# CERAMIC MATERIALS I


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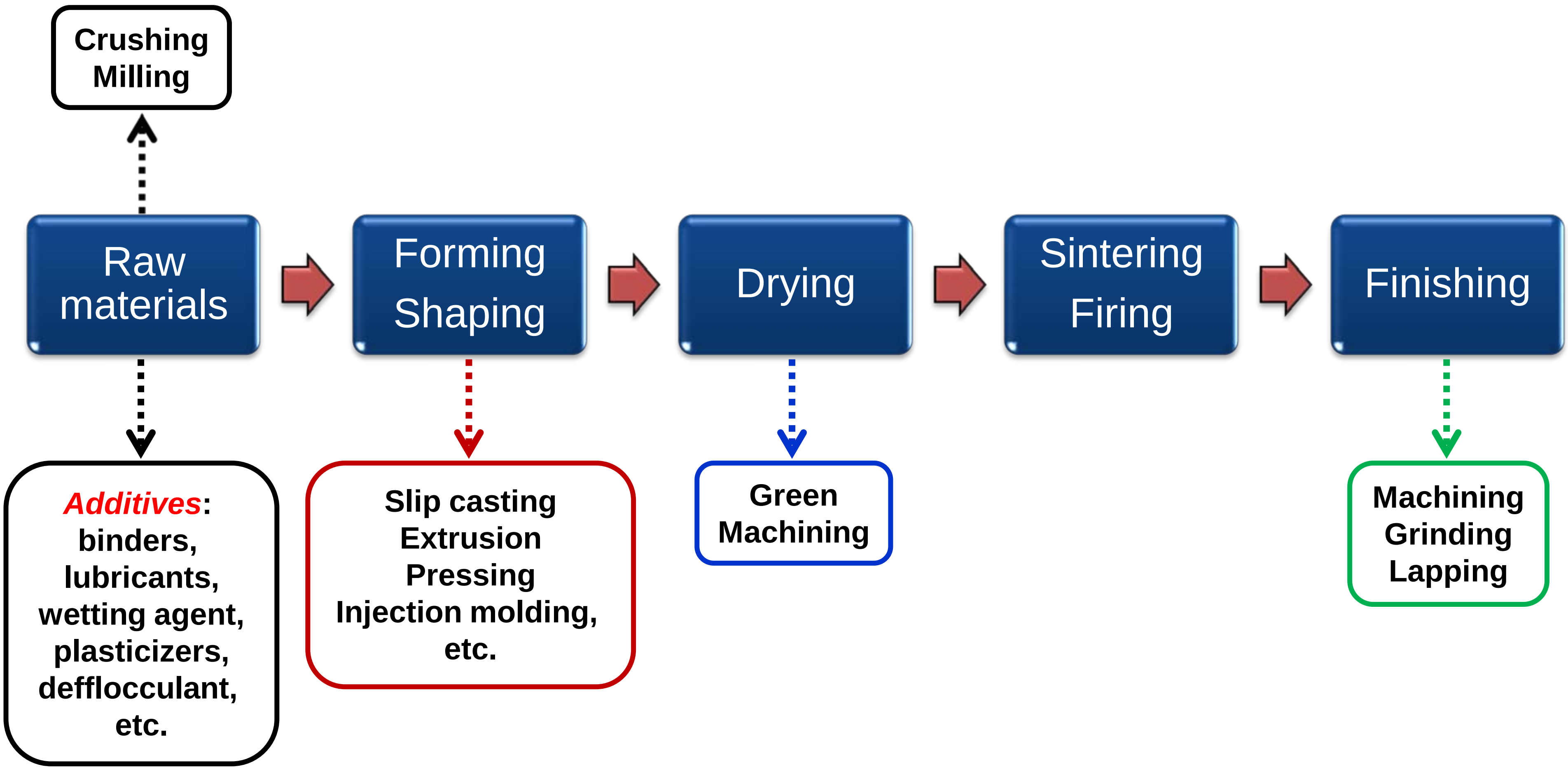
# FABRICATION OF CERAMICS



# CERAMIC MATERIALS

**Ceramic materials cannot be formed by the manufacturing processes known from metallic or organic materials. The energy to melt and cast ceramic raw materials would be far too costly.**

**The process used to form ceramic materials is a heat treatment of very fine powders of the raw materials called sintering.**

**The brittle nature of ceramic end products demands as little as possible machining after sintering. The ceramic parts have, therefore, to be shaped before sintering.**

# SHAPING OF CERAMICS

***Shaping*** transforms an unconsolidated powder mixture into a coherent, consolidated body having a chosen geometry.

Selection of a shaping technique

- size and dimensional tolerances of the product
- the requisite microstructural characteristics
- the levels of reproducibility required
- economic considerations
- required shape

# SHAPING OF CERAMICS

Many shaping methods are used for ceramic products and these can be grouped into three basic categories, which are not necessarily independent.

**Factors to be considered:**

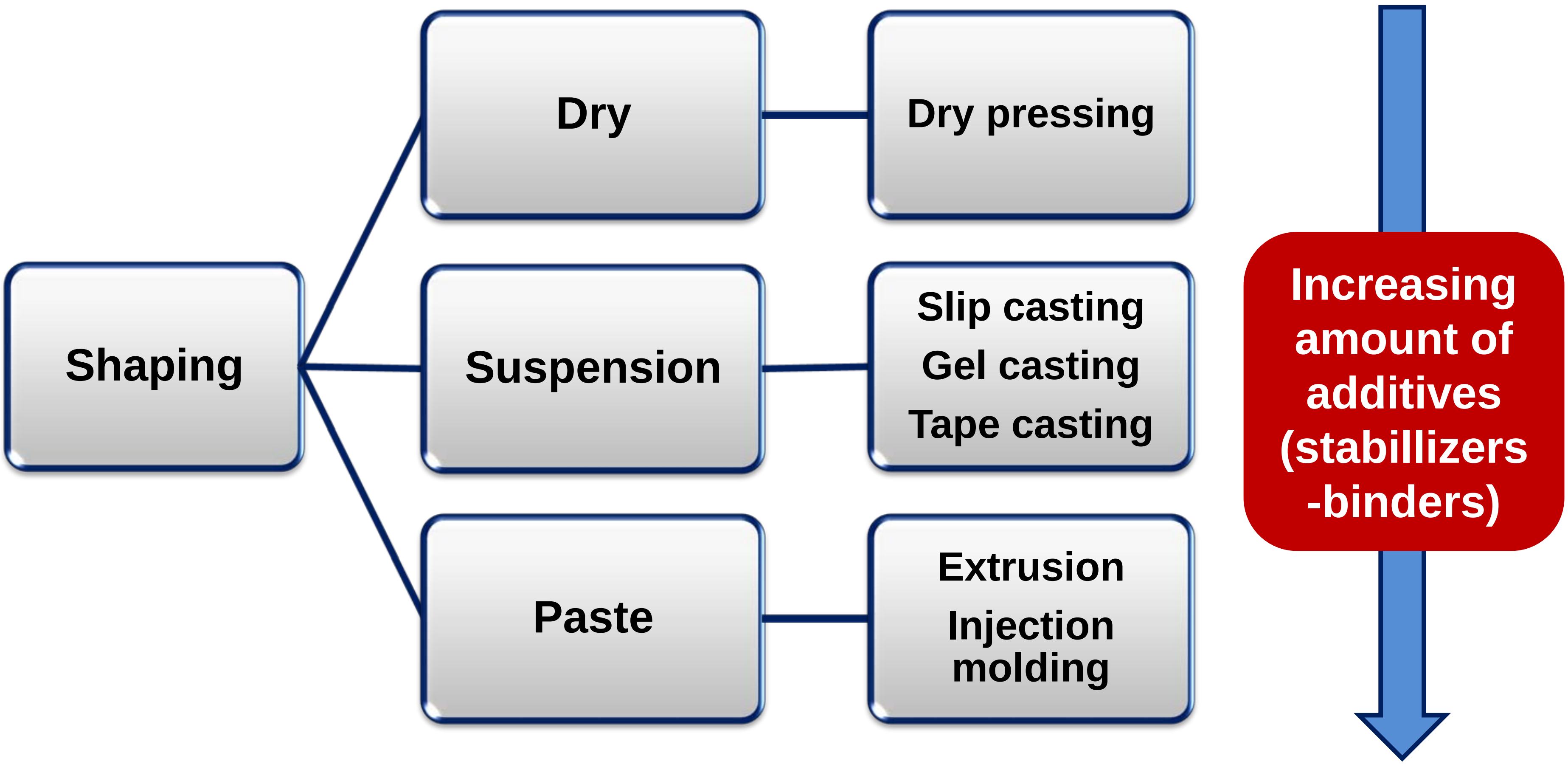
- **complexity of object**
- **size**
- **quantity (production rate) etc.**

# SHAPING OF CERAMICS

Shaping techniques

| Shaping techniques | |
|---|---|
| Powder Compaction | Dry pressing, hot pressing, cold isostatic pressing, hot isostatic pressing, etc. |
| Casting | Using a mold with the ceramic as, or containing, a liquid or slurry. Slip casting, gel casting, electrophoresis casting, etc. |
| Plastic forming | Extrusion, injection molding, transfer molding, etc. Using pressure to shape the green ceramic |

# SHAPING OF CERAMICS



# Common Ceramic Forming Methods

| Forming method | Feed material | Shape of green body |
|---|---|---|
| **Dry or semi-dry pressing** | | |
| Uniaxial pressing (Die compaction) | Powder or free-flowing granules | Small simple shapes |
| Isostatic pressing | Powder or fragile granules | Larger, more intricate Shapes |
| | | |
| **Casting of a slurry** | | |
| Slip casting | Free-flowing slurry with low binder content | Thin intricate shapes |
| Tape casting | Free-flowing slurry with high binder content | Thin sheets |
| | | |
| **Deformation of a plastic mass** | | |
| Extrusion | Moist mixture of powder and binder solution | Elongated shapes with uniform cross section |
| Injection molding | Granulated mixture of powder and solid binder | Small intricate shapes |

## Dimensional Control

**Tight control of dimension** → superior control of process through forming and sintering → plus final machining (polishing) – an expensive step

**Total volume shrinkage** = (drying stage) + (calcination stage) + (sintering stage) …..

Precise control depends on the control at this three stages

**Dry pressed, injection molded** → drying stage shrinkage ~ 0;

extruded and slip casted parts → drying stage shrinkage ~ 3-12%

**Shrinkage during calcination**: high for injection molding and tape casting

# POWDER COMPACTION

- Powder compaction is simply the pressing of a free flowing powder.

- The powder may be dry pressed (i.e., without the addition of a binder) or pressed with the addition of a small amount of a suitable binder.

- The pressure is applied either uniaxially or isostatically.

- The choice of pressing method depends on the shape of the final product.

- We make simple shapes by applying the pressure **uniaxially**; more complex shapes require **isostatic pressing**

# POWDER COMPACTION

- Mechanical compaction of dry or semidry powders in a die is **one of the most widely used forming operations** in the ceramic industry.

- In general the applied pressure is not transmitted uniformly because of friction between the particles and the die walls as well as between the particles themselves.

- The stress variations lead to **density variations** in the green body, thereby placing considerable limits on the degree of packing uniformity that can be achieved.

- Although the density variations can be reduced significantly by isostatic pressing, mechanical compaction provides **far less control in the manipulation of the green body microstructure** than the casting methods.

# POWDER COMPACTION

- The aim of the process is to transform loose powders into a green compact with a desired shape and a maximal overall density.

- Close geometrical tolerances, minimal variations of density, packing homogeneity, and sufficient strengths and integrity to withstand the stresses occurring during the subsequent handling, debinding and sintering treatment are further properties required of the green compact.

- These properties are determined by the behavior of the powders during the pressing process. The unit operations of this process are filling of the die or mold, compaction of the powder under a particular state of stress and, in the case of uniaxial die pressing, ejection of the green compact from the die.

# POWDER COMPACTION

- Powder compaction by dry pressing is widely used in industry for shaping of ceramic products.

- This can be explained by the high efficiency of the process, which has two variants: uniaxial die pressing; and isostatic pressing.

- Both methods can be automated to a high degree and are used in the mass production of parts such as ceramic cutting tools (via uniaxial pressing) or spark plug insulators (via isostatic pressing).

# POWDER COMPACTION

- Powders used in the industrial production of ceramics very rarely have spherical particles.

- The surfaces of the particles are also rarely smooth.

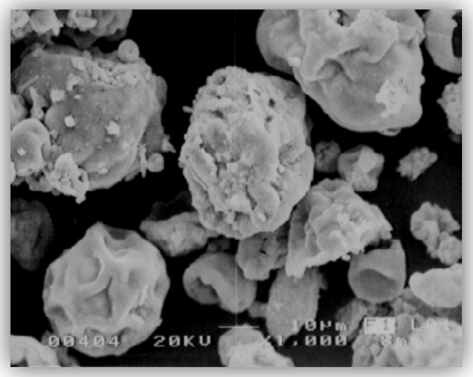
- Particles with rough surface textures or shapes suffer from agglomeration because of increased interparticle friction, and the packing density decreases as the particle shape departs from that of a sphere.

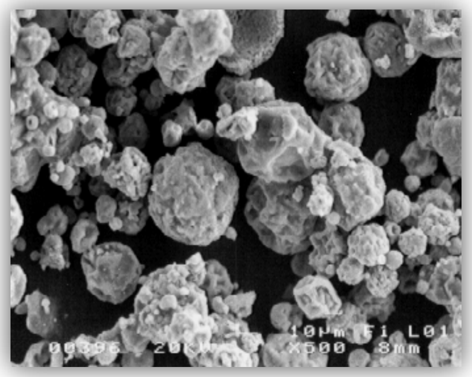
- Spherical particles are normally desirable when a high packing density is required. However, the use of non-spherical particles does not always lead to a reduction in the packing density if the particles have a regular geometry. The highest packing density and most isotropic structures are obtained with spheres and with particles having simple, equiaxial shapes (e.g., cubes).

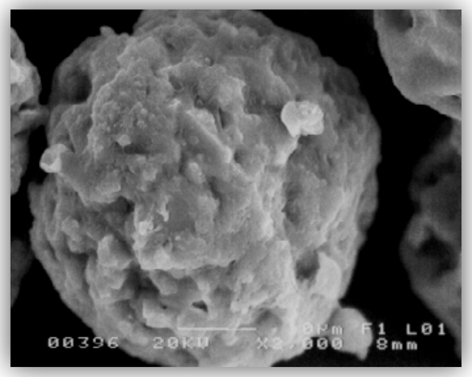
- Anisotropic particles can be packed to high packing density if they are ordered, but in random packing, the packing density can be quite low.

# WHY GRANULATION???

***Goal of Spray Drying:***







Drying step after wet milling
Free flowing powder
Good packing

# POWDER COMPACTION

- Uniaxial die pressing produces shapes with accurate dimensions in large quantities, in the shortest cycle times.

- Compared to injection molding, dry pressing requires a relatively small amount of additives (~2%), and thus allows for less expensive additive removal operations.

- Fine powders lack the flowability required for the process, in general they must be transformed into a free-flowing press granulate, by employing a granulation process.

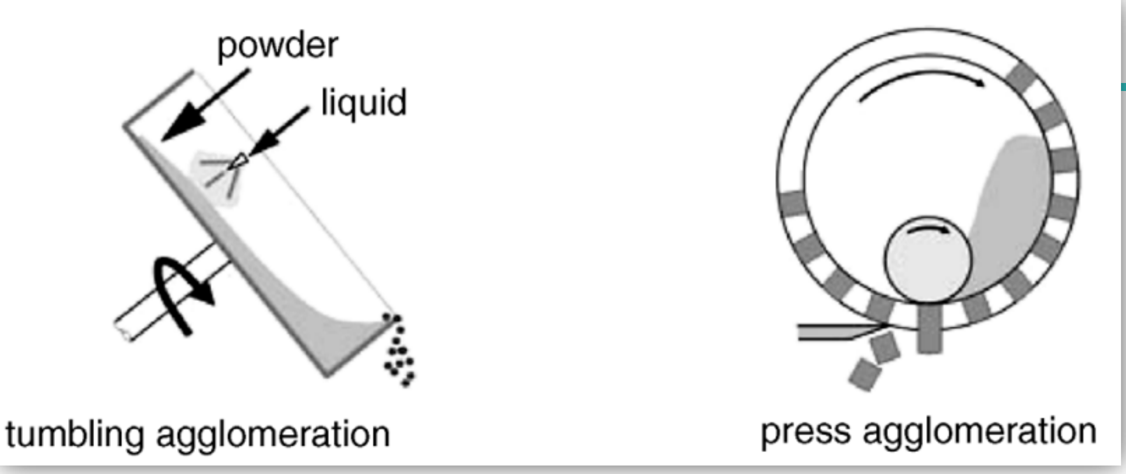
- A second problem results from the nonuniform pressure transmission, leading to nonuniform particle arrangements and density variations in the compacts, which is a well-known source of nonuniform grain growth and other sintering defects.

# GRANULATION

- For the production of technical ceramics, the poor flowability of the micron or submicron powders makes it necessary to form press granulates by the controlled agglomeration of the primary particles.

- Granulation methods can be divided into agitation, pressure, or **spray techniques.**

- Agitation methods use moist particles, bringing them into contact by mixing or tumbling so that the particle bonding forces can cause agglomeration.



# GRANULATION

Main method of granulation is spray drying: produce spherical particles (~20 μm), high productivity (e.g. ~ 10-100 kg/h); suitable for subsequent pressing process.

- Use hot air to dry flowing solids
- Droplet size ~ product size
- Slurry viscosity: important operation variable, should be shear thinning

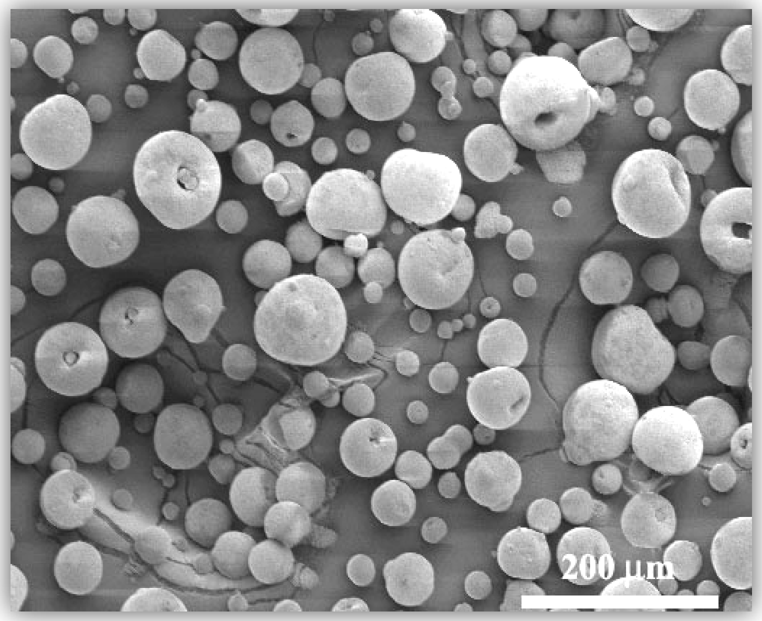
***Applications of spray granulation***

- Traditional ceramics
- Advanced ceramics
- Refractories

# GRANULATION

To transform a concentrate into many small droplets that are then exposed to a fast current of hot air.

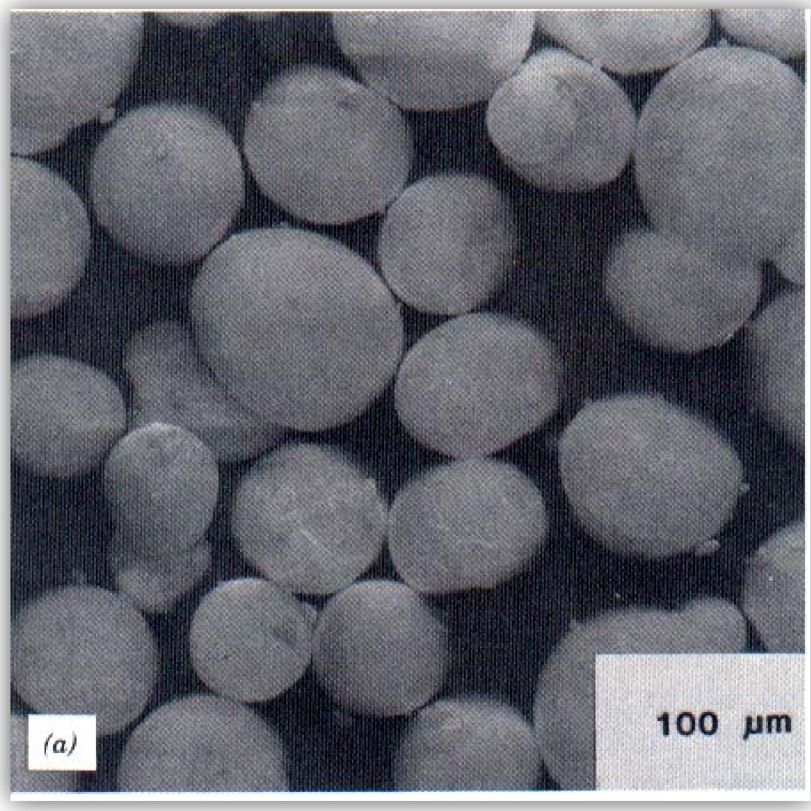
Because of the very large surface area of the droplets, the water evaporates almost instantaneously and the droplets are transformed into powder particles.

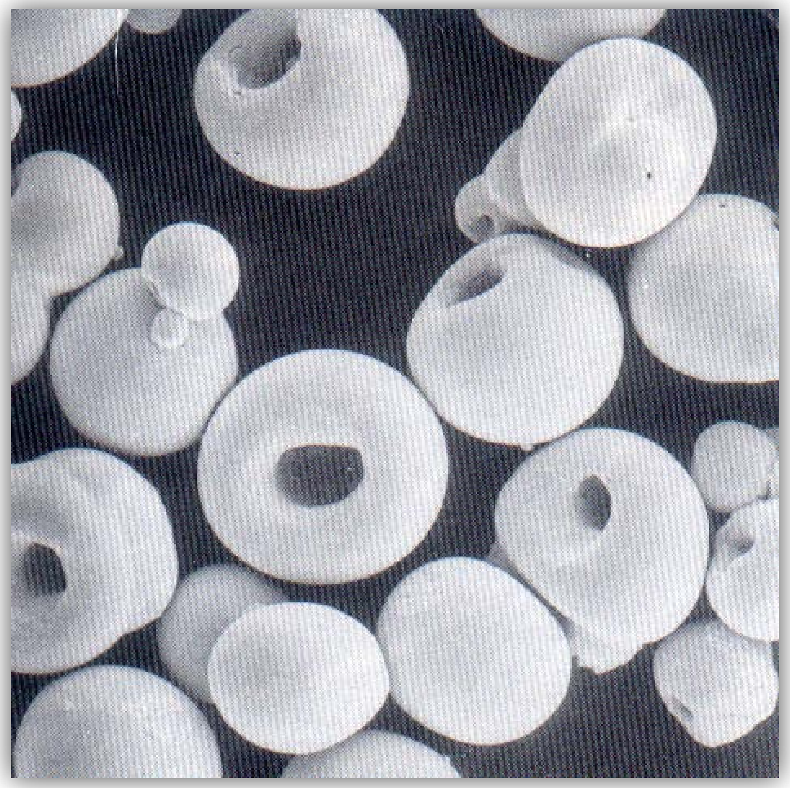


# Spray Drying

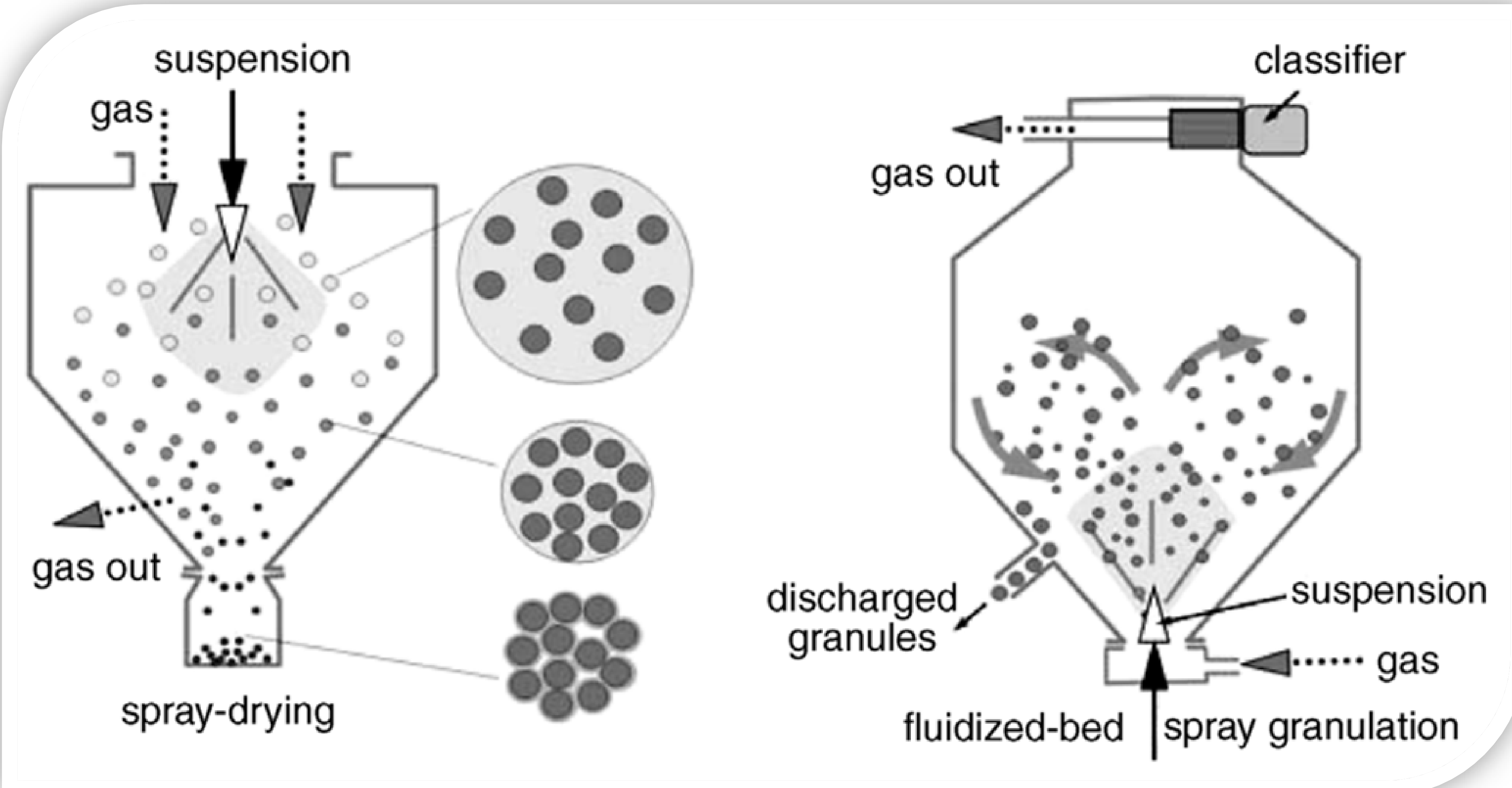
**Spray dried samples:**

Donut particle , temperature rise too fast , surface dried (sealed), vaporization of internal liquid → pores (viscous binder fluid may flow toward inside)

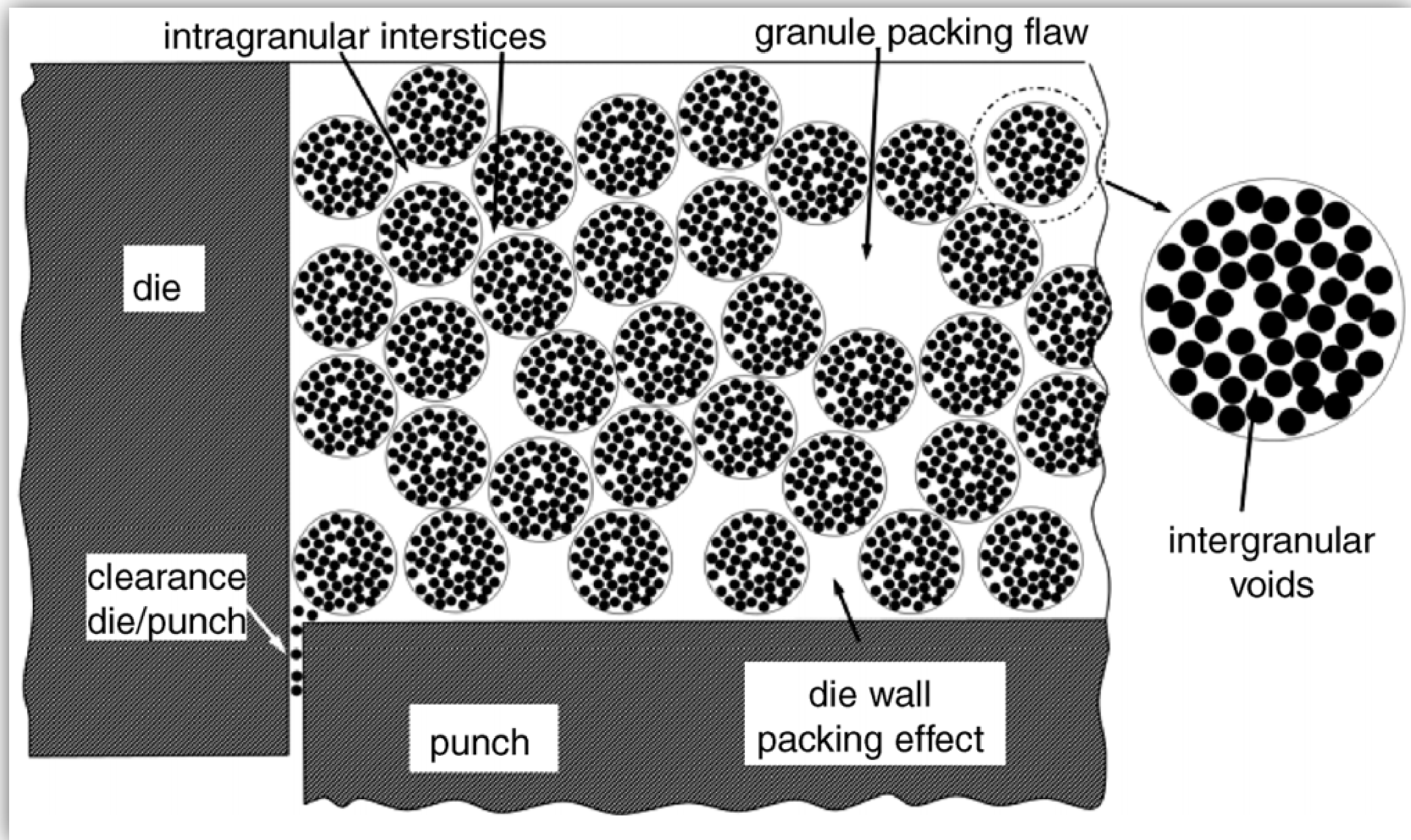


# Granulation of Ceramic Powders

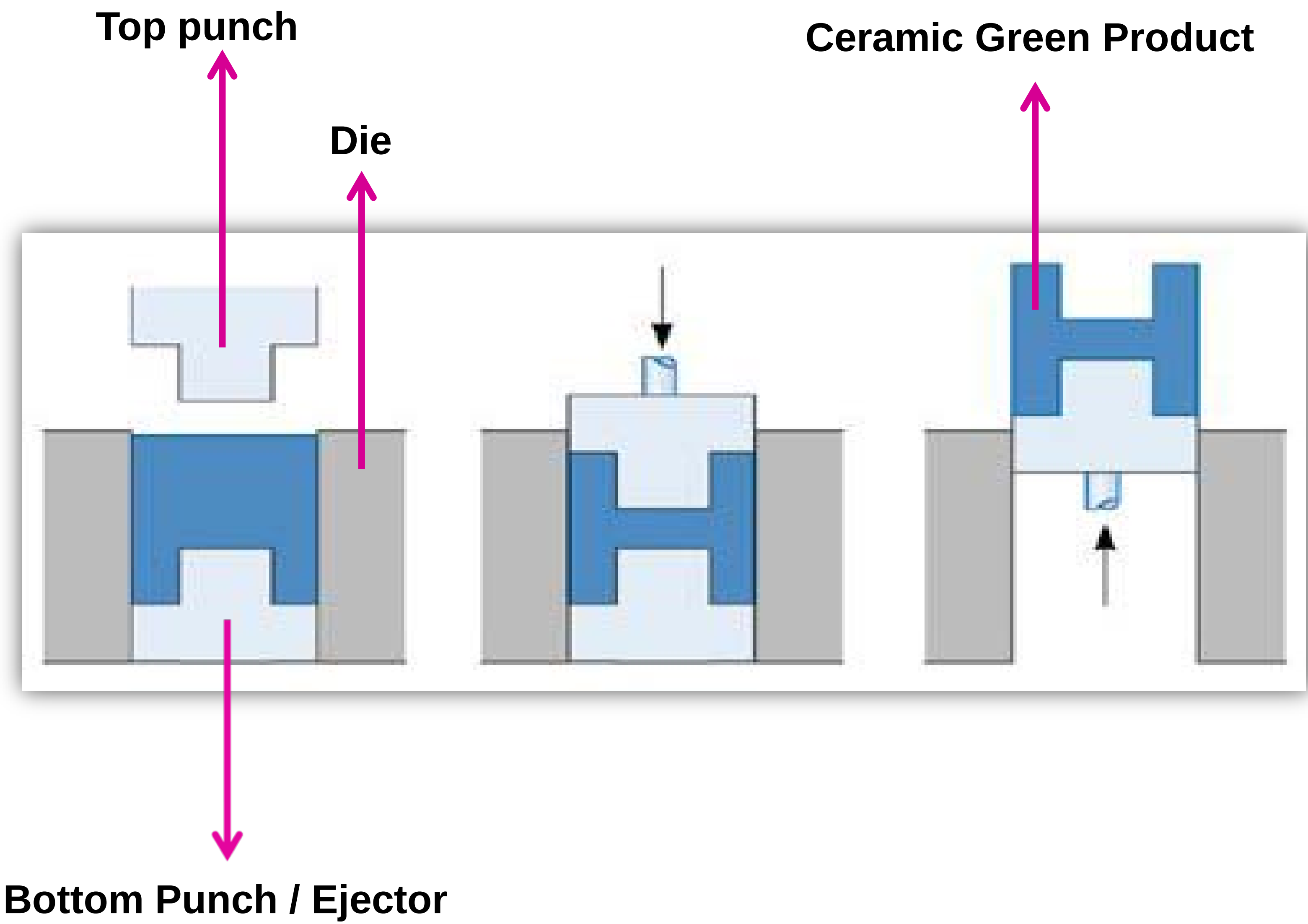


# POWDER COMPACTION

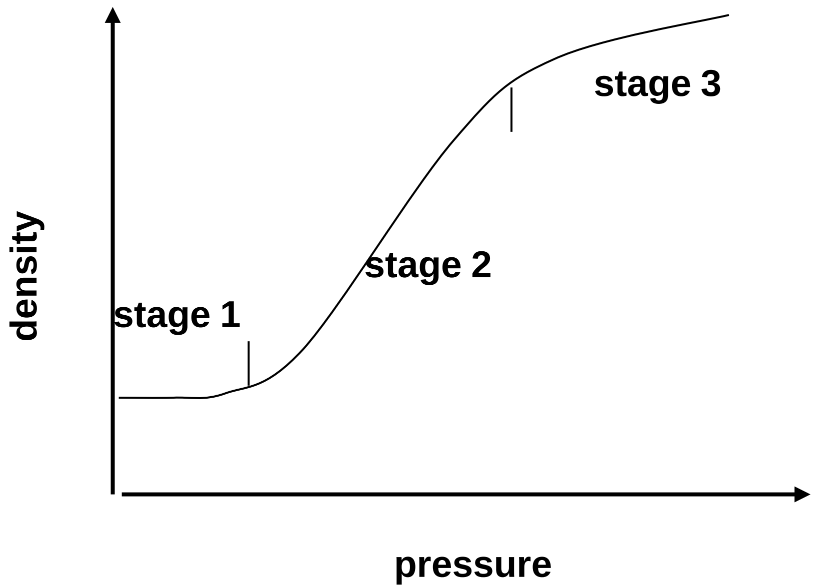


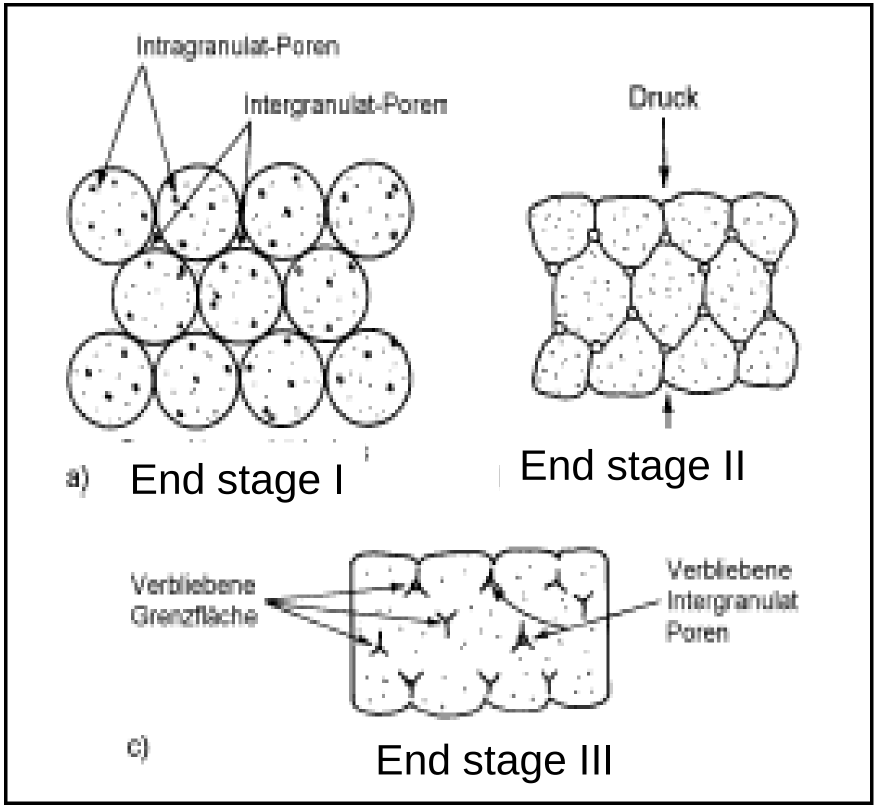

**Hierarchic packing structure of a press granulate**

# PRESSING



## Compaction of granules




**Compaction behavior of granulated powders**

**Evolution of the green-body microstructure during compaction of granules**

| | |
|---|---|
| **stage I** | **granule flow and rearrangement** |
| **stage II** | **granule deformation** |
| **stage III** | **granule densification** |

## Die pressing additives

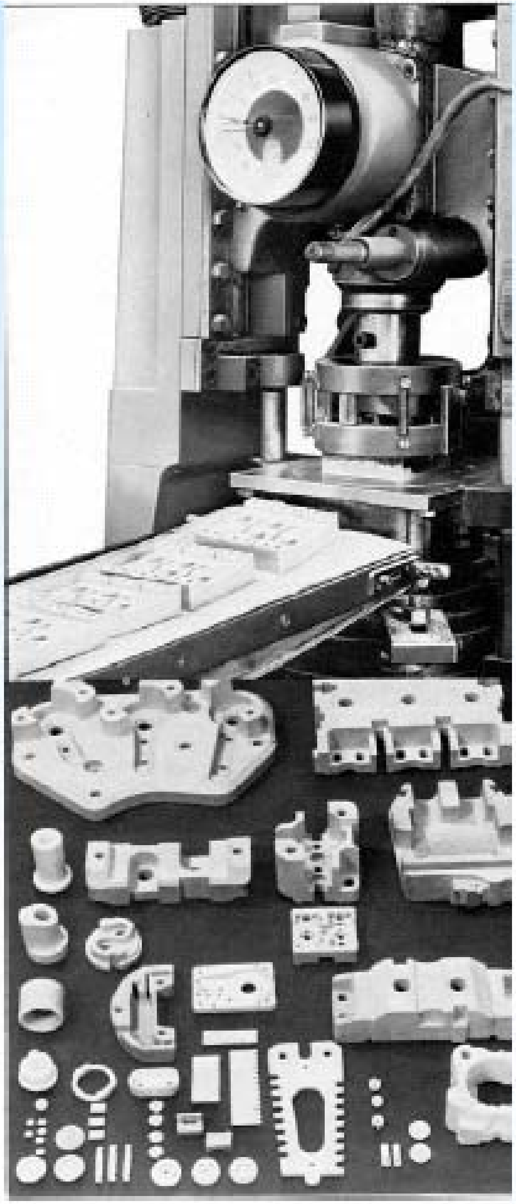
**TABLE 22.3 Additives Used in Industrial Pressing Powders**

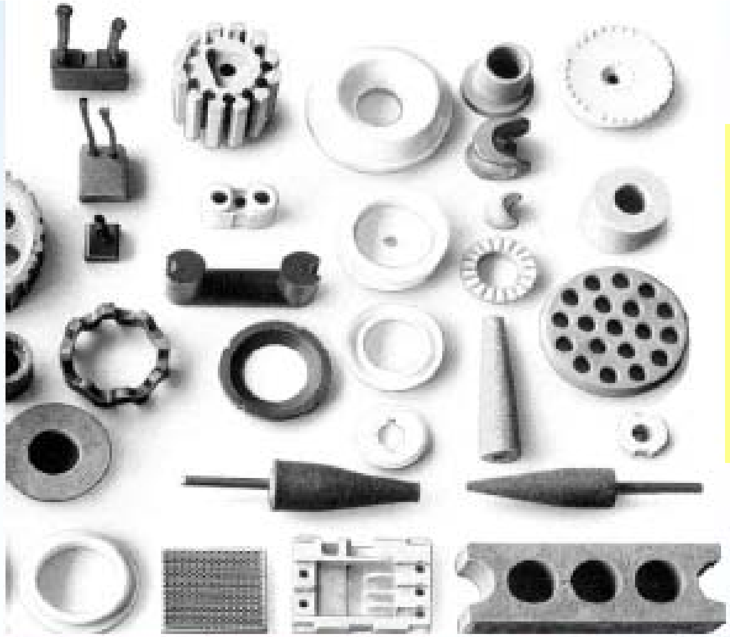
| Product | Binder | Plasticizer | Lubricant |
|---|---|---|---|
| Alumina | Polyvinyl alcohol[a] | Polyethylene glycol[b] | Mg Stearate |
| 96% alumina substrates | Polyethylene glycol[c] | None | Talc,[d] clay[d] |
| Alumina spark plug insulation | Microcrystalline wax emulsion | KOH + tannic acid | Wax, talc[d] clay[d] |
| MnZn Ferrites | Polyvinyl alcohol[a] | Polyethylene glycol[b] | Zn Stearate |
| Ba Titanate | Polyvinyl alcohol[a] | Polyethylene glycol[b] | |
| Steatite | Microcrystalline wax, clay | Water | Wax, talc,[d] clay[d] |
| Ceramic tile | Clay | Water | Talc,[d] clay[d] |
| Hotel china | Clay, polysaccharide | Water | Clay[d] |
| Refractories | Ca/Na lignosulfonate | Water | Stearate |

[a]Low-viscosity grade.
[b]400 molecular weight.
[c]20,000 molecular weight.
[d]Colloidal size.

Reed, 1995

# PRESSING





Products shaped by axial die pressing

# ISOSTATIC PRESSING

**Cold isostatic pressing** is a powder-forming process where compaction takes place under isostatic or near-isostatic pressure conditions.

Two main process variants exist, namely **wet-bag** and **dry-bag isostatic pressing**. In both techniques, the powder isfirst sealed in an elastomeric mold, which is then pressurized by a liquid, such that the powders become set under (hydrostatic) pressure. Typically, pressures up to 400 MPa are used on an industrial scale, although some laboratory equipment is designed to operate at pressures up to 1 GPa. The pressure medium must be compatible with the tool, the vessel, and the pumping system. In practice, special oils, glycerin or water with anticorrosive and lubricating additives are used. As these fluids are not incompressible at high pressures, they can store considerable elastic energy and, consequently, safety aspects must be considered when designing and operating the pressing equipment.

**Wet-bag isostatic pressing** requires extensive handling, and is used mainly for the production of prototypes or the low-volume production of parts.

In contrast, **dry-bag isostatic pressing** is a mass production process; an example is the production of spark plug insulators, for which several million must be produced worldwide on a daily basis.

**The main advantages of isostatic pressing** are that it produces a much more uniform density distribution than does uniaxial pressing, and the ejection stage – which often causes pressing defects – is avoided. **One disadvantage**, however, is the lower geometric precision of the compacts.

# ISOSTATIC PRESSING

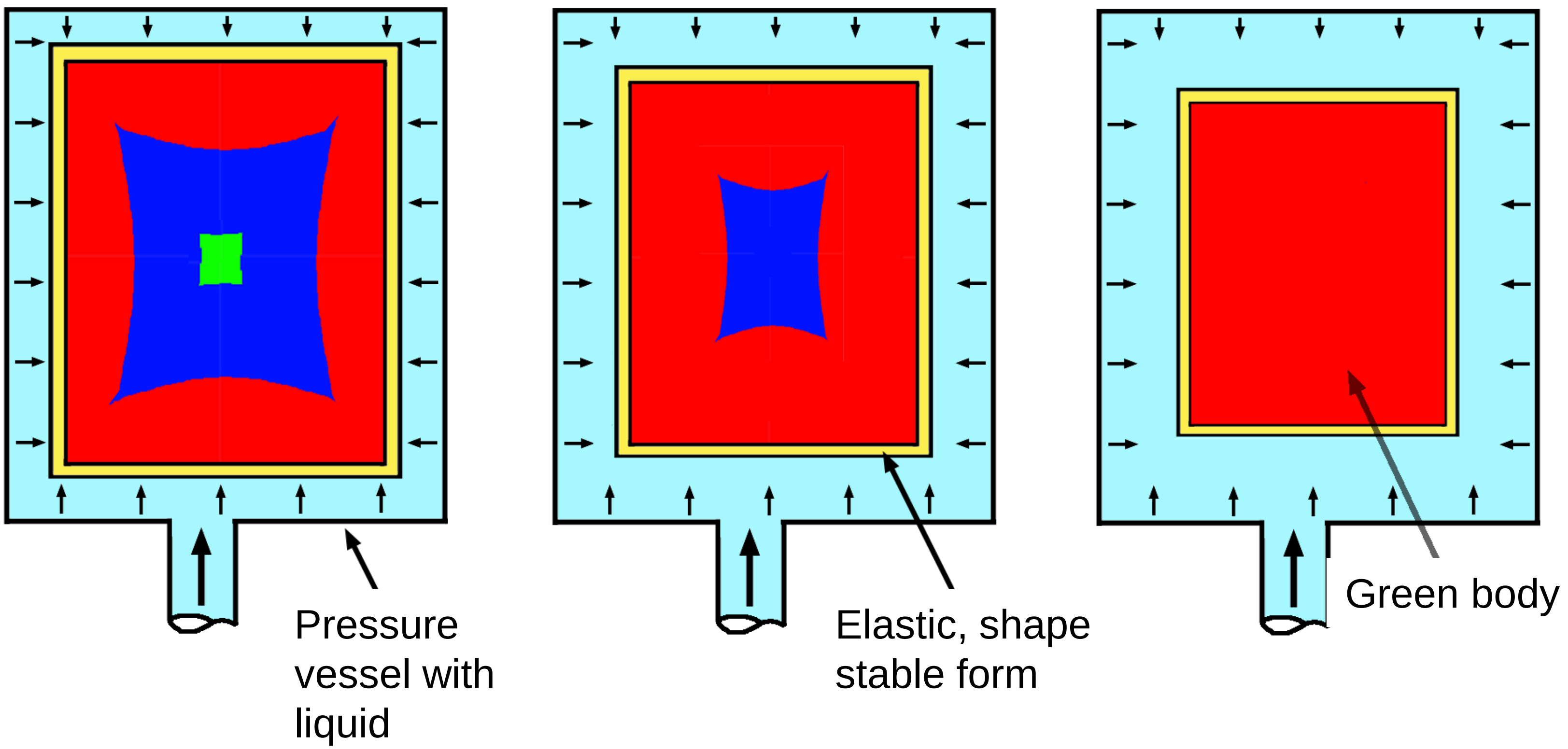
**Isostatic Pressing:** **Ceramic powder is loaded into a flexible chamber and pressure is applied outside the chamber with hydraulic fluid.**

**Examples: Spark plug insulators, carbide tools.**

Uses hydrostatic pressure to compact the ceramic powders from all directions

- Avoids the problem of non-uniform density in the final product that is often observed in conventional uniaxial pressing
- Same process used in powder metallurgy

# ISOSTATIC PRESSING




**The advantage of isostatic compaction is a more homogeneous density distribution. The complexity of the mold is, however, limited.**

# ISOSTATIC PRESSING

- Cold isostatic Pressing (CIP)
  - Powder is placed in a flexible rubber mold
  - Pressurized hydrostatically
  - Uses pressures up to 150 KSI
  - Typical application is automotive cylinder liners

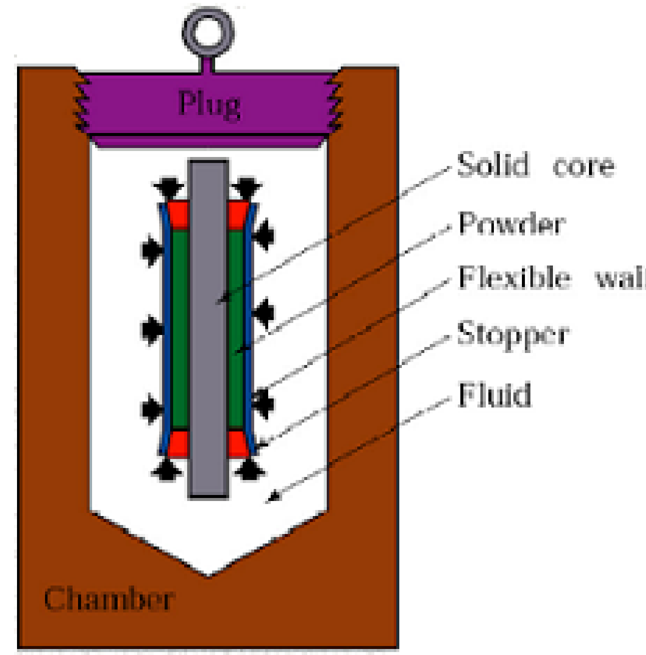



Fig: Schematic diagram, of cold isostatic, as applied to forming a tube.The powder is enclosed in a flexible container around a solid core rod.Pressure is applied iso-statically to the assembly inside a high-pressure chamber.

# ISOSTATIC PRESSING

- Hot Isostatic pressing
  - Container is made of high-melting-point sheet metal
  - Uses a inert gas as the pressurizing  medium
  - Common conditions for HIP are 15KSI at 2000F
  - Mainly used for super alloy casting

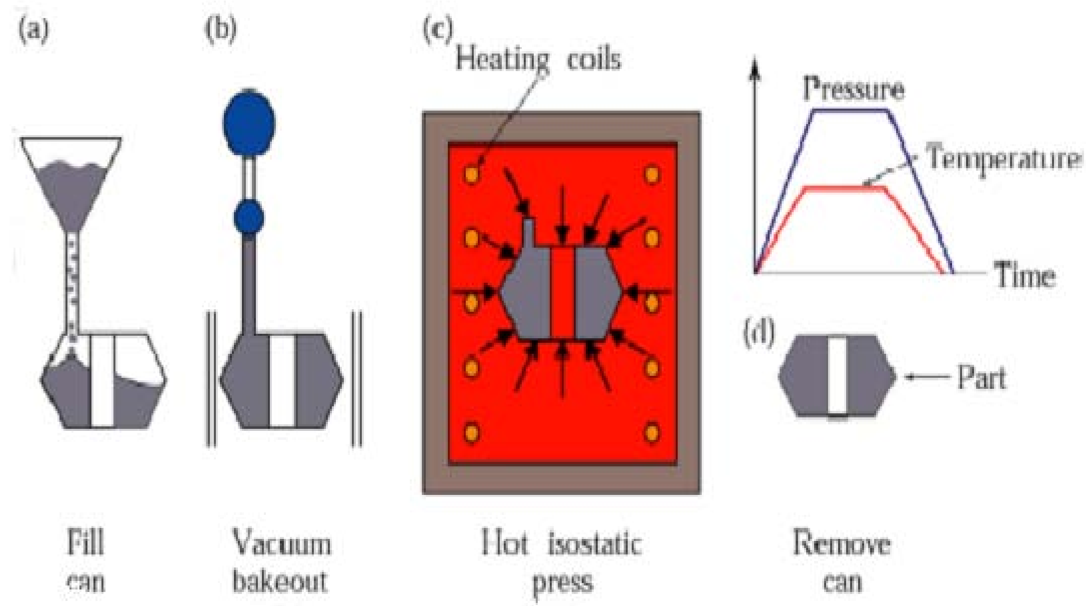



Fig: Schematic illustration of hot isostatic pressing.The pressure and temperature variation vs.time are shown in the diagram

# ISOSTATIC PRESSING

## Punch and Die Materials

- Depends on the abrasiveness of the powder metal
- Tungsten-carbide dies are used
- Punches are generally made of the similar materials
- Dimensions are watched very close

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# CASTING

- Casting ceramics is carried out at room temperature and generally requires the ceramic powder particles to be suspended in a liquid to form a slurry; note this process is quite unlike the casting of metals.

- The slurry is then poured into a porous mold that removes the liquid (it diffuses out through the mold) and leaves a particulate compact in the mold. This process is known as slip casting.

- The process has been used to form many traditional ceramic products (e.g., sanitary ware) and more recently has been used in forming advanced ceramic products (e.g., rotor blades for gas turbines).

- The other main casting process for ceramics is tape casting, which, as you would guess, is used to make thick films or sheets.

## *History of Slip Casting*

- This process was introduced into many European porcelain factories in the eighteenth century, and was commonly employed for the casting of terra cotta sculpture in the nineteenth century.

- Today you may find that many common things you have such as: figurines, doll faces, dishes, flower pots, lamp bases, toilets, etc. are made from this technique of mass production.

# SLIP CASTING

- A suspension of ceramic powders in water, called a *slip*, is poured into a porous plaster of paris mold so that water from the mix is absorbed into the plaster to form a firm layer of clay at the mold surface.
- The slip composition is 25% to 40% water.
- Two principal variations:

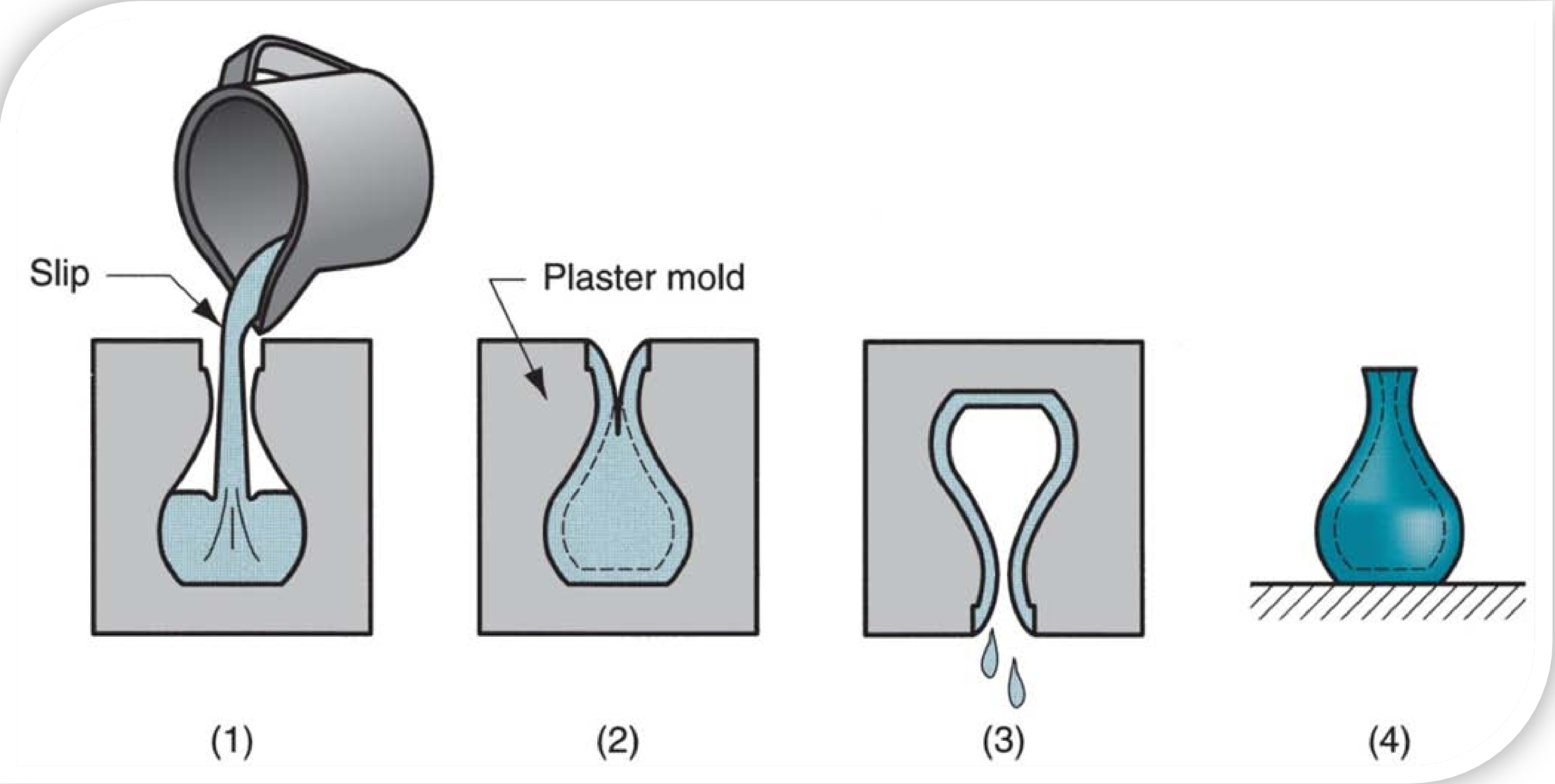
  – *Drain casting* - the mold is inverted to drain excess slip after a semi-solid layer has been formed, thus producing a hollow product.

  – *Solid casting* - to produce solid products, adequate time is allowed for entire body to become firm.

# SLIP CASTING

## Drain Casting

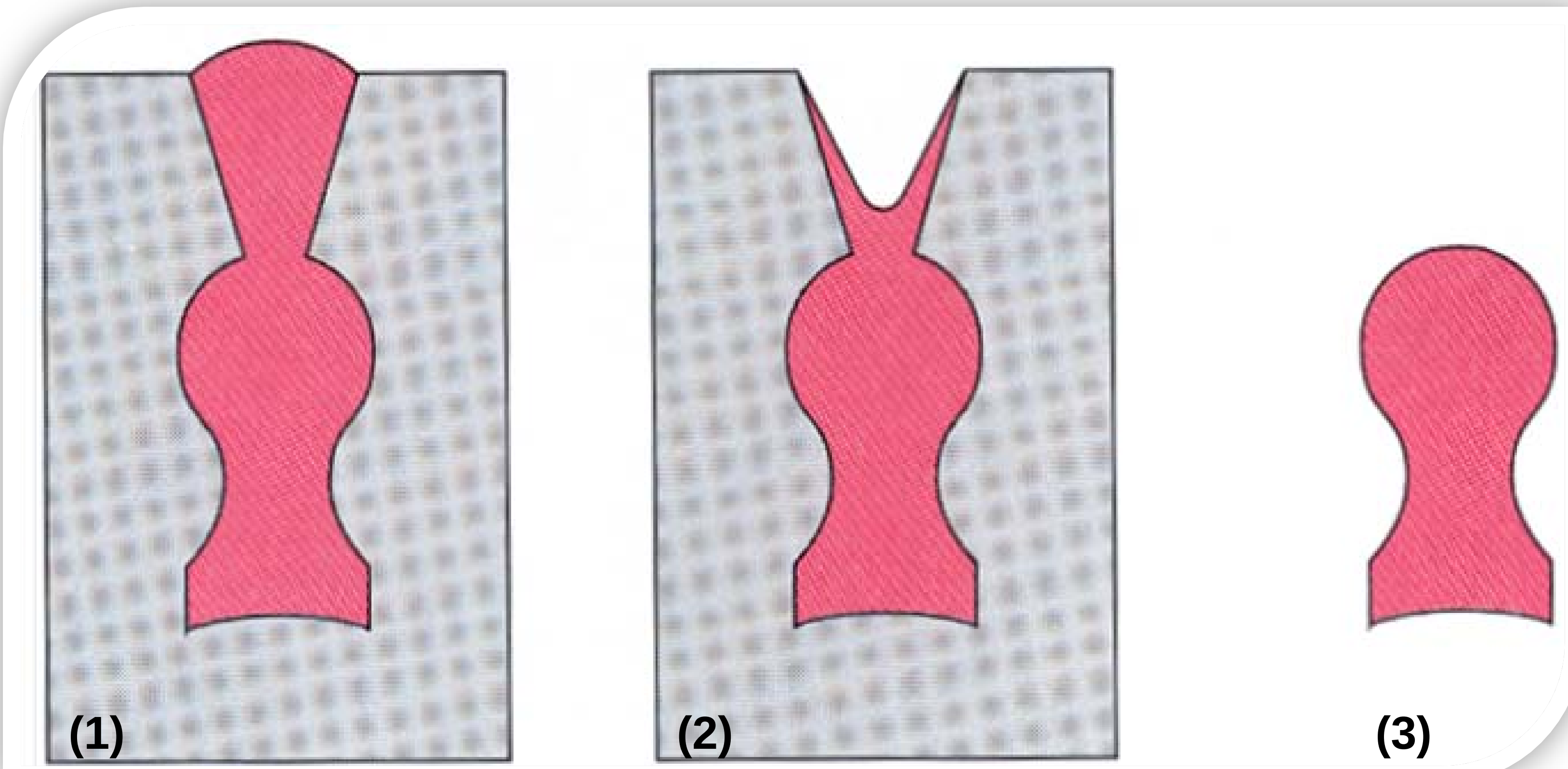
(1) Slip is poured into plaster of Paris mold cavity, (2) water is absorbed into plaster mold to form a firm layer, (3) excess slip is poured out, and (4) green body is removed from the mold



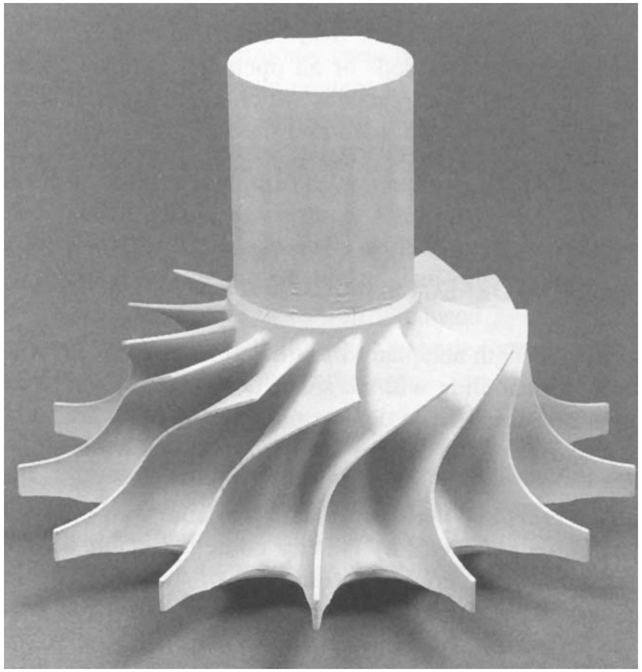
# SLIP CASTING

## Solid Casting

(1) Slip is poured into plaster of Paris mold cavity, (2) water is absorbed into plaster mold and (3) green body



# SLIP CASTING

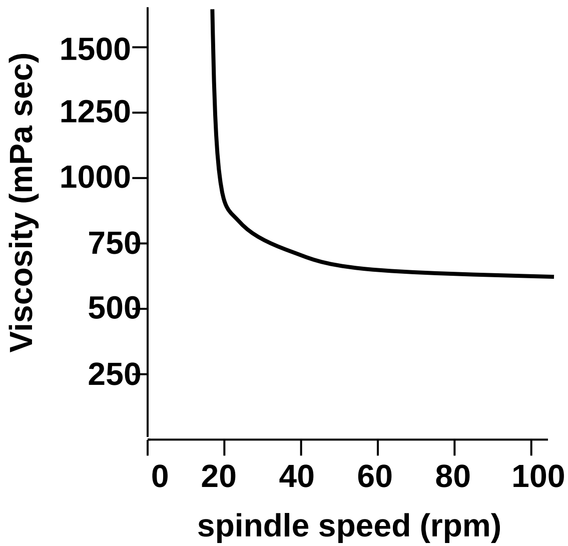


**Slip casted silicon nitride turbine (Allied Signal)**

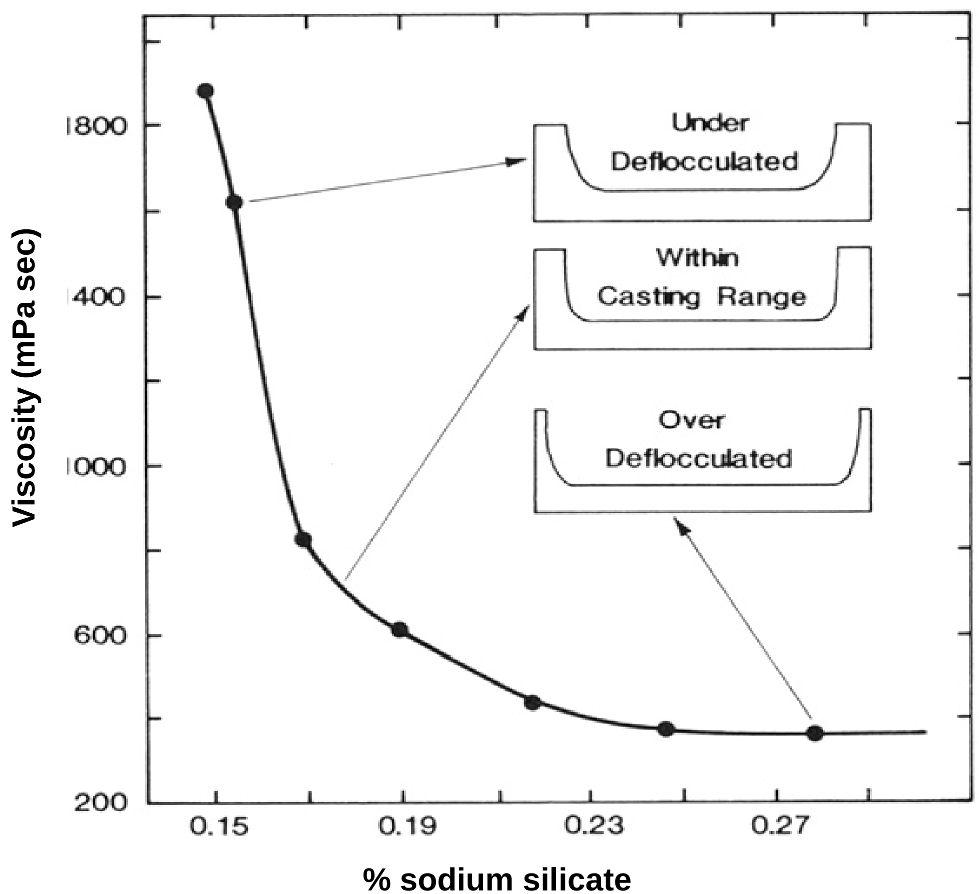
# SLIP CASTING

## Rheology in slip casting

*Slip casting of porcellaine*




The rheology of the cast is shear thinning. Before mixing, pumping and pouring the slurry has to be stirred



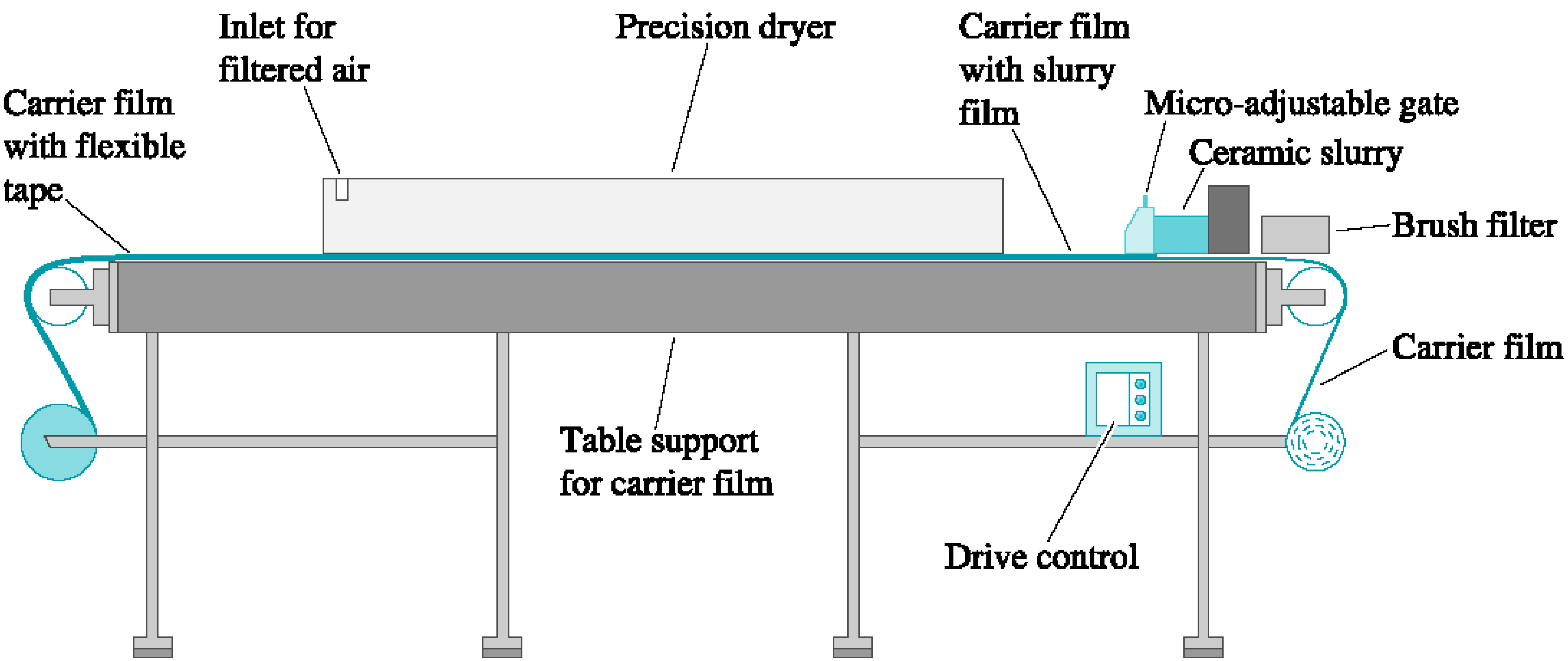

Influence of the viscosity on the shape of the slip casted white ware part

# SLIP CASTING

## Slip casting of sanitary ceramics

# TAPE CASTING

- Tape casting - A process for making thin sheets of ceramics using a ceramic slurry consisting of binders, plasticizers, etc. The slurry is cast with the help of a blade onto a plastic substrate.

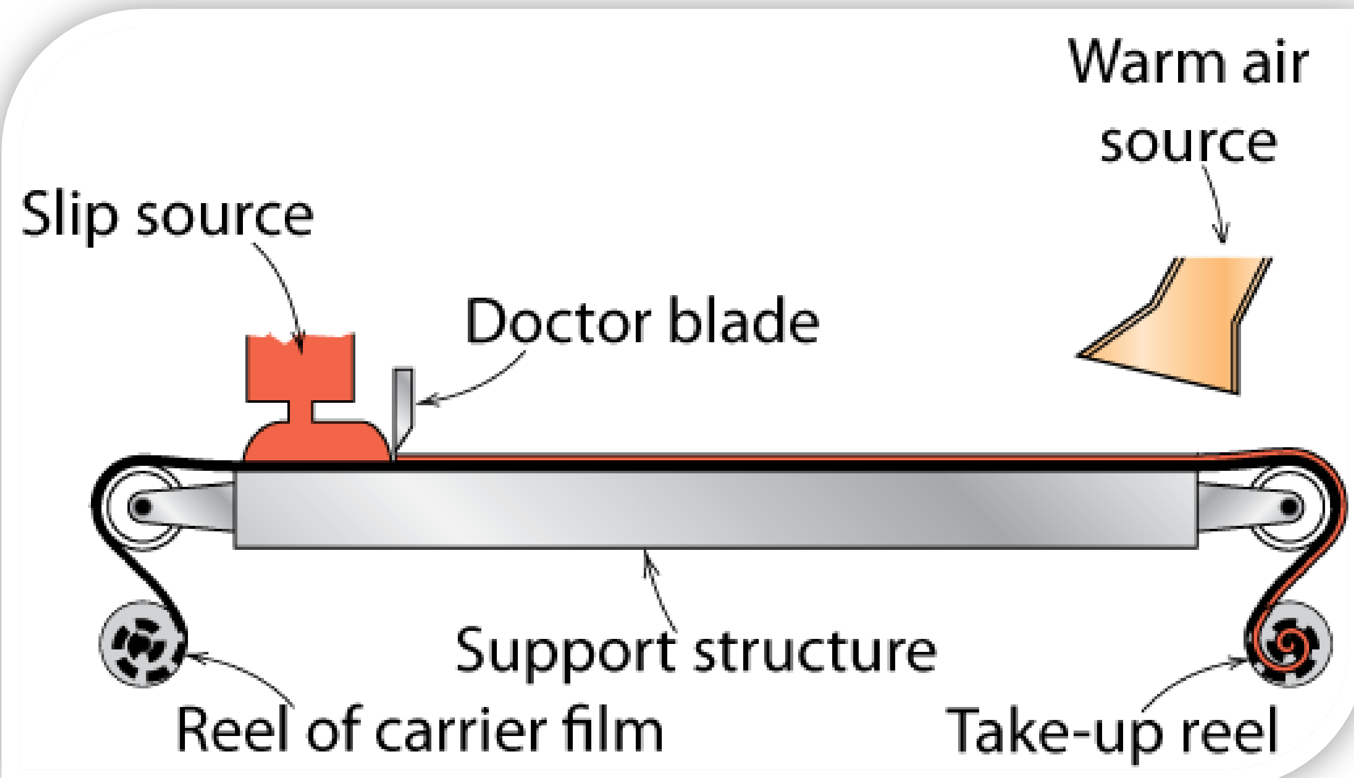



**Schematic of a tape casting machine.**

**(*Source: From* Principles of Ceramics Processing, *Second Edition, by J.S. Reed, p. 532, Fig. 26-6. Copyright © 1995 John Wiley & Sons, Inc. Reprinted by permission*.)**

# TAPE CASTING

- Thin sheets of green ceramic cast as flexible tape
- Used for integrated circuits and capacitors
- **Slip** = suspended ceramic particles + organic liquid (contains binders, plasticizers)



# PLASTIC FORMING

- Plastic forming methods in which a mixture of the ceramic powder and additives is deformed plastically through a nozzle or in a die provide a convenient route for the mass production of ceramic green bodies.

- Extrusion is used extensively in the traditional ceramics industry and to a lesser extent in the advanced ceramics sector.

- Injection molding has been the subject of intense investigation in recent years, but it has not yet made any significant inroads in the forming of ceramics for industrial applications.

# PLASTIC FORMING

- Plastic forming consists of mixing the ceramic powder with a large volume fraction of a liquid to produce a mass that is deformable (plastic) under pressure.

- Such processes were developed and used originally for clay and have since been adapted to polymeric materials.

- For traditional clay based ceramics the liquid is mainly water.

- For ceramic systems that are not based on clay, an organic may be used in place of, or in addition to, water.

- The binders are often complex and contain multiple components to achieve the required viscosity and burn-out characteristics.

# EXTRUSION

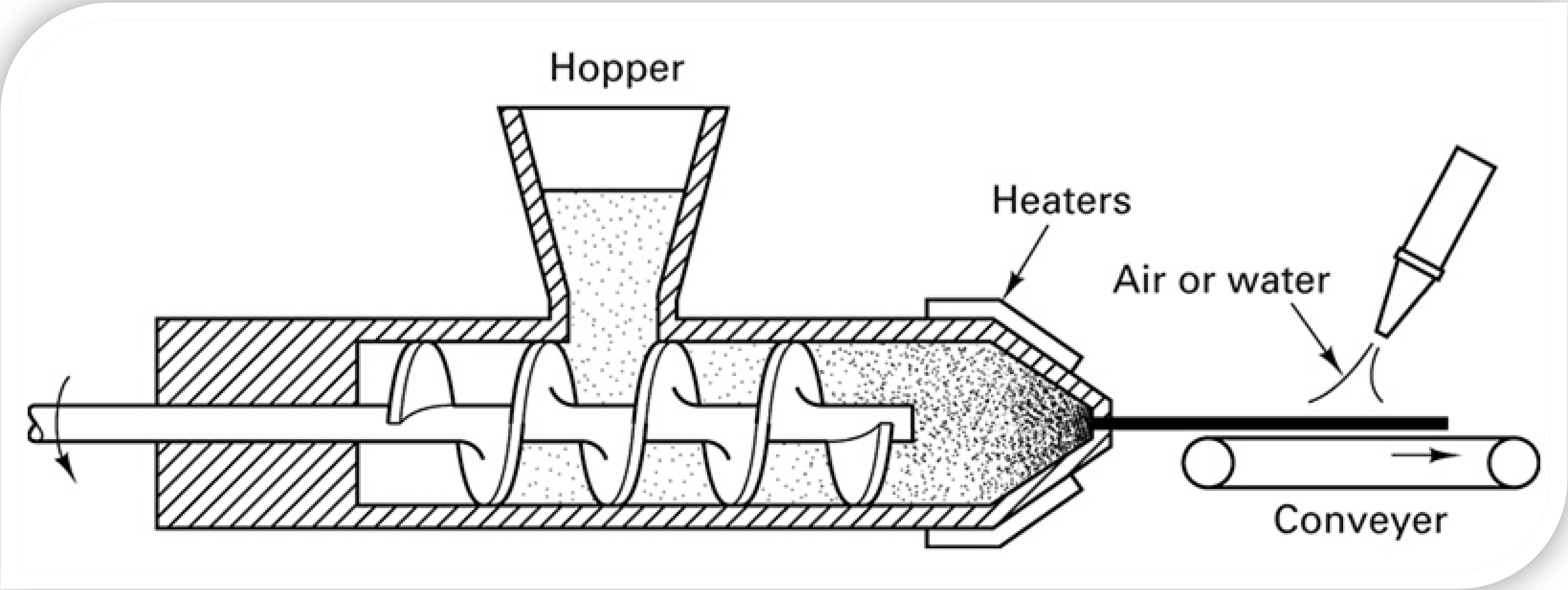
- Used for long products with a uniform cross-section
- Pellets or powders are fed through a hopper and then into a chamber with a large screw
- The screw rotates and propels the material through a preheating section where it is heated, homogenized, and compressed
- To preserve its shape, the material is cooled by jets of air or water spraying

# EXTRUSION

- Single cross sections and hollow shapes of ceramics can be produced by extrusion.

- Plastic ceramic material is forced through a hard steel or alloy die by a motor driven augur.

- Examples: Refractory brick, sewer pipe, hollow tubes.




**A screw extruder producing thermoplastic product. Some units may have a changeable die at the exit to permit production of different-shaped parts.**

# INJECTION MOLDING

Powder injection molding (PIM), which encompasses metal injection molding (MIM) and ceramic injection molding (CIM), is a net-shaping process which enables large scale production of complex-shaped components for use in a diverse range of industries.

Ceramic injection molding (CIM) uses ceramic powders such as alumina, zirconia, titania, ferrite powders, etc. It was introduced in 1940's, but for the next thirty years it was of minor interest to ceramic industry. In 1970's and 1980's CIM provided cost-effective fabrication method for mass production of ceramic parts for automotive industry.

Today more than 300 companies practise PIM. Most of them practise MIM technology (>70%). Small percentage (5%) produce metals, ceramics and carbide components and about 25% practice CIM technology. This positive tendency can be attributed to unique properties of ceramic materials. They have excellent mechanical properties and low specific weight. Also, they are suitable for applications under extreme conditions (high temperatures, corrosive atmospheres, abrasive conditions, high loads at high temperatures). This combination makes them interesting for a wide variety of applications.

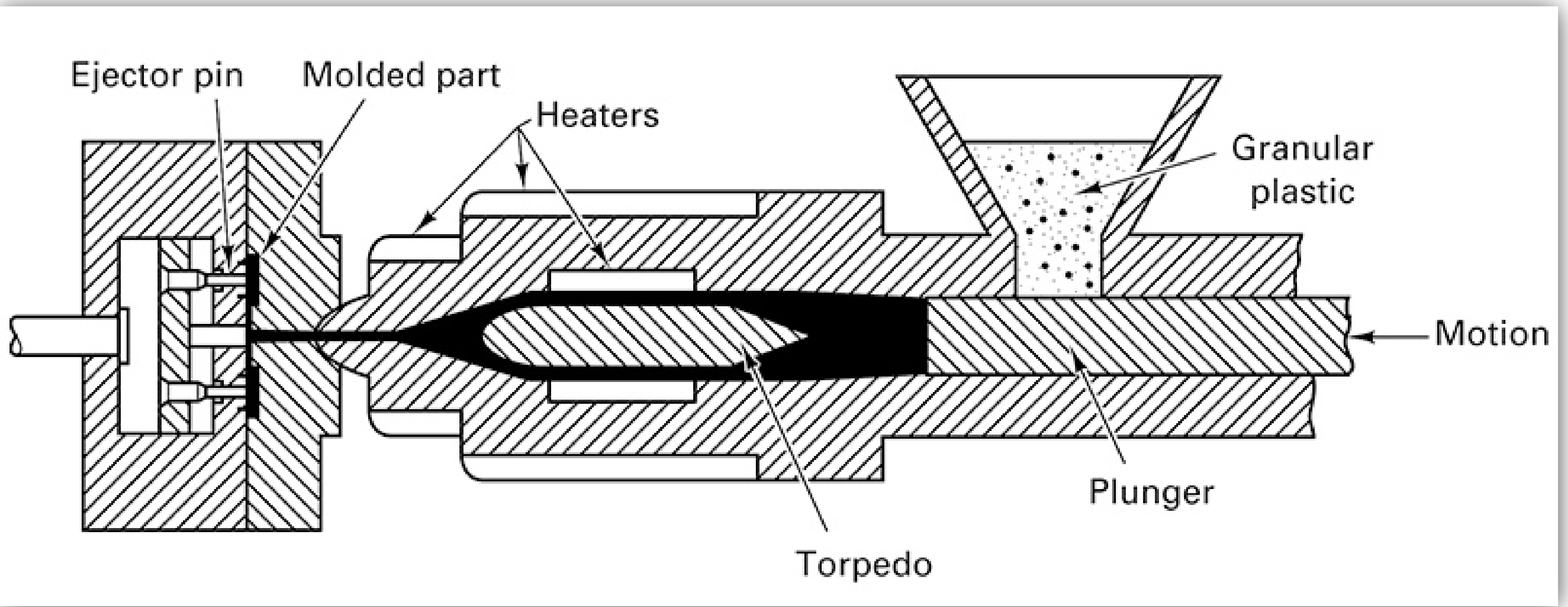
# INJECTION MOLDING

- Ceramic particles are mixed with a thermoplastic, then heated and injected into a mold cavity
- Polymer acts as a carrier and provides flow characteristics for molding
- Upon cooling which hardens the polymer, the mold is opened and part is removed
- The plastic binder is removed and the remaining ceramic part is sintered

# INJECTION MOLDING

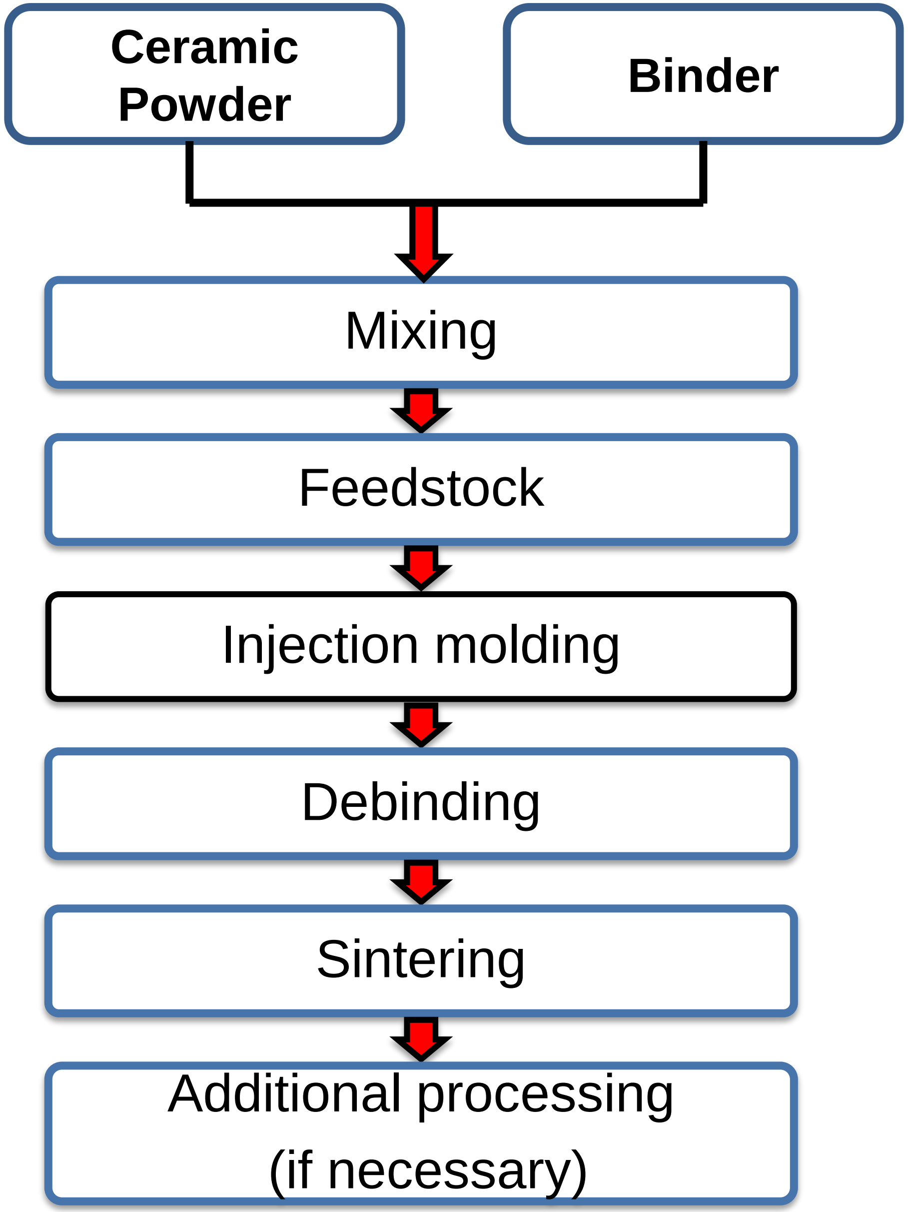
- Used for high-volume production of complex parts
- Granules of a raw material are fed through a hopper into a cavity that is ahead of a plunger
- The plunger moves forward and the material is heated
- In the torpedo section, the material is mixed, melted, and superheated
- The fluid then flows through a nozzle that is against the mold
- Sprues and runners are used in the same way as in metal casting

# INJECTION MOLDING




Schematic diagram of the injection molding process. A moving plunger advances material through a heating region (in this case, through a heated manifold and over a heated torpedo) and further through runners into a mold where the molten thermoplastic cools and solidifies.

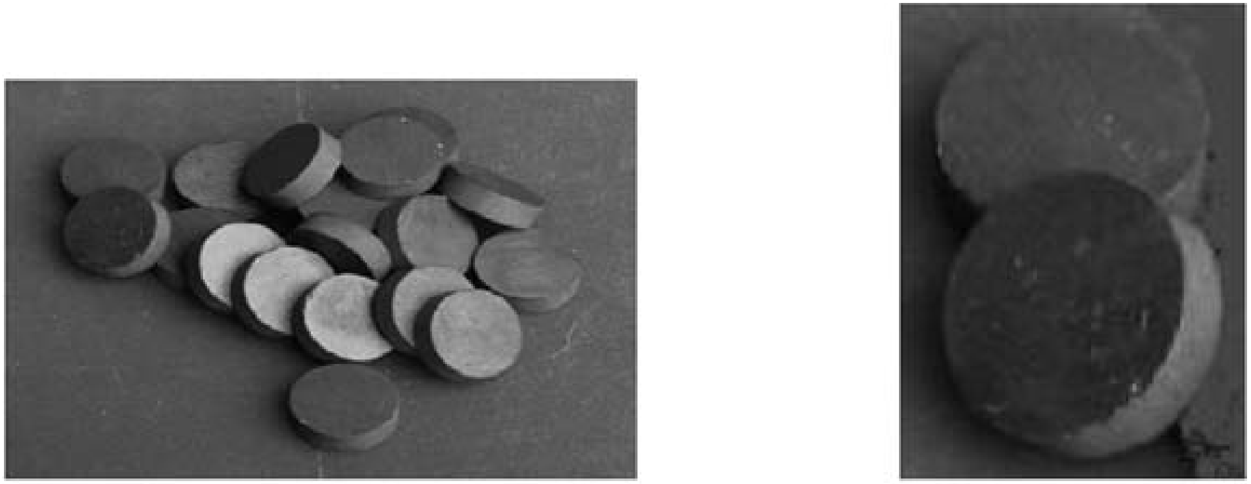
# INJECTION MOLDING




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

**CIM component: green body, brown body and sintered part, respectively.**

# INJECTION MOLDING



Disc shaped CIM Mn-Zn ferrite samples (diameter d=16mm, thickness t=5mm).

Ring shaped CIM Mn-Zn ferrite samples (outer diameter $d_o$=15mm, inner diameter $d_i$=6mm, thickness t=5mm).

# INJECTION MOLDING

- Powders blended with a polymer

- The molded greens are then placed in a furnace to burn off the plastics

- Advantages of injection molding
  - Produces complex shapes
  - Mechanical properties are nearly equal to those of wrought products

- Injection molding - A processing technique in which a thermoplastic mass (loaded with ceramic powder) is mixed in an extruder-like setup and then injected into a die to form complex parts. In the case of ceramics, the thermoplastic is burnt off.

# SHAPING

***Plasticizer*** *is the component of a binder that keeps it soft or pliable; it improves the rheological properties.*

***Green ceramic*** *is a ceramic* that has been shaped into a desired form but has not yet been sintered.

***Slip*** *is the liquid-like coating used to form the glaze when fired.*

***Binder*** *is a component that is added to hold the powder together while we shape the body.*

***Slurry*** *is a suspension of ceramic particles in a liquid.*

***Calcination:*** Heating of chemicals to decompose and or react with different chemicals; used in traditional synthesis of ceramics.

# SHAPING OF CERAMICS

## General considerations

- Both technical and economic factors should be considered
- For advanced ceramics, microstructure control is a critical issue
- Process window reflects the easiness of control; (reliability, reproducibility issue)
- Cost

## Various Shaping Methods for Ceramic Components

| *Shaping method* | *Type of feed material* | *Type of shape* |
|---|---|---|
| **Dry pressing** | Free-flowing granules | Small and simple |
| **Isostatic pressing** | Fragile granules | Larger and more intricate |
| **Extrusion** | Plastic mass using a viscous polymer solution | Elongated with constant cross section |
| **Injection molding** | Organic binder giving fluidity when hot | Complex |
| **Slip casting** | Free-flowing cream | Mainly hollow |

# Overview of shaping technologies

| method | product geometry | Starting material | mold costs | product examples |
|---|---|---|---|---|
| **axial die pressing** | simple- **complex** | **granulate** | **high** | **ferrite cores, piezo ceramics** |
| **isostatic pressing** | **simple** | **granulate** | **medium** | **tubes, spark plug, pistons** |
| **tape casting** | **simple (tape)** | **Concancrated suspension** | **very low** | **condensator substrates** |
| **extrusion** | **simple** | **plastic mass** | **low** | **tubes** |
| **pressure slip casting** | **simple** | **Concantrated suspension** | **low** | **sanitary ceramics** |
| **slip casting** | **complex** | **Concantrated suspension** | **low** | **sanitary ceramics** |
| **injection molding** | **complex** | **plastic mass** | **high** | **turbine blades** |

**Liquid content of the starting material for the different shaping processes**

- **Compaction of granulates ca. 5%**
- **Extrusion, injection molding ca. 25-30**
- **Casting ca. 60-70%**

**increasing liquid content**

**Asst. Prof. Dr. Ayşe KALEMTAŞ**

THE END

Thanks for your kind attention

# Any Questions