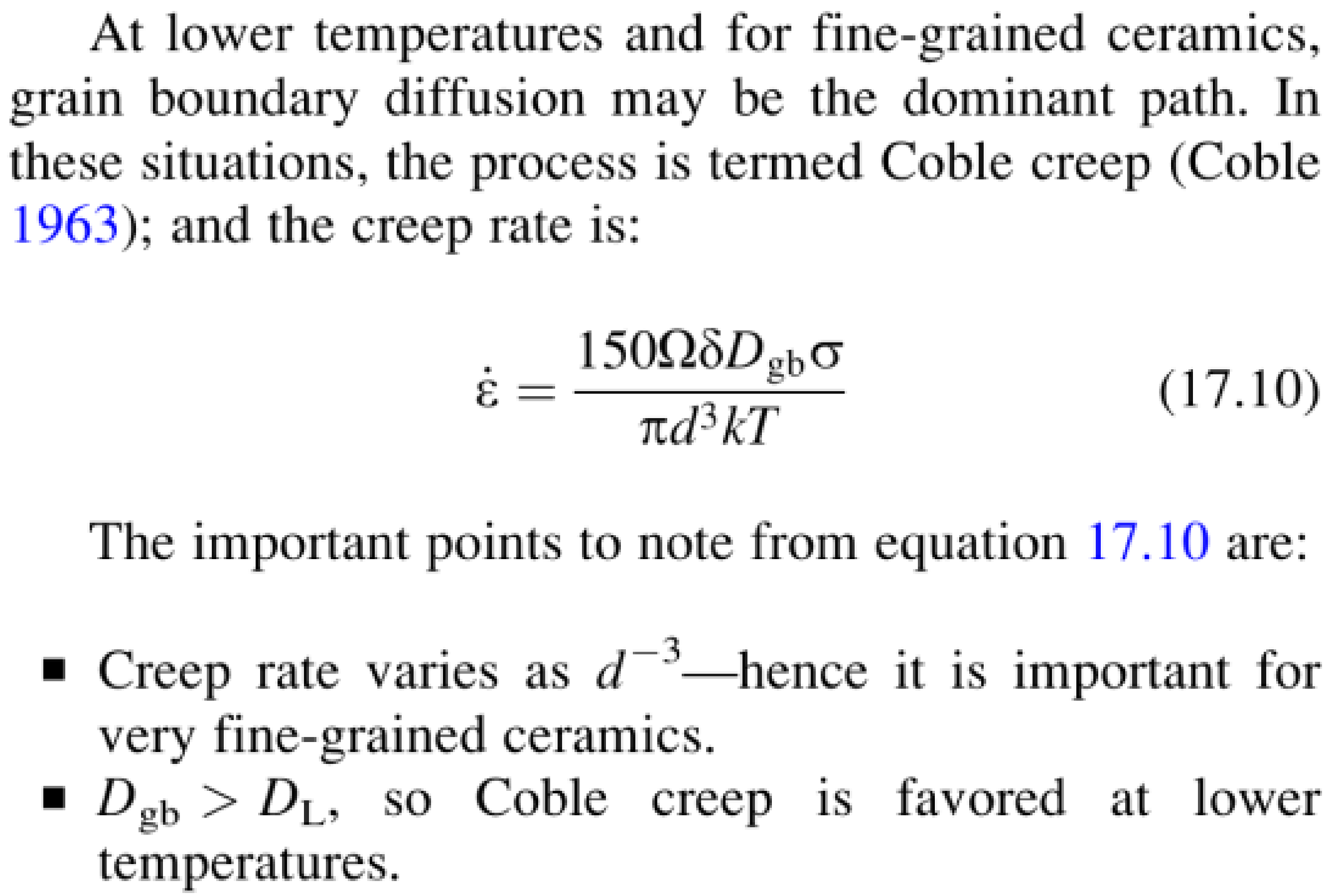
Important points about Nabarro-Herring Creep;

- T has to be high enough to allow vacancy diffusion
- Diffusion is considered to occur through the bulk
- Creep rate increases with decreasing grain size (d)
- Creep rate is proportional to the applied stress
- There is linear dependence between strain rate and stress

Properties of Ceramics

Mechanical Properties

CREEP



At lower temperatures and for fine-grained ceramics, grain boundary diffusion may be the dominant path. In these situations, the process is termed Coble creep (Coble 1963); and the creep rate is:

$$\dot{\varepsilon} = \frac{150\Omega\delta D_{\mathrm{gb}}\sigma}{\pi d^3 kT} \qquad (17.10)$$

The important points to note from equation 17.10 are:

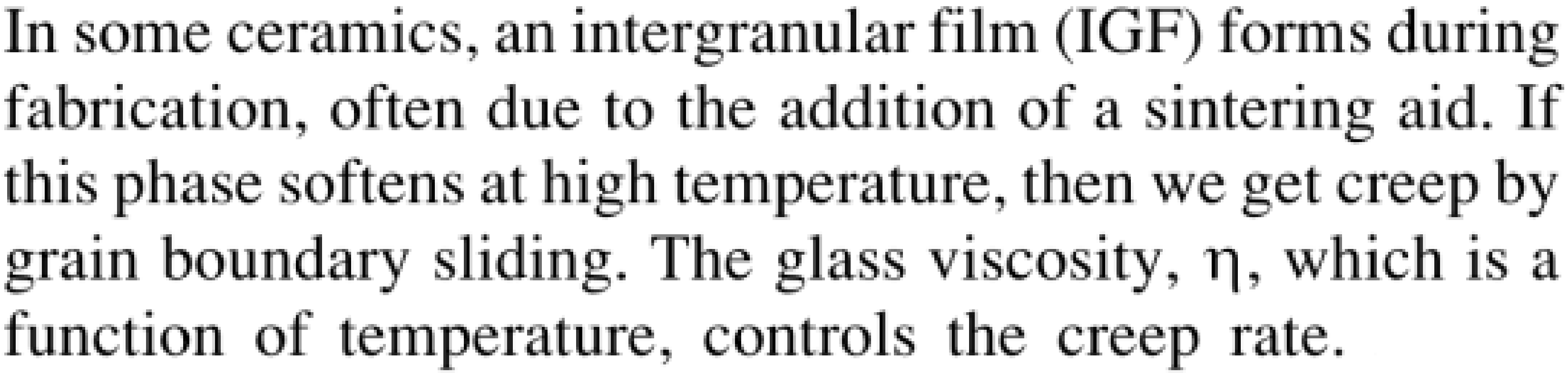
- Creep rate varies as d^{-3}—hence it is important for very fine-grained ceramics.
- $D_{\mathrm{gb}} > D_{\mathrm{L}}$, so Coble creep is favored at lower temperatures.

Properties of Ceramics

Mechanical Properties

CREEP

Grain Boundary Sliding



In some ceramics, an intergranular film (IGF) forms during fabrication, often due to the addition of a sintering aid. If this phase softens at high temperature, then we get creep by grain boundary sliding. The glass viscosity, η, which is a function of temperature, controls the creep rate.

At low temperatures the grain boundaries are '*stronger'* than the crystal interior and impede the motion of dislocations

Being a higher energy region, the grain boundaries *melt* before the crystal interior. At high temperatures grain boundaries are weaker than grain and slide past one another to cause plastic deformation

Properties of Ceramics

Mechanical Properties

CREEP

Dislocation Core Diffusion Creep

$$\dot{\varepsilon} = \frac{\alpha D_L \mu b}{kT}\left(\frac{\sigma}{\mu}\right)^n$$

The equation of dislocation creep is incapable of explaining certain experimental facts, notably an increase in the exponent *n* and a drop in the activation energy for creep at lower temperatures. To do so it is necessary to assume that the transport of matter via *dislocation core diffusion* contributes significantly to the overall diffusive transport of matter, and—under certain circumstances—becomes the dominant transport mechanism (Robinson and Sherby, 1969). The contribution of core diffusion is included by defining an effective diffusion coefficient (Hart, 1957 and Robinson and Sherby, 1969).

Robinson, S.L. and O.D. Sherby, *Mechanical behaviour of polycrystalline tungsten at elevated temperature.* Acta Met., 1969. **17**: p. 109.

Hart, E.W., *On the role of dislocations in bulk diffusion.* Acta Metallurgica (pre 1990), 1957. **5**: p. 597

Properties of Ceramics

Mechanical Properties

CREEP

Summary

Creep is the slow plastic deformation due to diffusion of atoms at high temperatures ($T > 0.5\ T_m$). Creep occurs at stresses **below the yield stress**. Note the difference: plastic deformation is not dependent on time; modern manufacturing uses the fact that metals can be shaped very rapidly. Creep is a viscous-like deformation and the stress rules the rate of deformation.