



# Ceramics

- Processing -



# Processing Ceramics

## a) Glasses

viscous liquid  $\sim 700$  °C, they can be cast (at 1.000 °C) and formed by methods used for metals (e.g., rolling, pressing, forging)

## b) High-performance engineering ceramics

$T_M > 2.000$  °C  $\rightarrow$  no casting, no secondary forming processes possible BUT made from powders which are pressed and fired ( $\rightarrow$  sintering)



# Production of Engineering Ceramics

- Starting point of the forming processes of engineering ceramics is the production of **ceramics powders**
- The basic chemistry of powders production is fairly simple but the production process can be highly complicated as fine powders (diameter  $< 1 \mu\text{m}$ ) are often required

Alumina powder made of bauxite (hydrated aluminum oxide)

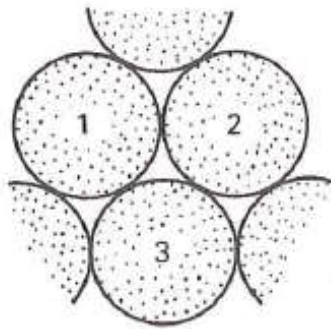
- crushing, purification
- heating to  $1.150 \text{ }^\circ\text{C}$ :



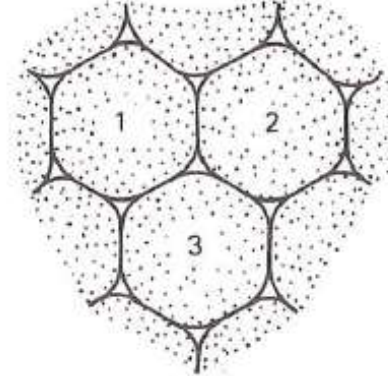


# Forming of Engineering Ceramics

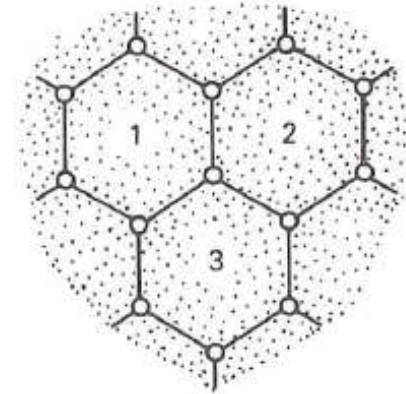
- Fine powders have extremely high surface energy
  - a cup of 1  $\mu\text{m}$  sized particles  $\rightarrow 10^3 \text{ m}^2$  surface area.
  - $\text{Al}_2\text{O}_3$  surface energy  $1 \text{ J m}^{-2} \rightarrow$  one cup of alumina powders: 1 kJ
- High surface energy is the “driving force” for **sintering**  
particles packed and heated ( $\sim 2/3 T_M$ ) sinter: they bond together forming necks which then grow reducing surface area and increasing particle density



(a)



(b)



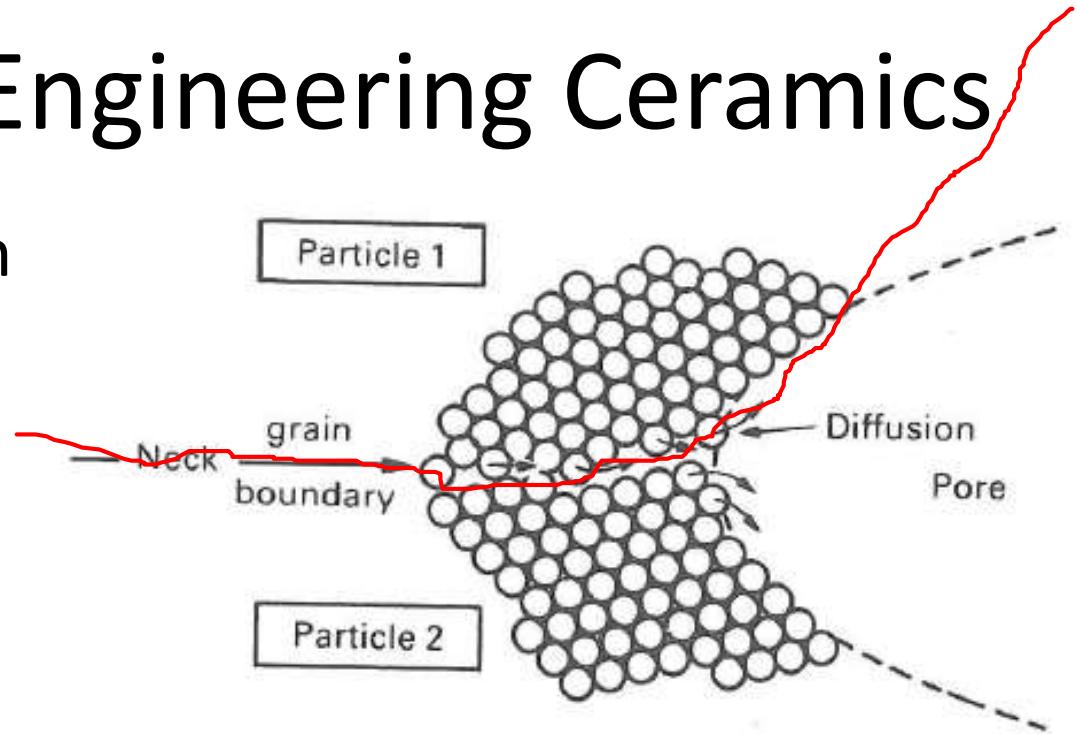
(c)

$\rightarrow$  full density is never reached, and small rounded holes are often left (relatively small effect on mechanical strength)



# Forming of Engineering Ceramics

## Microscopic description

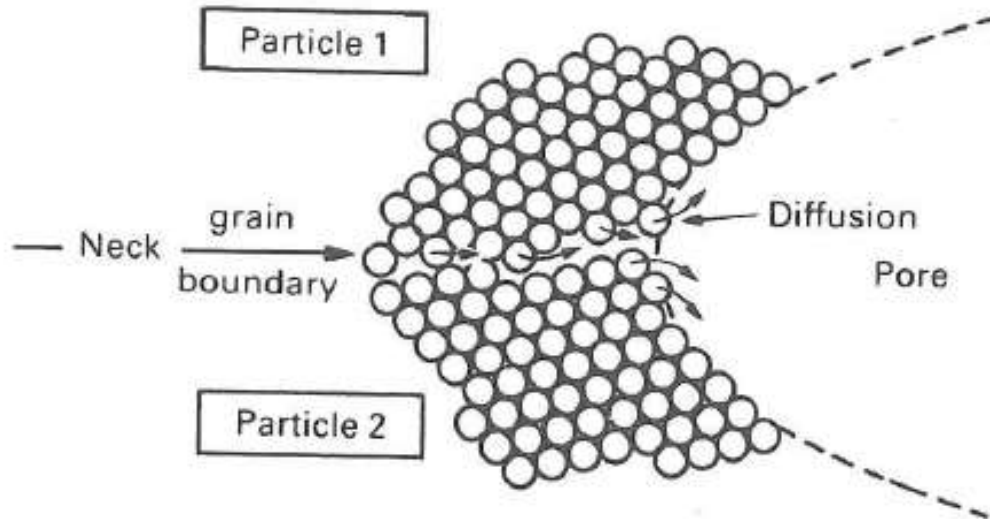


- Upon increasing packing pressure and temperature, powder particles bond together by forming **small necks**
- At each neck, there is a **grain boundary** since particles meet (most likely) with different orientations. If temperature is sufficiently high, atoms diffuse from the grain boundary to the **pore space**
- This “pore filling” process is:
  - i) driven by the reduction in surface area
  - ii) controlled by the rate of diffusion



# Forming of Engineering Ceramics

## Microscopic description



1. Fine particles sinter much faster than coarse ones because **surface area is higher** and **diffusion distance is lower**
2. The rate of sintering varies with temperature in the same way as the diffusion coefficient, thus the rate of densification is:

$$\frac{d\rho}{dt} = \frac{C}{a^n} \exp\left(-\frac{Q}{RT}\right)$$

$\rho$ : density  
 $a$ : particle size

$C, n$ : constants ( $n = 3$ )  
 $Q$ : activation energy for sintering  
(= to activation energy for grain-boundary diffusion)



# Forming of Engineering Ceramics

## Sintering Methods: General features

- Powder is pressed to an initial shape inside a die [in combination with binder to provide enough strength to be moved into furnace]
- Compacted powder (within die) is heated into a sintering furnace and during sintering
  - considerable shrinkage → shape changes within the die
  - grain growth → final grain size can be larger than initial particle size
- Powders of different sizes are often mixed to have a high density to start with and also shrinkage can be taken into account in the design of the die to minimize finishing by machining or grinding
- The final microstructures show grains with distribution of small circular pores at the edge of the gains, with **pore size and spacing** directly proportional to **particle size**

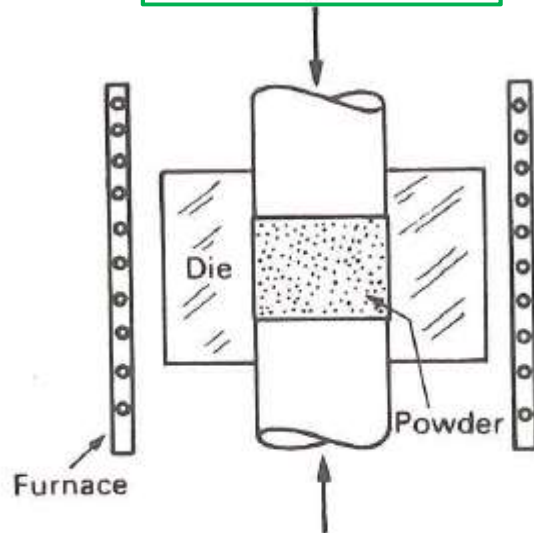


# Forming of Engineering Ceramics

## Sintering Methods: HOT PRESSING

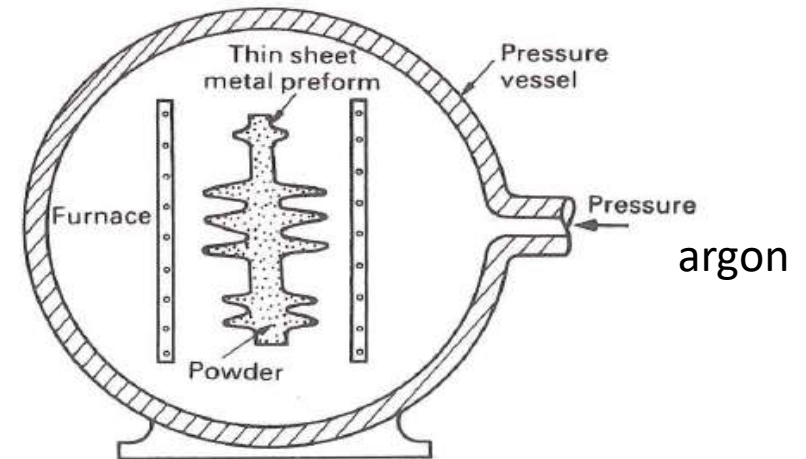
- Method used to obtain high density and small grains ( $\uparrow$  mech. prop.)
- Simultaneous application of **pressure** and **temperature**  $\rightarrow$  pressure adds up to surface energy to speed-up sintering (from hours to minutes) and increase density
- Short time reduces grain growth  $\rightarrow$  higher mechanical properties
- No subsequent finishing is needed BUT dies are expensive

### Die pressing



powder heated and compressed in a shaped die  $\rightarrow$  anisotropic properties

### Hot isostatic pressing



powder (in a thin steel preform) is heated and compressed by high pressure argon  $\rightarrow$  isotropic properties

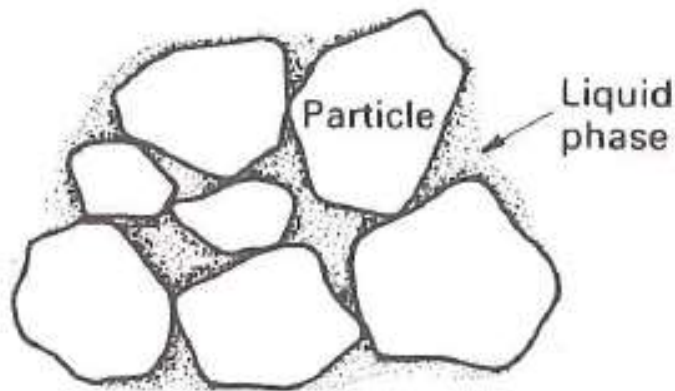




# Forming of Engineering Ceramics

## Sintering Methods: LIQUID PHASE SINTERING

- Alternative (and less expensive) method to hot pressing to obtain high density but with some loss in mechanical properties
  - Powder (e.g.,  $\text{Al}_2\text{O}_3$  or  $\text{Si}_3\text{N}_4$ ) + small amounts (1%) of additive (MgO)
  - Additive reacts with the powders to form a low melting point glass which flows between the powder particles at the sintering temperature
- diffusional transport through the melt is high and the rate of sintering is increased
- due to the presence of the glass, porosity is highly reduced



### However:

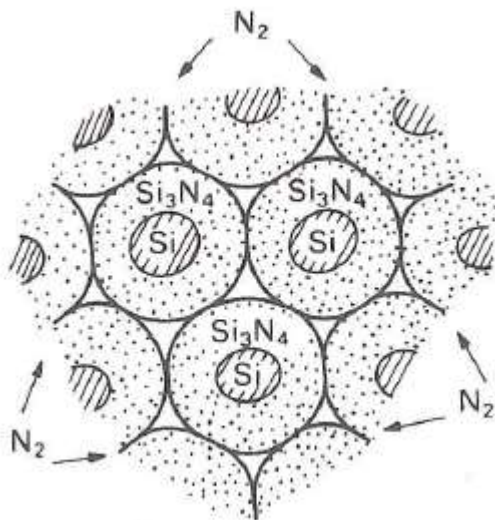
As the glass remains at the boundaries of the grains, it can melt again

→ **reduces high temperature strength**

# Forming of Engineering Ceramics

## Sintering Methods: REACTION BONDING

- Fairly new route to fabricate silicon-based ceramics which is cheaper than hot-pressing and gives good precision
- Pure silicon powders heated in nitrogen gas:
  - $3 \text{ Si} + 2 \text{ N}_2 = \text{Si}_3\text{N}_4$  (silicon nitride)
- Mixture of silicon and carbon powders sintered together
  - $\text{Si} + \text{C} = \text{SiC}$  (silicon carbide)



→ These chemical reactions take place during sintering and bonding occurs simultaneously

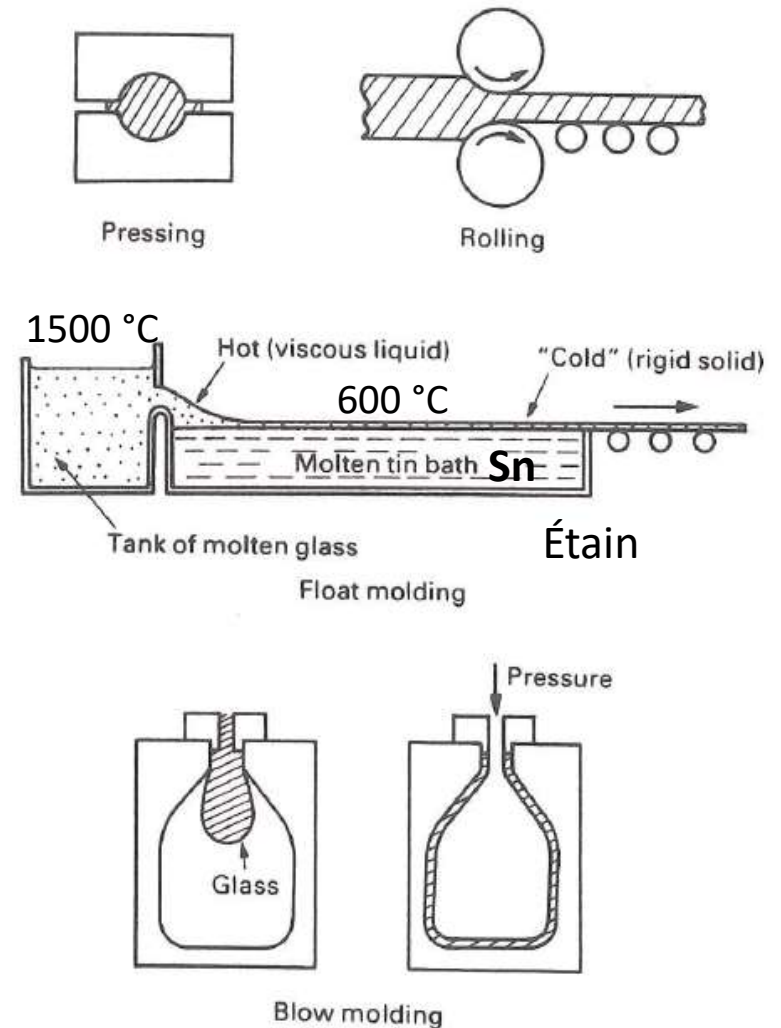
### SiC

- Ceramics powder is mixed with a polymer to make it “plastic” and then shaped with methods used for polymers (rolling, extrusion, pressing) so to obtain complex shapes
- The polymeric additive is burnt out and the powder is heated so that Si and C reacts. Final porosity is fairly high but dimensional change is small (<0.1%)



# Production and Forming of Glass

- Glasses are based on silica ( $\text{SiO}_2$ ) with additives: 30% for soda-glass, 20% high temperature glass (Pyrex)
- Raw glasses are produced by **melting** the components together and **casting** them (like metals)  $\rightarrow$  deformation of viscous flow
- Typical processes:
  1. **Hot-pressing:** a slug of hot glass is pressed between dies (requires high viscosity): use to make heavy glass insulators
  2. **Rolling:** to produce a glass sheet (high viscosity)
  3. **Float molding:** to produce optically smooth and thin window glass (low viscosity)
  4. **Blow molding:** to produce bottle or thin envelopes for light bulbs

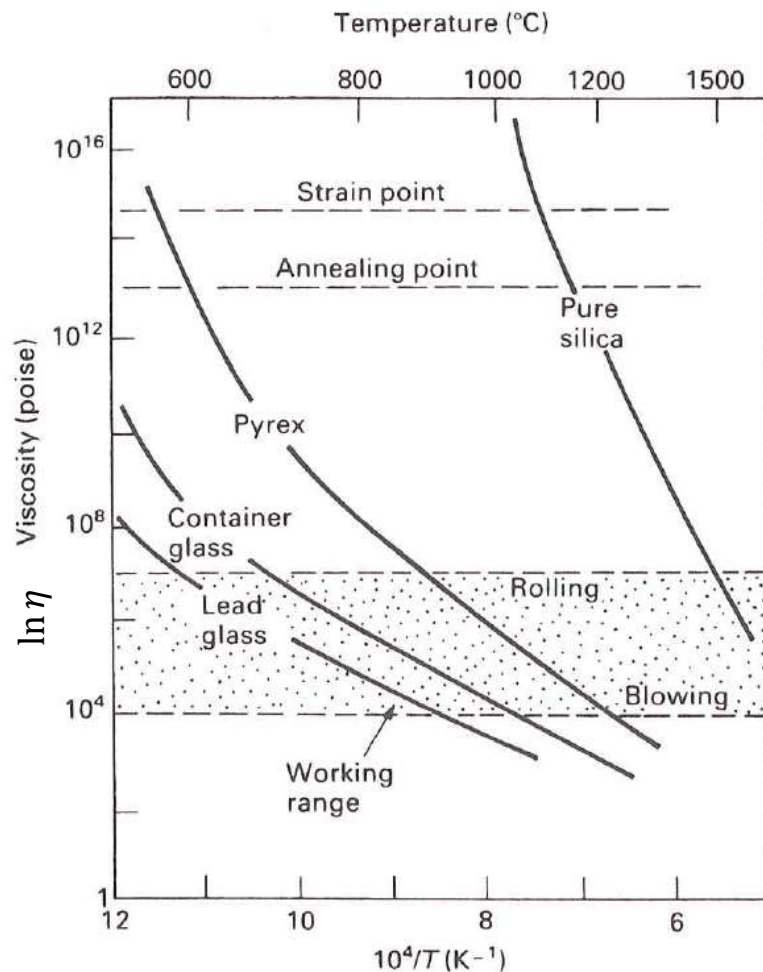


# Production and Forming of Glass

In addition to glass temperature ( $10^{17}$  P) two other temperatures are important in the forming of glass:

- **annealing point** → there is enough “fluidity” to relax internal stresses most glasses are held for about 15 min at this temperature to relax internal stresses that might induce fracture ( $\eta \sim 10^{13}$  Poise)
- **strain point** → here atom motion is “slow” and from this temperature rapid cooling does not introduce new stresses ( $\eta \sim 10^{14}$  Poise)

In glass processing: slow cooling from annealing point to strain point, faster cooling from strain point to room temperature



$$\eta = \frac{\sigma_s}{\dot{\gamma}} \quad \eta \propto \exp\left(\frac{Q}{RT}\right)$$



# Production and Forming of Glass

## **toughened glass (up to 4 times stronger than ordinary glass)**

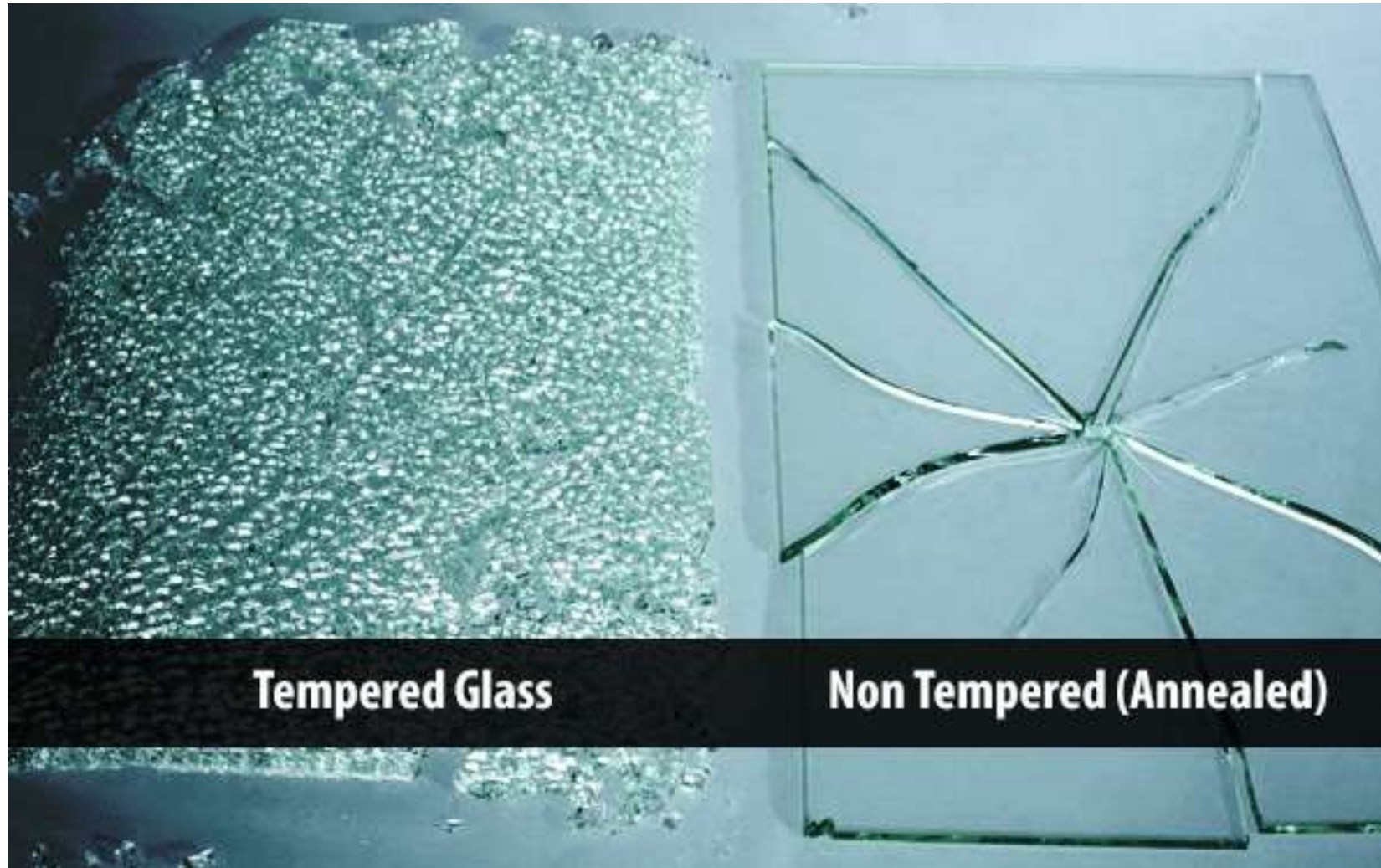
Tensile stresses are problematic (→ brittle fracture) but compressive stresses can be useful.

Toughened (or tempered glass) is made by heating glass above the annealing point and then cooling rapidly the surface of the glass (~10 sec.):

- The surface of the glass contracts and hardens while the interior is still hot and more fluid
- The interior also cools and contract but the surface is below the strain point (cannot flow) so it is put in compression by the interior
- With the surface in compression the glass is stronger as microcrack that induce failure always start from the surface
- However, the interior is put in tension by the surface and if a crack penetrate inside → the glass shatters



# Fracture of Tempered vs. Non-Tempered Glass





# Improving Ceramics

$$\sigma_{TS} \approx \frac{K_C}{\sqrt{\pi a_m}}$$

Reduce flaw:  $a_m$

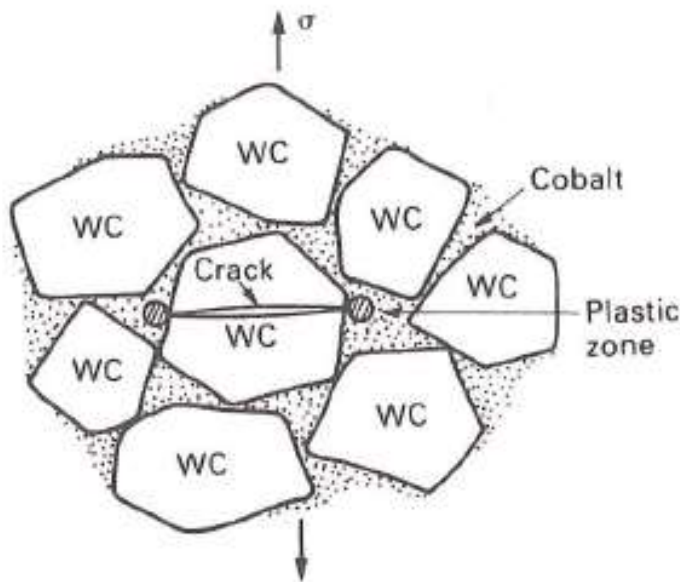
Increase:  $K_C$

- Flaws cannot be avoided (even in defect free ceramics)
- Flaws have roughly the size of powder particles
- Flaw size can be reduced by manufacturing methods
- Samples with abnormally large flaws can be detected and discarded → **quality control**
- Fracture toughness of pure ceramics is low:  $[0.2 - 2] \text{ MNm}^{-3/2}$
- Fracture toughness can be increased by
  - 1) Making “alloys” (partially stabilized zirconia, PSZ):  
 $\text{ZrO}_2 + \text{MgO} \quad K_C: 2 \rightarrow 8 \text{ MNm}^{-3/2}$
  - 1) Fiber strengthened: cement toughened with glass fibers  $\sim 10 \text{ MNm}^{-3/2}$
  - 2) Making a composite: cerment

# Improving Ceramics: Cerment

Cerment is a composite of a ceramic (tungsten carbide, WC) and a metal (cobalt, Co)

Brittle particles of tungsten carbide are bonded together with a thin film of cobalt by sintering mixed powders



A crack which is formed into WC immediately run into the cobalt film which deforms plastically and absorbed energy

$K_C$  of WC :  $1 \text{ MNm}^{-3/2}$

$K_C$  of cerment:  $15 \text{ MNm}^{-3/2}$





**Table 20.1** Applications of High-Performance Ceramics

Application	Property	Material
Cutting tools	Hardness, toughness	Alumina, sialons
Bearings, liners, seals	Wear resistance	Alumina, zirconia
Agricultural machinery	Wear resistance	Alumina, zirconia
Engine and turbine parts, burner nozzles	Heat and wear resistance	SiC, Si <sub>3</sub> N <sub>4</sub> , alumina, sialons, ceramic–ceramic composites
Shielding, armor	Hardness, toughness	Alumina, boron carbide
High-performance windows	Translucence and strength	Alumina, magnesia
Artificial bone, teeth, joints	Wear resistance, strength	Zirconia, alumina
Integrated circuit substrates	Insulation, heat resistance	Alumina, magnesia