Week 12

Ceramics and colloids

A. Testino

Sintering_1

References:

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- M.N. Rahaman - Ceramic processing and sintering. Taylor & Francis. Second edition (2003). Chapters 7-10
- A. Leriche, F. Cambier, S. Hampshire – Sintering of Ceramics. Reference Module in Materials Science and Materials Engineering (2017)
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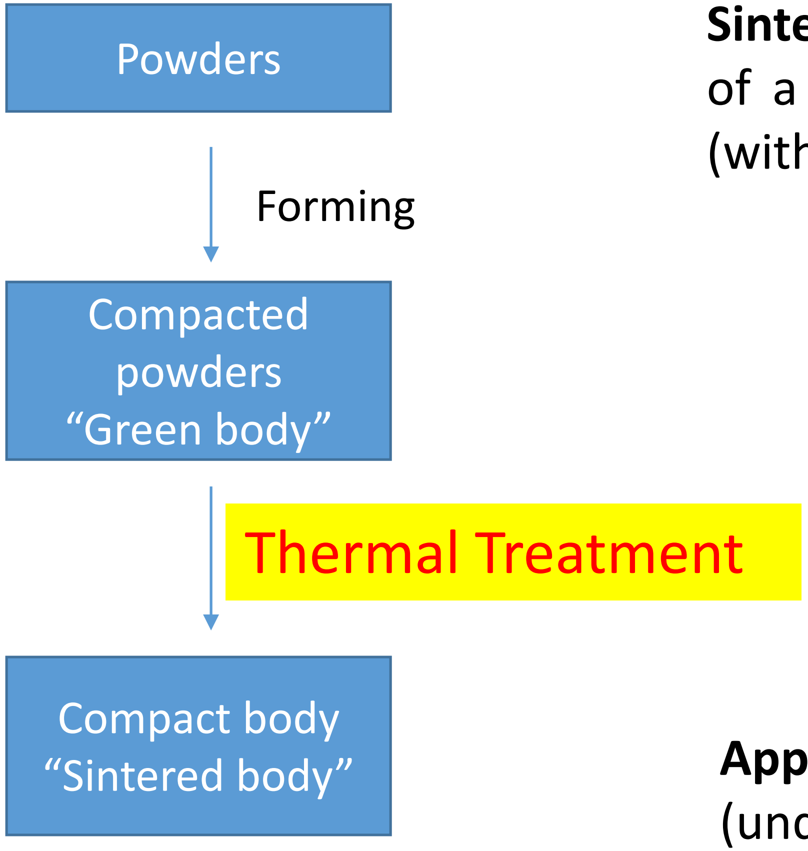
- W. D. Kingery - Densification during Sintering in the Presence of a Liquid Phase. I. Theory, J. Appl. Physics, 30, 302-306 (1958)

Summary Week 12-13-14

1. Sintering fundamental (10)
2. Solid state sintering (16)
3. Grain growth & microstructure (22)
4. Liquid phase sintering (13)
5. Examples and practice (11)

Recall: processing



Powders

Forming

Compacted powders “Green body”

Thermal Treatment

Compact body “Sintered body”

Sintering: thermal treatment which allows the transformation of a compacted powder body (green body) into a solid body (without fusion).

Key objectives: understand how the process variables influence the microstructure evolution.

Approach: experimental trials (trial-and-error) or theoretical basis (understanding of the elementary mechanisms which are governing the consolidation process).

Some key parameters that can be controlled with accuracy:

- Temperature (thermal profile of the oven);
- Pressure (applied on the green body);
- Average particle size;
- Gaseous atmosphere.

Other parameters are more complicated to control:

- Particle size distribution;
- Particle packing (green body density);
- Powder characteristics (chemical homogeneity);
- Thermal homogeneity into the oven;
- Reproducibility.

Other parameters might be unknown:

- Surface energy;
- Grain boundary energy;
- Diffusion coefficients.

Sintering behavior: very difficult to predict even for the simplest system

Driving force: decrease the free energy of the system! Influenced by:

- **Curvature of the particle (overall surface)**
- **External applied pressure (external applied fields)**
- **Chemical reactions (within the solid or with a gas phase)**

- The driving force define the **thermodynamics** of the system change. As usual, the **kinetics** define how much time is needed to fulfill the TD wishes!

- Kinetics refers to the **mass transport**, which occurs predominantly by **diffusion (Fick's low).** The understanding of the diffusion mechanism is crucial to achieve a controlled process.

- The diffusion rate depends on defects (type and concentration). Therefore, the **defect chemistry** of the system is important and can be largely modified by using dopants, atmosphere, and temperature.

- **Atoms** (ions) diffuse from area at higher chemical potential to regions of lower chemical potential or, equivalently, vacancies counterflow.

- In **ionic solid** the local eletroneutrality needs to be preserved and diffusion fluxes are coupled (**ambipolar diffusion**)

Example: surface free energy change (thermodynamic driving force)

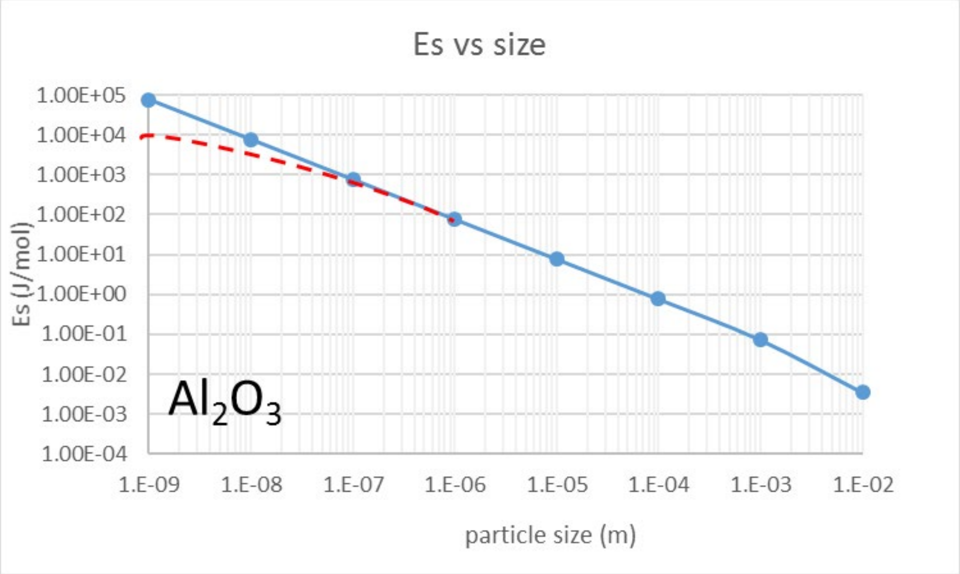
Consider a mole of spherical particles with radius *a*:

M: molecular weight	[M mol^{-1}]
ρ: density	[M L^{-3}]
V_m: molar volume	[L^3 mol^{-1}]
γ: specific surface energy	[M L^2 t^{-2} L^{-2}] = [M t^{-2}]

Number of particles per mol: $N = \frac{3M}{4\pi a^3 \rho} = \frac{3V_m}{4\pi a^3}$ [mol^{-1}]

Surface area: $S_A = 4\pi a^2 N = \frac{3V_m}{a}$ [L^2 mole^{-1}]

Surface energy: $E_s = \frac{3\gamma V_m}{a}$ [M L^2 t^{-2} mol^{-1}]



Considering that the surface energy of a macroscopic (fully dense) solid is negligible, E_s represents the decrease in surface energy of the system upon sintering/coarsening ($\Delta E \cong E_s$).

If γ is 1 J m^{-2}, *a*= 1 μm and V_m = 25 x 10^{-6} m^3 mol^{-1}
E_s = 77 J mol^{-1} (for instance Al_2O_3)

Remember:

smaller particle = higher driving force
γ is size dependent (for *a*<1μm, ------)
For *a*>100 μm almost no driving force!

Kinetics: solid state diffusion

Fick’s laws of diffusion.

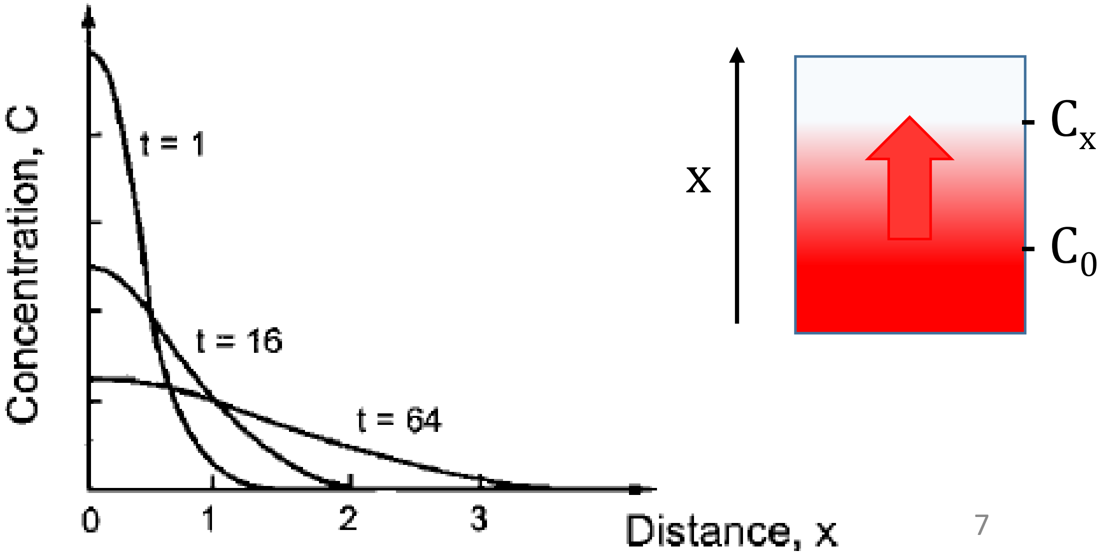
The movement of diffusing species is considered to be driven by gradients in the concentration. The approach is similar to that of heat transfer (continuum approach). The concentration can vary as a function of distance and time. When the concentration is independent of time → **Fick’s first law**

$$\boxed{J_x = -D\frac{dC}{dx}}$$

The proportionally constant D is the **diffusion coefficient** (diffusivity, [lenght^2 time^{-1}]). It depends on T.
J is the **flux** of diffusing species (number of crossing per unit of area, normal to the direction of the flux, per unit of time [# length^{-2} time^{-1}]).

If the concentration change with time: → **Fick’s second law** (it can be derived from the first law considering the conservation of matter)

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2}$$



Mechanism of diffusion

Different types of defects determine the path of matter transport → The major mechanism of matter transport:

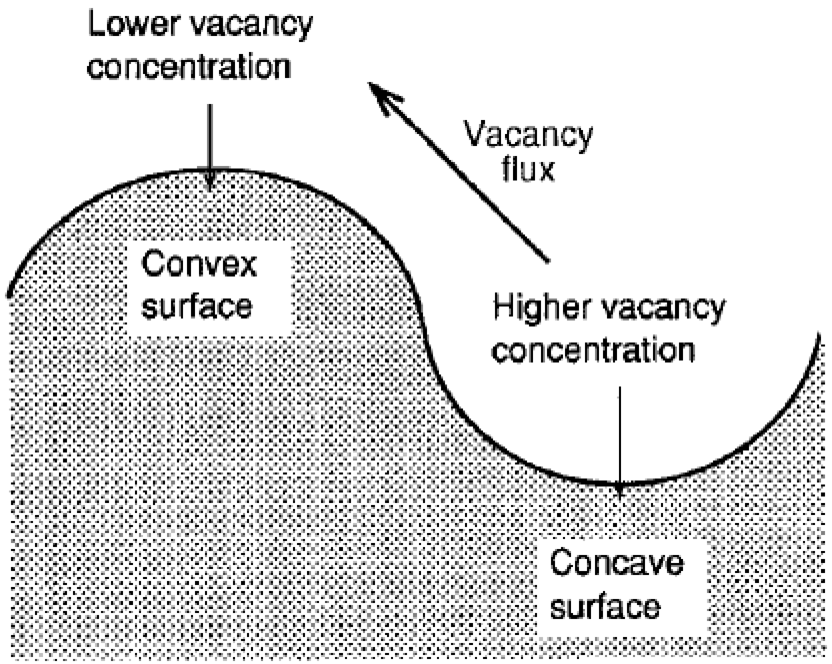
- **Lattice diffusion** (bulk diffusion): movement of point defects (vacancies, interstitial) through the bulk of the lattice;

- **Grain boundary diffusion**: polycrystals are separated by region of lattice mismatch and disorder, called grain boundaries. This 2D area (0.5-1 nm thick) are highly defective and the mass transport is more rapid than lattice diffusion in the adjacent grains. It depends on grain size;

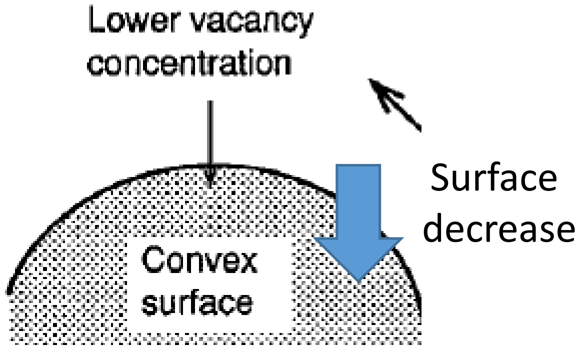
- **Surface diffusion**: the surface is a defective area. Atoms (ions) move on the surface, looking for an energy minimum. The curvature of the surface plays a crucial role.

Diffusion and curvature:

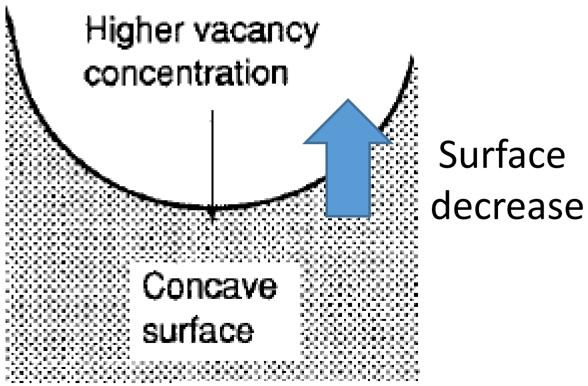
Let's assume that vacancies are the only punctual defect.



Schematic diagram showing the direction of flux for vacancies in a curved surface. The flux of atoms is the opposite.
(Rahaman - Fig. 7.12; p.456)



= decrease the vacancy concentration



= increase the vacancy concentration

Concentration difference → flux
Flux of vacancies → counter flux of matter. Therefore, matter diffuse from convex to concave

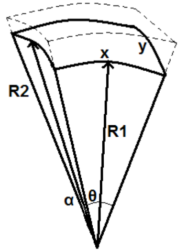
Vapor pressure and curvature:

Matter transport by evaporation-condensation is treated alongside the solid state diffusion.

$$P_{vap} = P_0 \exp\left(\frac{\gamma_{SV} K \Omega}{kT}\right)$$

γ_{SV}: interfacial energy S/V, $\gamma_{SV}=\gamma_{SV}(\mathrm{T})$
P_0: vapor pressure over a flat surface
K: curvature parameter (positive for convex surface)
Ω: atomic volume
k: Boltzmann constant
T: temperature (K)
P_{vap}: vapor pressure over the curved surface

$$K = \left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$



Remember:
2D surface

If $\gamma_{SV} K \Omega << kT$:

$$\boxed{P_{vap} = P_0\left(1 + \frac{\gamma_{SV} K \Omega}{kT}\right)}$$

Kelvin equation, p.462

Thus, for a given system under isothermal conditions, the vapor pressure **increase with the curvature of the surface.**

In a liquid-gas system: small droplet evaporate faster (and easier) than large droplet;

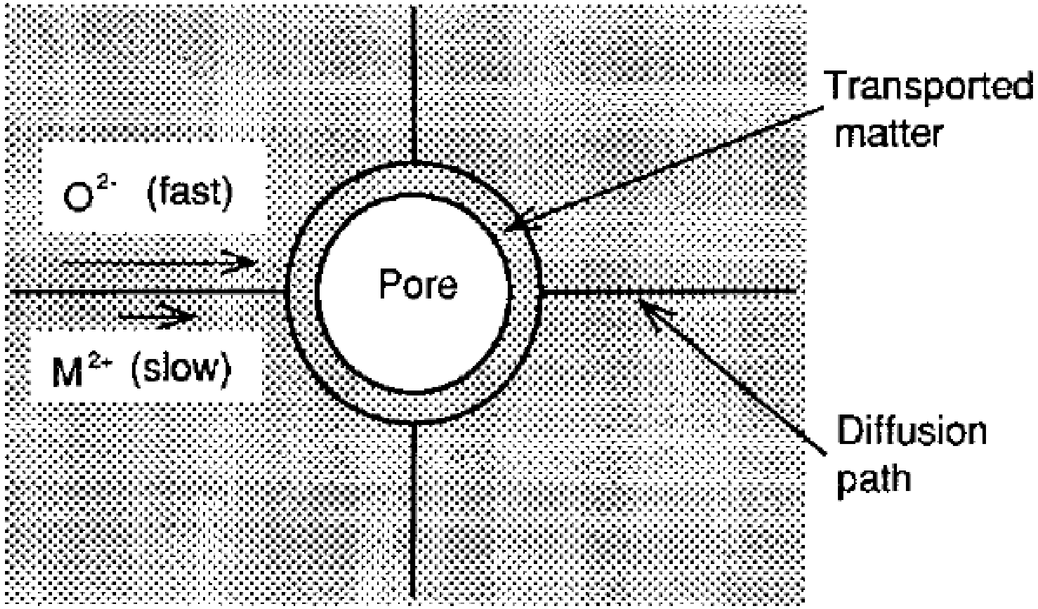
In a solid-liquid system: small particles are more soluble than large particles; small particles dissolve whereas large particles grow, etc;

In solid-gas system: small pores disappears whereas large pores grow (or pores are segregated).

Ambipolar diffusion

So far we consider diffusion of atomic species. In case of ceramics, we deal with ions. Each ion has a diffusion rate and a preferential diffusion mechanism.

The local eletroneutrality and local stoichiometry of the solid matter need to be preserved. Therefore:



- The more slowly diffusing ion determines the rate of matter transport.
- The effect of the faster diffusing species is to accelerate the motion of the slower ion (charge effect)
- The transport occurs predominately along the fastest path.

The rate controlling mechanism becomes the slowest diffusing species along its fastest path, which is accelerated by the fastest diffusing species

Remarks of the section

- Matter transport during sintering occurs by **diffusion**;
- Diffusion is a **thermally activated** process;
- Diffusion can occurs along **different paths** (lattice, grain boundary, surface);
- Diffusion needs a **driving force** (gradient, Fick's law);
- Remember influence of **curved surfaces**;
- The diffusion kinetics depends on the concentration of **defect**;
- The concentration of **defect can be influenced** by many parameter, such as temperature, atmosphere, doping, …
- Matter flux can be seen in term of **flux of atoms or counterflux of vacancies**;
- In ionic solid the mass transport is coupled in such a way that **stoichiometry and eletroneutrality** of the solid is preserved;
- The mass transport rate is controlled by the **slowest diffusing species along its fastest path.**

Solid state sintering: introduction

Matter transport can occurs by at least **six different paths**: these sintering mechanisms are convoluted and can change their relative relevance during the evolution of sintering process.

During sintering grains and pores grow: this process is referred to as **coarsening.**

Coarsening reduce the driving force for densification. Therefore, **a competition between sintering (densification) and coarsening** take place.

The **microstructure evolves** during these processes (grain and pore sizes and their size distribution) with fundamental implication to the material properties.

Some mathematical models exits but only a **qualitative understanding** of sintering can be achieved.

Other **phenomenological approach** attempts to represent the sintering data but not much insight into the mechanism are provided.

Sintering without (too much) coarsening provides **nanostructured dense ceramics**.

Mechanisms

Matter is transported from a higher chemical potential (source) to a lower chemical potential area (sink).

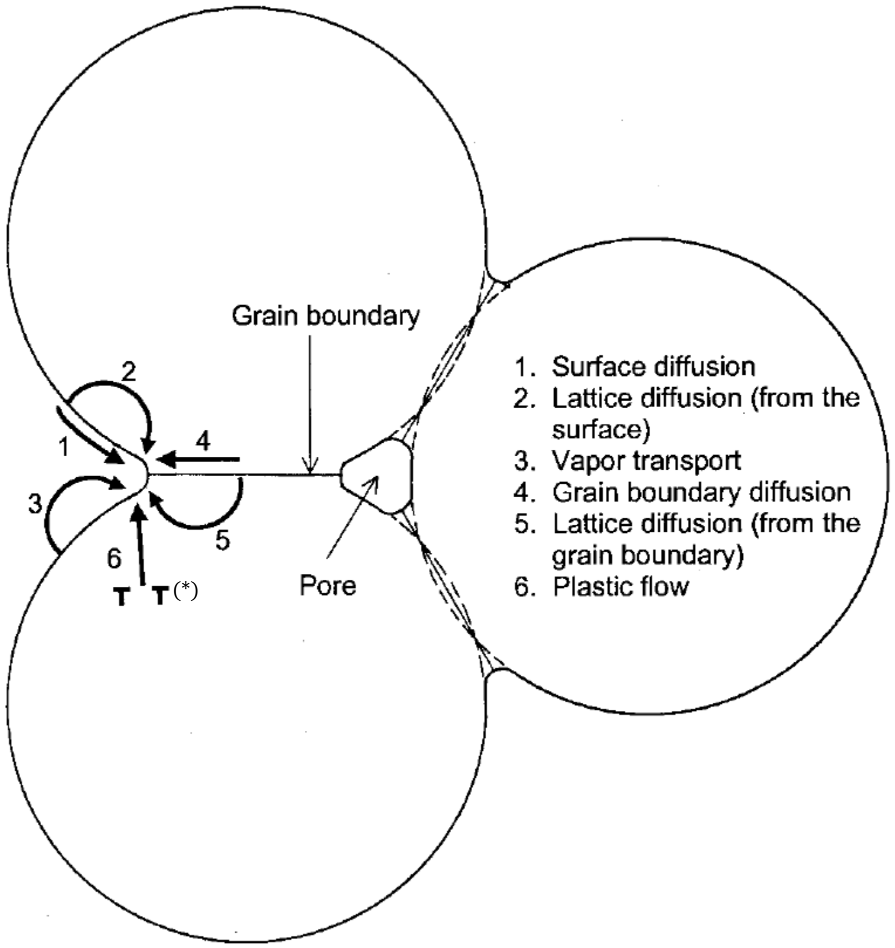


FIGURE 8.1 Six distinct mechanisms can contribute to the sintering of a consolidated mass of crystalline particles:(1) surface diffusion, (2) lattice diffusion from the surface, (3) vapor transport, (4) grain boundary diffusion, (5) lattice diffusion from the grain boundary, and (6) plastic flow. Only mechanisms 1 to 3 lead to densification, but all cause the necks to grow and so influence the rate of densification.

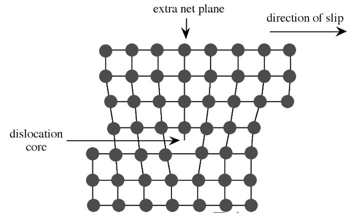
4 to 6

TABLE 8.1 Mechanisms of Sintering in Polycrystalline and Amorphous Solids

Type of solid	Mechanism	Source of matter	Sink of matter	Densifying	Non densifying
Polycrystalline	Surface diffusion	Surface	Neck		x
	Lattice diffusion	Surface	Neck		x
	Vapor transport	Surface	Neck		x
	Grain boundary diffusion	Grain boundary	Neck	x	
	Lattice diffusion	Grain boundary	Neck	x	
	Plastic flow	Dislocations	Neck	x	
Amorphous	Viscous flow	Unspecified	Unspecified	x	

Densify mechanism = shrinkage

(*) edge dislocation (⊥)



Analytical models

A relatively **simple geometry** is assumed for the powders and the mass balance equations are analytically solved for each mechanism. But the **microstructure is evolving during sintering** and the **geometrical model changes too.** Therefore, it is **difficult to define a single geometrical** model for the entire process.

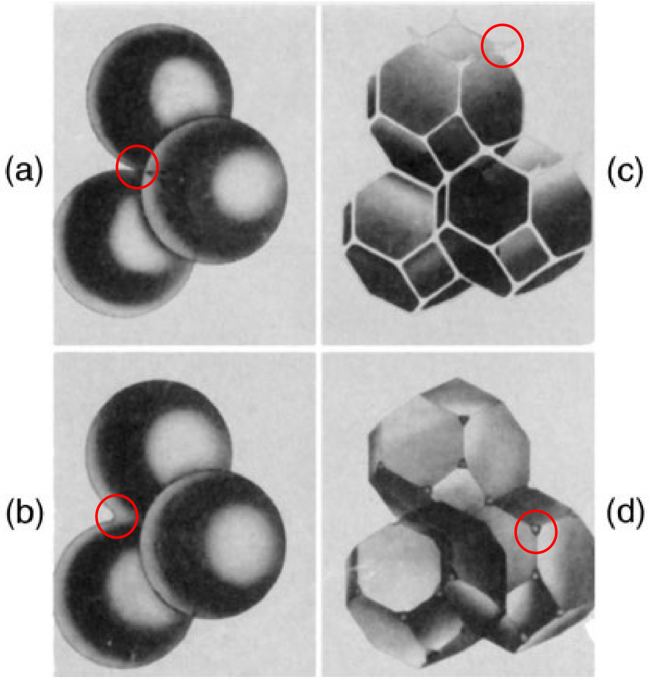


Figure 8.8 Idealized models for the three stages of sintering. (a) Initial stage: Model structure represented by spheres in tangential contact. (b) Near the end of the initial stage: Spheres have begun to coalesce. The neck growth illustrated is for center-to-center shrinkage of 4%. (c) Intermediate stage: Dark grains have adopted the shape of a tetrakaidecahedron, enclosing white pore channels at the grain edges. (d) Final stage: Pores are tetrahedral inclusions at the corners where four tetrakaidecahedra meet. (From Ref. 10.)

To overcome this difficulty, the sintering process can be **portioned in three sequential stages.** For each of them an **idealized geometry** is defined with a **<u>rough</u>** similarity with the microstructure.

Stage of sintering:

- **initial (a-b);**
- **intermediate (c)**;
- **final (d)**.

Stages: qualitative description

Initial

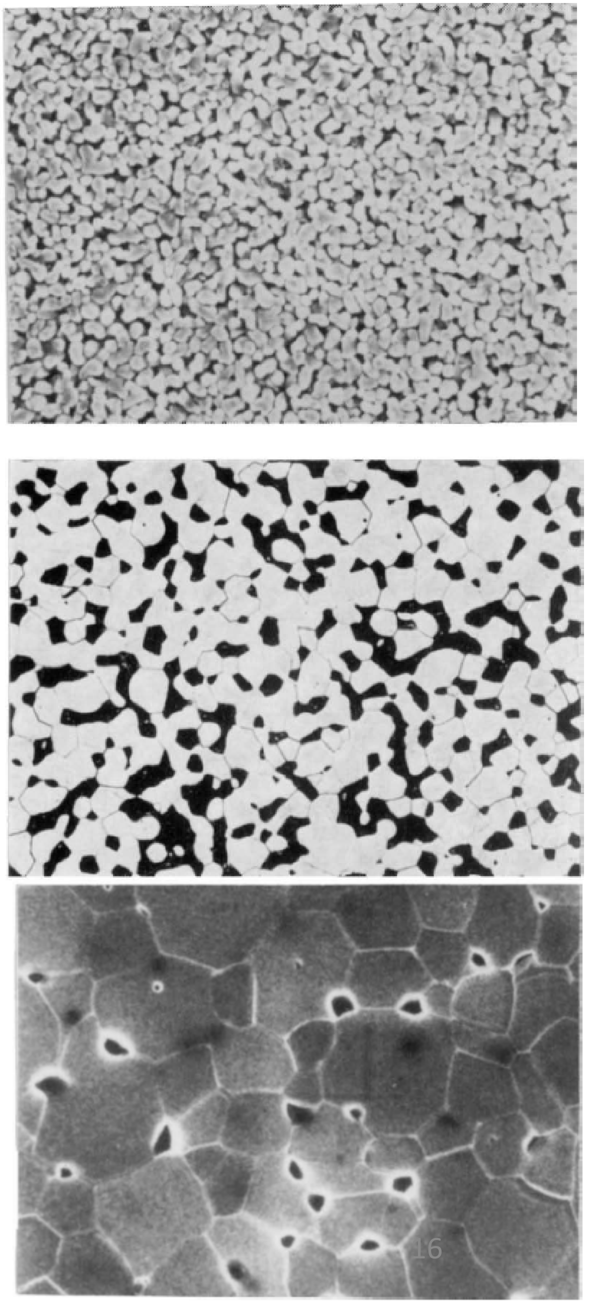
- Rapid interpaticle neck growth (diffusion, vapor transport, plastic and viscous flows);
- Main differences in curvature are removed;
- Densification starts: from 50% to 65% of the theoretical density (linear shrinkage 3-5%)
- Neck radius between particles = 0.4 – 0.5 of the particle radius.

Intermediate

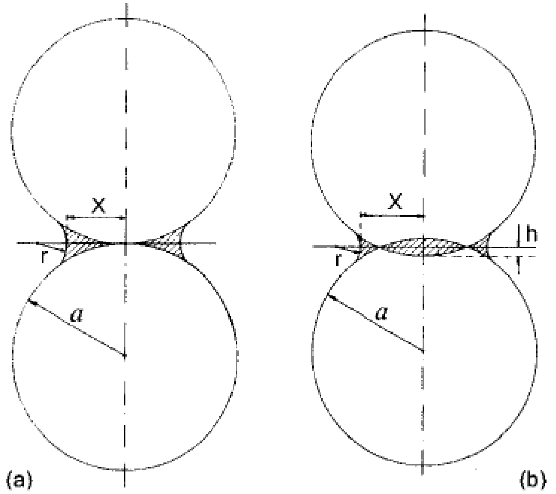
- This stage covers the major part of the sintering process;
- Pores reach their equilibrium shape but they are still interconected (open porosity);
- Pore shrinks, segregates. Isolated pores;
- The density reaches 90% of the theoretical value.

Final

- Pores are segregated and isolated at the grain corners;
- Over time pores may disappears. Density increase approaching the theoretical value.



Initial stages: the two sphere model



(a)		(b)
$r \approx \frac{X^2}{2a}$	Radius of neck	$r \approx \frac{X^2}{\boxed{4}a}$
$A \approx \frac{\pi^2 X^3}{a}$	Area of neck surface	$A \approx \frac{\pi^2 X^3}{\boxed{2}a}$
$V \approx \frac{\pi X^4}{2a}$	Volume transported into neck	$V \approx \frac{\pi X^4}{\boxed{8}a}$

Figure 8.10 Geometrical parameters for the two-sphere model used in the derivation of the initial stage sintering equations for crystalline particles. The geometries shown correspond to those for (a) the nondensifying mechanisms and (b) the densifying mechanisms.

The geometrical model:

- circular neck with radius X and with a circular cross section r; small difference between densifying (shrink) and nondensifying models.

Kinetics:

- let’s consider the diffusion transport of vacancies and the most common mechanism : **grain boundary diffusion**

Grain boundary (GB) diffusion (1)

Ω: vacancy volume
D_v: Diffusion coefficient of v.
$\frac{dC_v}{dx}$: vacancy concentration gradient
in one dimension, otherwise ∇C_v
A_{gb}: cross section of the GB with thickness δ_{gb}

$$A_{gb} = 2\pi X\delta_{gb}$$

r_1, r_2: the two principal radii of curvature
$r_1 = \mathrm{r}\,;\, r_2 = -\mathrm{X}$ (fig. 8.10)

Flux of vacancies: $J_a = \frac{D_v}{\Omega}\frac{dC_v}{dx}$

Volumetric rate of v. transport: $\frac{dV}{dt} = J_a A_{gb}\Omega$

Thus: $\frac{dV}{dt} = 2\pi D_v X\delta_{gb}\frac{dC_v}{dx}$

Assuming a constant concentration of vacancies at the neck surface and at the center : $\frac{dC_v}{dx} = \frac{\Delta C_v}{X}$

And that the concentration at the center of the neck is equal to that of a flat surface: C_{v0}

$$\Delta C_v = C_v - C_{v0} = \frac{C_{v0}\gamma_{sv}\Omega}{kT}\left(\frac{1}{r_1} - \frac{1}{r_2}\right)$$

(Kelvin eq., see slide #10)

Considering X>>r $\frac{dV}{dt} = \frac{2\pi D_v\delta_{gb}\gamma_{sv}C_{v0}\Omega}{kTr}$

Grain boundary (GB) diffusion (2)

$$\frac{dV}{dt} = \frac{2\pi D_v \delta_{gb} \gamma_{sv} C_{v0} \Omega}{kTr}$$

Radius of neck	$r \approx \dfrac{X^2}{4a}$
Area of neck surface	$A \approx \dfrac{\pi^2 X^3}{2a}$
Volume transported into neck	$V \approx \dfrac{\pi X^4}{8a}$

$$D_{gb} = D_v C_{v0}$$

$$\frac{\pi X^3}{2a}\frac{dX}{dt} = \frac{2\pi D_{gb} \delta_{gb} \gamma_{sv} \Omega}{kT}\left(\frac{4a}{X^2}\right)$$

After integration
(X=0 @ t=0)

$$X^6 = \frac{96 D_{gb} \delta_{gb} \gamma_{sv} \Omega a^2}{kT} t$$

➡

$$\frac{X}{a} = \left(\frac{96 D_{gb} \delta_{gb} \gamma_{sv} \Omega}{kTa^4}\right)^{1/6} t^{1/6}$$

The ratio of the neck radius to the sphere radius increases as $t^{(1/6)}$

Grain boundary (GB) diffusion (3)

GB diffusion is a densify mechanism, therefore shrinkage occurs: $\frac{\Delta L}{L_0} = -\frac{h}{a} = -\frac{r}{a} = -\frac{X^2}{4a^2}$

$$\boxed{\frac{\Delta L}{L_0} = -\left(\frac{3D_{gb}\delta_{gb}\gamma_{sv}\Omega}{2kTa^4}\right)^{1/3} t^{1/3}}$$

It is predicted that the shrinkage increase as $t^{1/3}$

This is experimentally measurable by thermomechanical analysis (TMA, or dilatometry)

Generalized parametric equation

$$\boxed{\left(\frac{\Delta L}{L}\right)^{m/2} = -\frac{H}{2^m a^n} t}$$

m, n: numerical exponent that depend on the mechanism of sintering;
H: geometrical and material parameters

3

Generalized parametric equation

$$\left(\frac{\Delta L}{L}\right)^{m/2} = -\frac{H}{2^m a^n} t$$

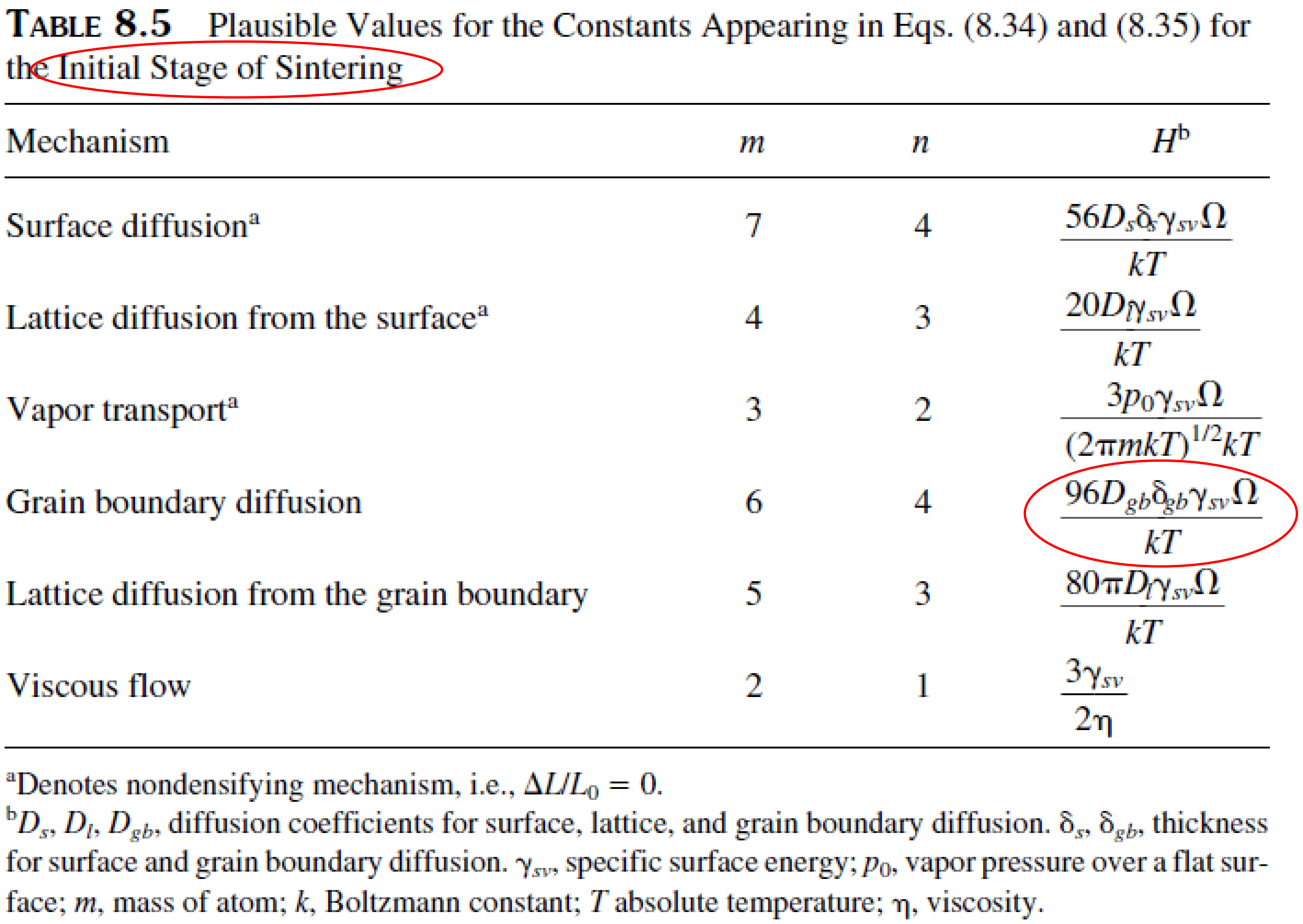


TABLE 8.5 Plausible Values for the Constants Appearing in Eqs. (8.34) and (8.35) for the Initial Stage of Sintering

Mechanism	m	n	H[b]
Surface diffusion[a]	7	4	$\frac{56 D_s \delta_s \gamma_{sv} \Omega}{kT}$
Lattice diffusion from the surface[a]	4	3	$\frac{20 D_l \gamma_{sv} \Omega}{kT}$
Vapor transport[a]	3	2	$\frac{3 p_0 \gamma_{sv} \Omega}{(2\pi mkT)^{1/2} kT}$
Grain boundary diffusion	6	4	$\frac{96 D_{gb} \delta_{gb} \gamma_{sv} \Omega}{kT}$
Lattice diffusion from the grain boundary	5	3	$\frac{80\pi D_l \gamma_{sv} \Omega}{kT}$
Viscous flow	2	1	$\frac{3\gamma_{sv}}{2\eta}$

[a] Denotes nondensifying mechanism, i.e., $\Delta L/L_0 = 0$.

[b] D_s, D_l, D_{gb}, diffusion coefficients for surface, lattice, and grain boundary diffusion. δ_s, δ_{gb}, thickness for surface and grain boundary diffusion. γ_{sv}, specific surface energy; p_0, vapor pressure over a flat surface; m, mass of atom; k, Boltzmann constant; T absolute temperature; η, viscosity.

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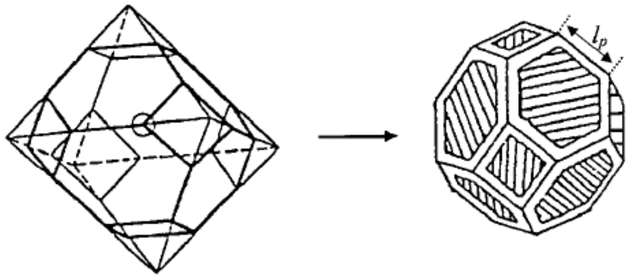
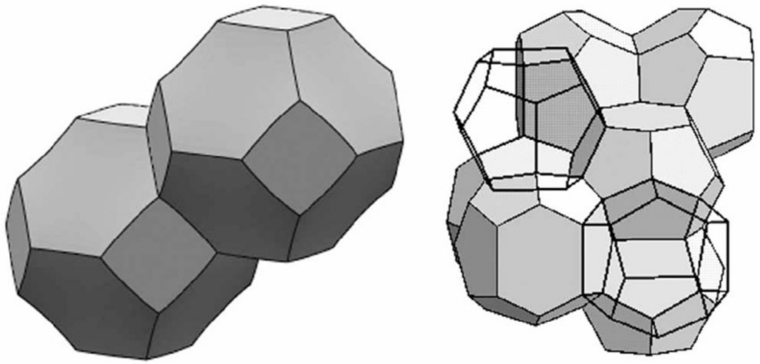
Intermediate stage



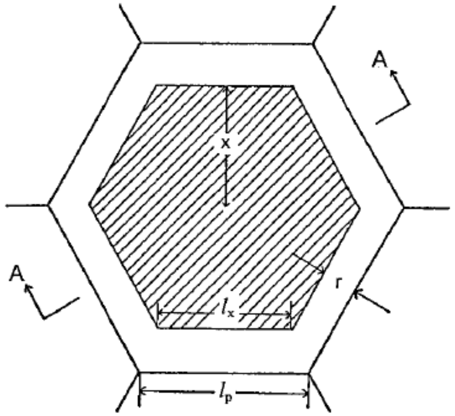


14 faces: 8 hexagonal, 6 squared

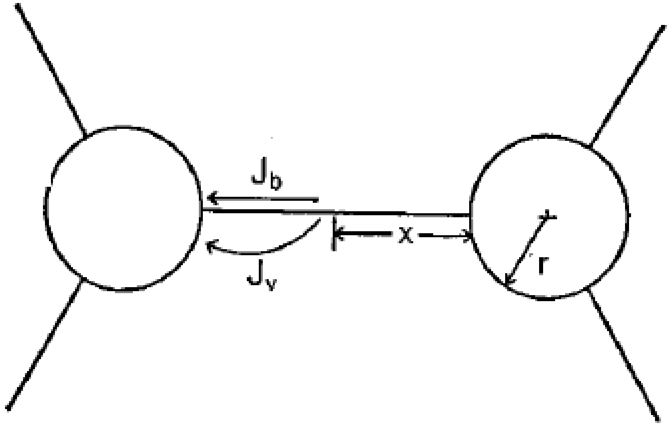
$$V_t = 8\sqrt{2}l_p^3 \qquad V_p = \frac{1}{3}\left(36\pi r^2 l_p\right)$$

Porosity: $$P_c = \frac{V_p}{V_t} = \frac{3\pi}{2\sqrt{2}}\left(\frac{r^2}{l_p^2}\right)$$

Geometrical model: space-filling array of equal-sized ***tetrakaidecahedra*** and cylindrical pores of volume V_p



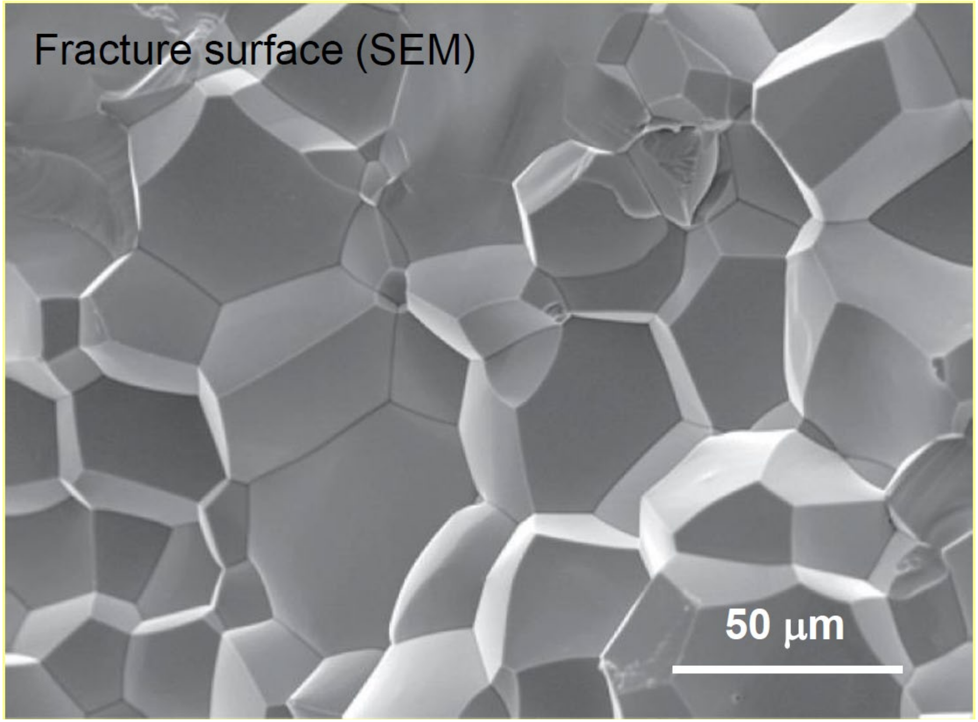
The intermediate stage sintering equations for polycrystalline solids are based on a hexagonal neck.

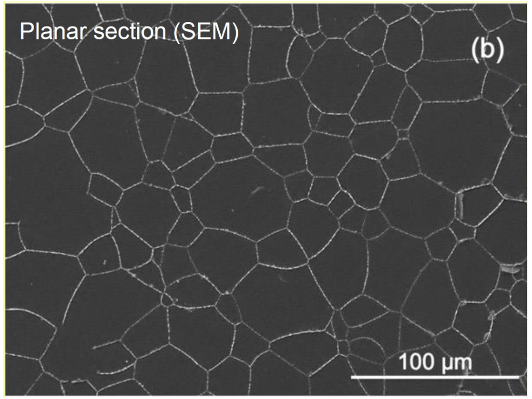


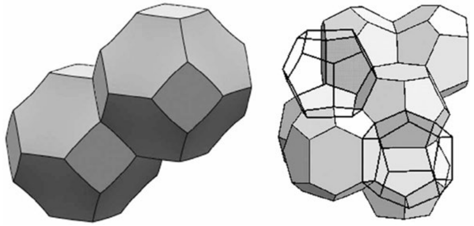
The section (on A–A) shows a cut through the neck with the atomic flux paths for **grain boundary** and **lattice diffusion**.

3

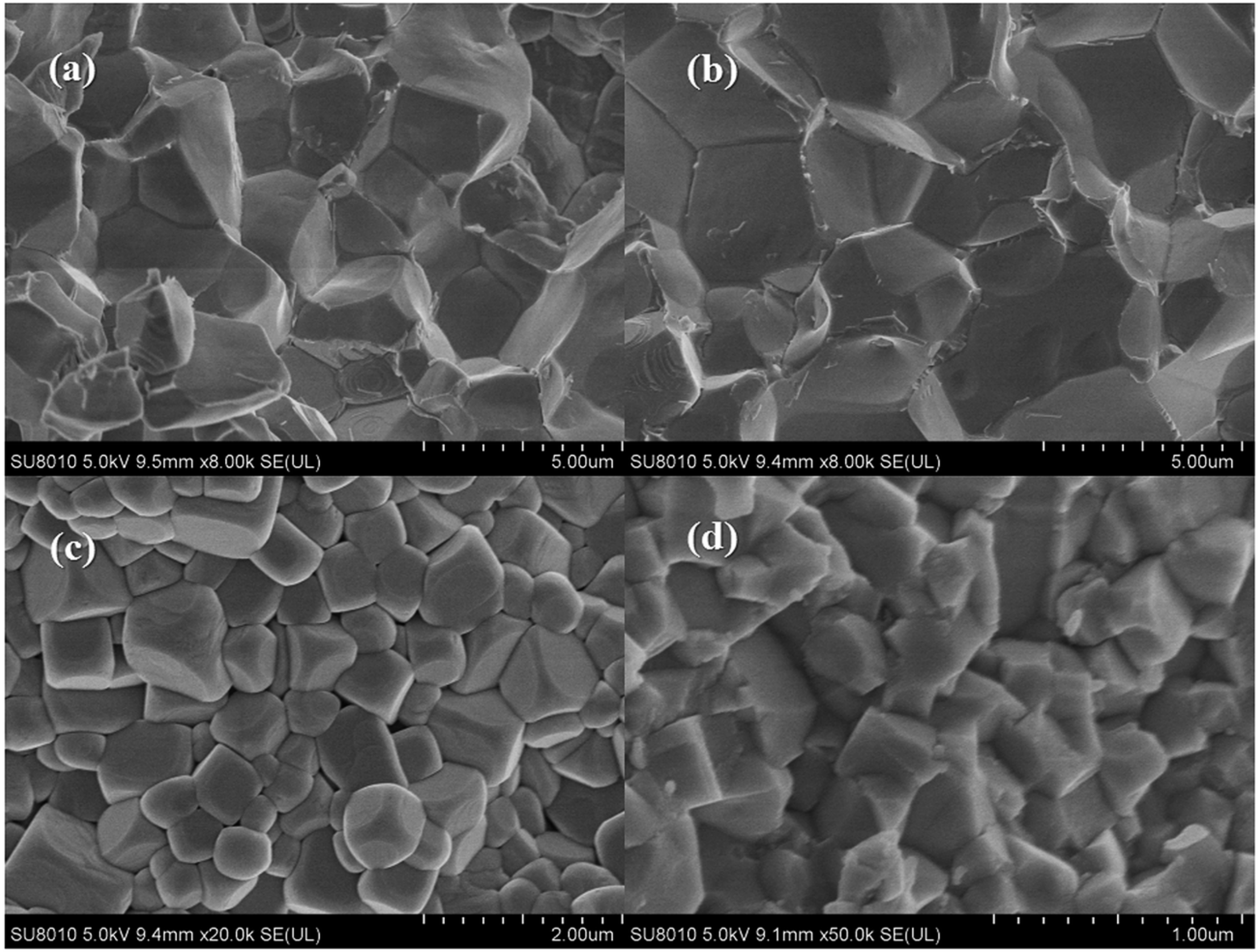
Examples: fracture surface







After lapping, polishing, etching



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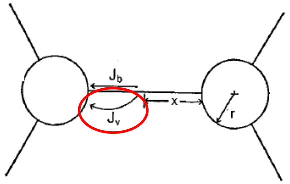
Lattice diffusion, J_v



The flux (J) per unit length (l) of the cylindrical pore: $$\frac{J}{l} = 4\pi D_v \Delta C$$

Including some assumption and approximation: $$J = 16\pi D_v \Delta C r$$

D_v: vacancies diffusion coefficient
ΔC: concentration gradient
$D_l = D_v C_{v0}$: lattice diff. coef.
t_f, t: final time, actual time

Since there are 14 faces, each sharing 2 pores: $$\frac{dV}{dt} = \frac{14}{2} J = 112\pi D_v \Delta C r$$

For curvature r and ∞

$$\Delta C = \frac{C_{v0}\gamma_{sv}\Omega}{kTr}$$

After some mathematics and integration: $$P_c \approx \frac{r^2}{l_p^2} \approx \frac{10 D_l \gamma_{sv}\Omega}{l_p^3 kT}(t_f - t)$$

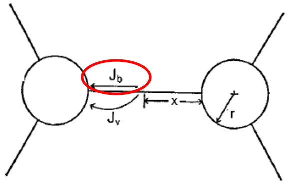
This equation works for order-of-magnitude calculation and until pores are pinched off and become isolated.

In term of densification, considering that P = 1-ρ (ρ : relative density), and $l_p \approx$ G (grain size), the densification rate reads:

$$\frac{1}{\rho}\frac{d\rho}{dt} \approx \frac{10 D_l \gamma_{sv}\Omega}{\rho G^3 kT}$$

Again, this equation can be experimentally validated

Grain boundary diffusion, J_b



The geometrical model is the same and it can be derived that:

$$P_c \approx \frac{r^2}{l_p^2} \approx \left(\frac{2D_{gb}\delta_{gb}\gamma_{sv}\Omega}{l_p^4 kT}\right)$$

And:

$$\frac{1}{\rho}\frac{d\rho}{dt} \approx \frac{4}{3}\left[\frac{D_{gb}\delta_{gb}\gamma_{sv}\Omega}{\rho\sqrt{1-\rho}G^4 kT}\right]$$

Grain boundary diffusion

$$\boxed{\sqrt{1-\rho}\frac{d\rho}{dt} \propto G^{-4}}$$

Lattice diffusion, J_v

$$\boxed{\frac{d\rho}{dt} \propto G^{-3}}$$

The dominant densification mechanism during the intermediate stage can be experimentally evaluated.

Final stages

The geometrical model: array of equal-sized ***tetrakaidecahedra***, with **spherical pores** of one size at each corner (24 pores), shared by four grains.

$$V_p = \frac{24}{4}\frac{4}{3}\pi r^3$$

$$P_s = \frac{\pi}{\sqrt{2}}\left(\frac{r^3}{l_p^3}\right)$$

(See slide #22)

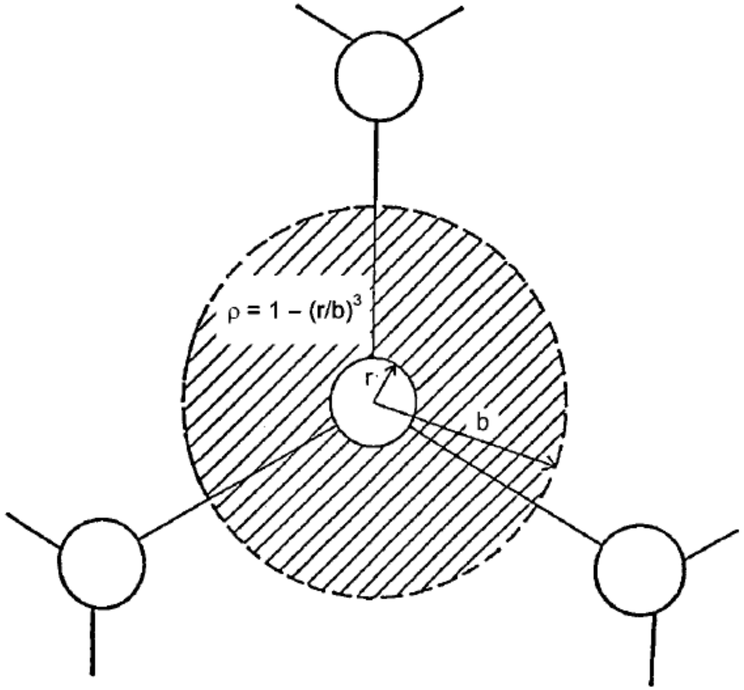


Figure 8.17 A porous solid during the final stage of sintering can be modeled by constructing a spherical shell centered on a single pore. The outer radius b is chosen such that the density of the shell matches that of the porous solid.

If the density of the sphere of radius b is assumed to be equal to the average density:

$$\rho = 1 - \left(\frac{r}{b}\right)^3$$

The volume of the solid, dashes volume, is: $\frac{4}{3}\pi(b^3 - r^3)$

And the number of pores per unit of solid phase is:

$$N = \frac{3}{4\pi}\left(\frac{1-\rho}{\rho r^3}\right)$$

This is about the geometrical model. Let’s see the mechanisms.

Final stages

Lattice diffusion:

Following a procedure similar to that for the intermediate stage, the porosity P_s as a function of time (t):

$$\boxed{P_s = \frac{6\pi}{\sqrt{2}}\left(\frac{D_l \gamma_{sv} \Omega}{l_p^3 kT}\right)\left(t_f - t\right)}$$

$l_p \approx G$

t_f: time needed for full density, pores vanished

This equation works for porosity <2%. For porosity in the range 2-5% a more complex equation need to be considered, which recall the equation derived for the intermediate stage.

Grain boundary diffusion:

The equations are similar to the intermediate stage, with some difference in the numerical constant

$$\boxed{P_c \approx \left(\frac{D_{gb} \delta_{gb} \gamma_{sv} \Omega}{l_p^4 kT}\right)}$$

$$\frac{1}{\rho}\frac{d\rho}{dt} \approx \left[\frac{D_{gb} \delta_{gb} \gamma_{sv} \Omega}{\rho\sqrt{1-\rho}\,G^4 kT}\right]$$

(See slide #25)

Remarks of the section

- The sintering of polycrystalline ceramics is **complex**;
- Mass transport can occur by at least **six different mechanisms**;
- Some mechanisms are **densifying** (shrinkage) whereas other are **nondensifying**;
- **Analytical model exist** and the sintering rate depends on primary variables, such as particle size and temperature;
- Nevertheless, due to **simplified geometrical** models and assumptions the models provides only a **qualitative** description;
- The microstructure **evolve** during sintering. Therefore, the description of the overall process need to be portioned in **stages**.