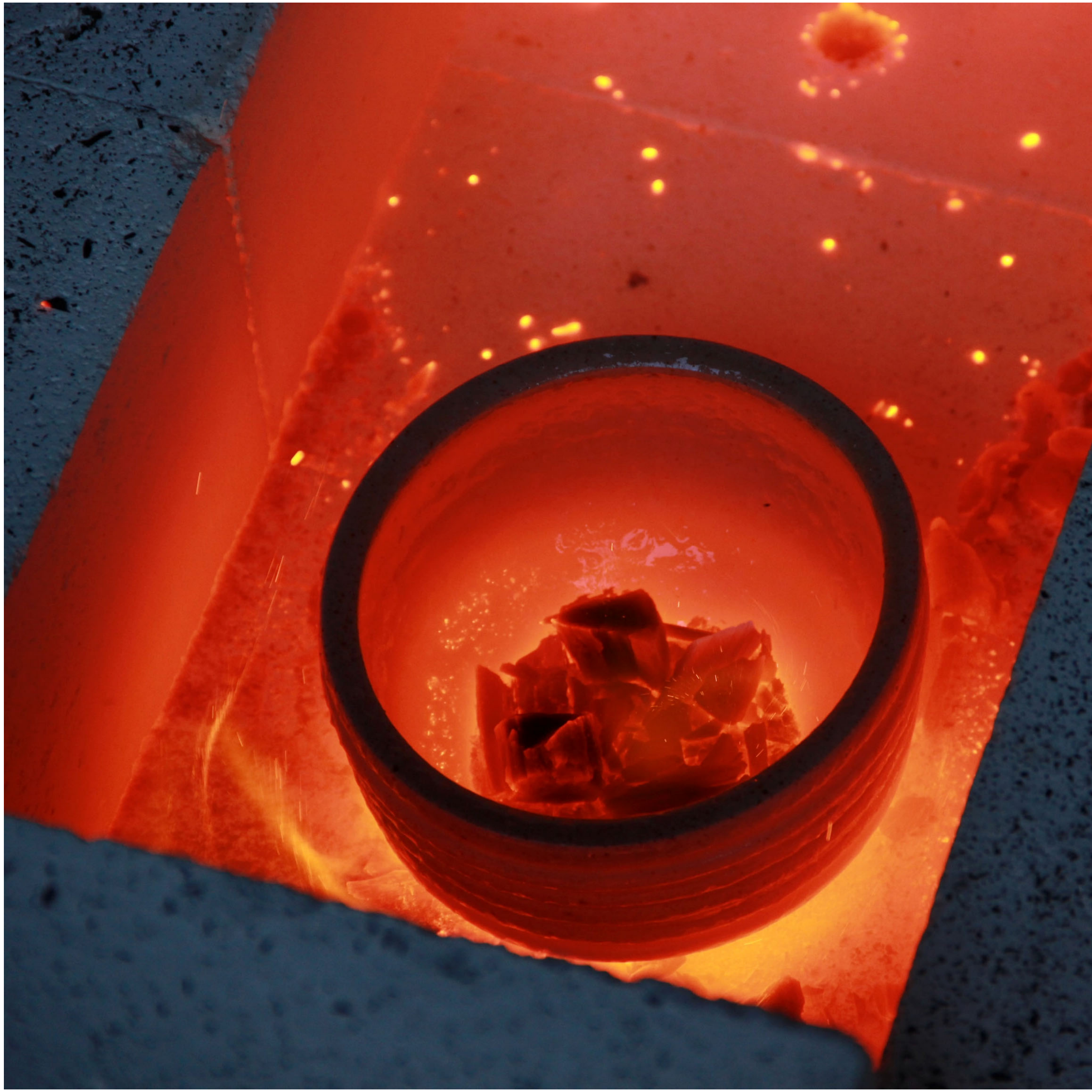
Advanced Ceramic Technologies

Sintering

M. Stuer



Outline

- Two major sintering classes
- Driving force for sintering
- Material transport mechanisms
- Grain growth mechanisms
- Microstructural control
- Sintering process analysis
  - Iso-density analysis
  - Master sintering curve

Learning objectives:

- Refresh sintering mechanisms and learn about the shortcoming of the Coble model
- Understand the grain growth mechanisms and how to modify grain growth during sintering
- Analysis of sintering

Sintering:
Types, driving forces and mechanisms

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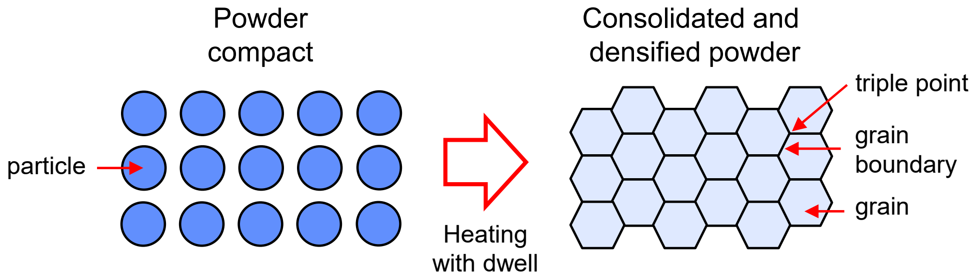
General sintering aspects

- **Sintering:** Heat treatment leading to the **formation of solid bonds** between particles **without total melting**.

One distinguishes between **two sintering classes**:

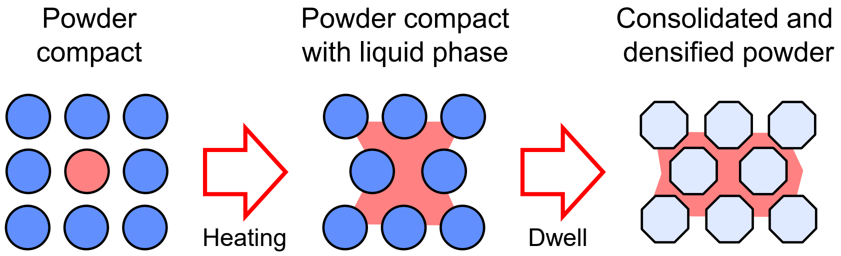
Solid state sintering



Temperatures **between 0.5 and 0.8 times** the fusion temperature of the material

Example: $Al_2O_3 \rightarrow T_{fusion}$: 2072°C
$\rightarrow T_{sintering}$: 1500°C (=0.72*2072°C)

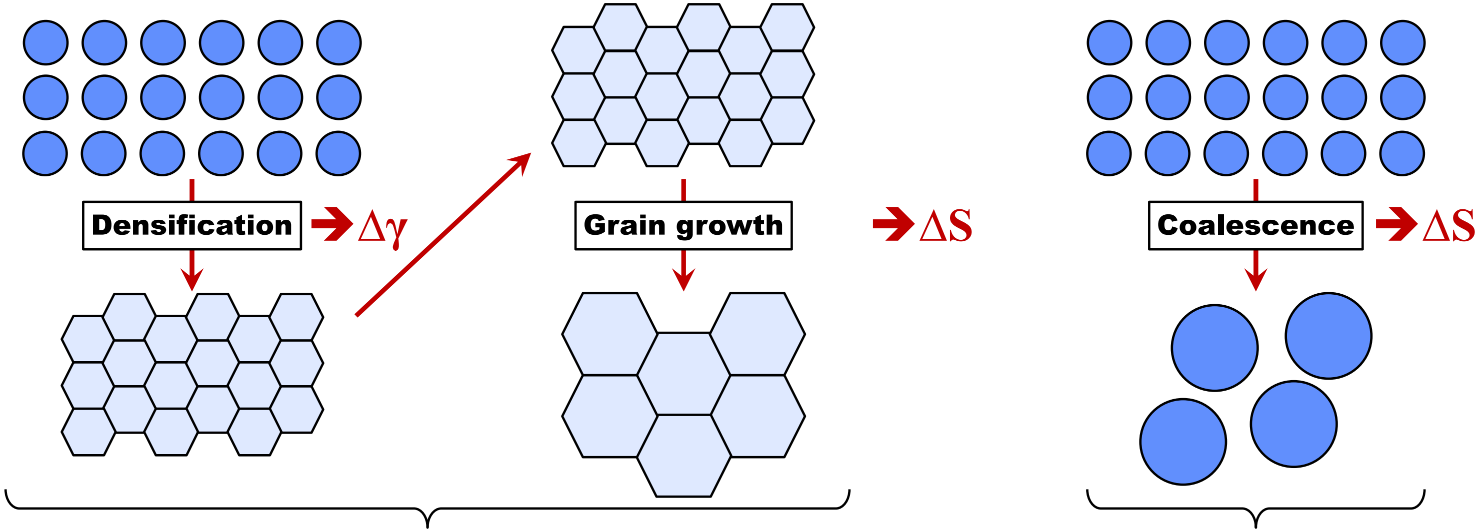
Liquid state sintering



Temperatures **above T_g** (glass transition temperature) **or T_s** (solidus) of the material (here: ●) intended to liquefy

Sintering driving forces

- Sintering **driving forces:**
  - **macroscopic:** **Excess energy** associated with the **solid-vapor surface**
  - **thermodynamic:** **Free energy** reduction of the system by replacing solid-vapor with solid-solid interfaces and reduction of the **total interface area**
- **Mechanisms** reducing the excess interfacial energy:



Densification and grain growth

Particle coalescence

M. Barsoum, Fundamentals of Ceramics, CRC Press (2020)

Estimation of the surface energy in a green body

- Number of particles N with radius r in a green body having a mass equivalent to 1 mole of the material:

$$N = \frac{3M}{4\pi r^3 \rho} = \frac{3V_m}{4\pi r^3}$$

  - M : molar mass
  - ρ : density
  - V_m : molar volume

- Surface area (solid-vapor) of the N particles in the green body:

$$S = (4\pi r^2) \cdot N = 3\,\frac{V_m}{r}$$

- Total surface energy E_s of the particles in the green body:

$$E_s = S \cdot \gamma_{sv} = \frac{3V_m \gamma_{sv}}{r} \quad \left[\frac{J}{mol}\right] \Rightarrow \boxed{E_s \propto \frac{\mathbf{1}}{\boldsymbol{r}}}$$

  - γ_{sv} : solid-vapor surface energy

- Since the solid-solid interface energy is “low”, the **overall sintering driving force** can be approximated by:

$E_s \approx \Delta E$ (corresponds to energy reduction of the system during sintering without grain growth)

Liquid state sintering

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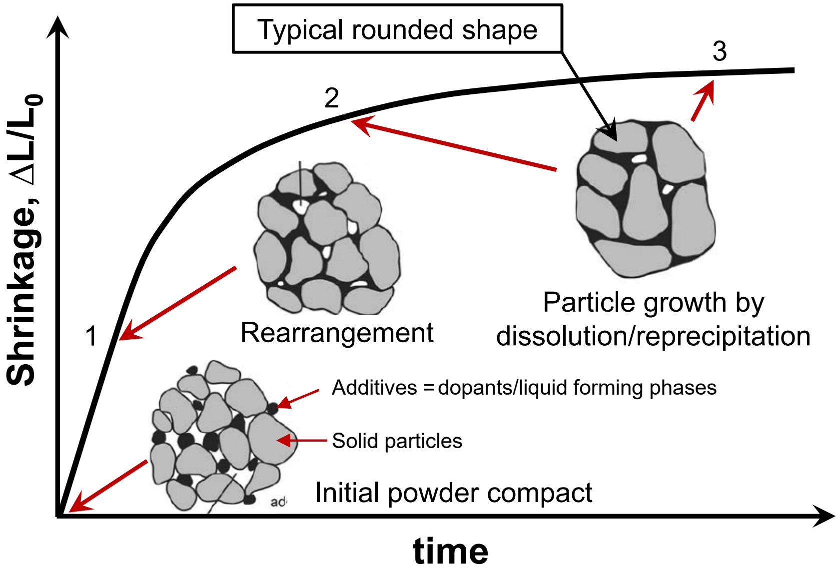
Liquid state sintering

- **Principle:**
  - Sintering takes place under conditions where **solid grains coexist with a liquid**
    ➔ The liquid needs to wet the solid!
  - Upon cooling, **liquid solidifies** to produce a **composite microstructure**
  - **Capillary forces** during sintering lead to high packing density of particles
- **Stages** (overlapping):
  - Melting and redistribution of liquid leading to **rearrangement/compacting** of solid particles by capillary forces
  - Densification and rounding of particles by **dissolution-reprecipitation**
  - **Particle growth** by Ostwald ripening (c.f. Laplace's law) and residual porosity reduction



- **Applications:**
  - Multiphase ceramics (ex. porcelain)
  - Densification of materials that cannot or are difficult to be sintered:
    - WC/Co (eutectic @ 1310°C) ➔ drilling/cutting tools
    - Si_3N_4 ➔ bearing balls

Liquid sintering

solid state sintering

Mass transport mechanisms

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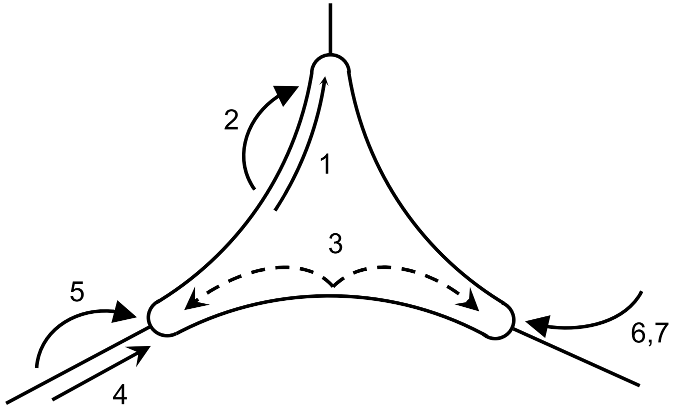
Mass transport mechanisms

- **Mass transport** during sintering takes place by:
  - **diffusion**
  - **plastic deformation** (under pressure)
- Diffusion may take place:
  - at the surface
  - at grain boundaries
  - within volume

interfaces

- A distinction is made between consolidation and densification:
  - **Consolidation**: **all** sintering mechanisms are consolidating
  - **Densification**: only mechanisms with material **source** in the **volume** or at the **grain boundaries** are densifying (e.g. sintering shrinkage)



Mass transport mechanisms

Consolidating but not densifying:

1. Surface diffusion from the surface
2. Volume diffusion from the surface
3. Vapor diffusion from the surface

Consolidating and densifying:

4. Grain boundary diffusion from the grain boundaries
5. Volume diffusion from the grain boundaries
6. Volume diffusion of dislocations
7. Plastic or viscous flow

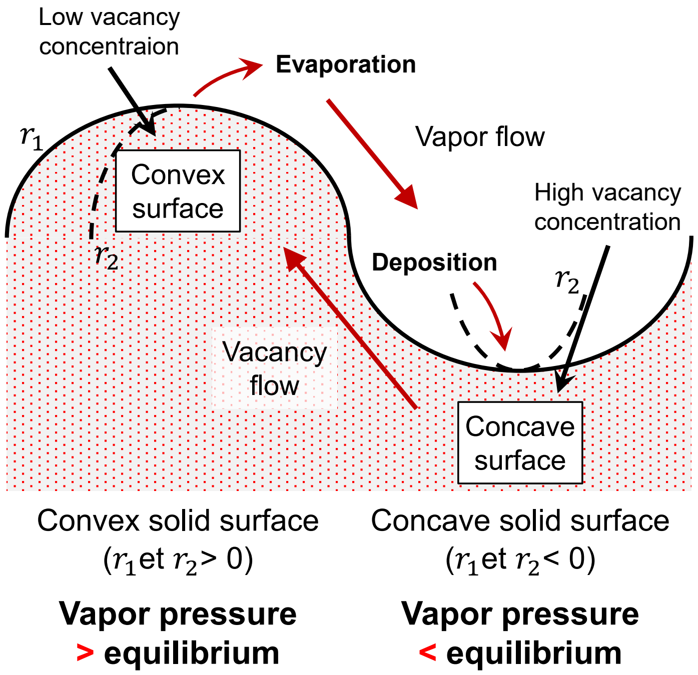
Rahaman, M.N. Ceramic Processing and sintering, Marcel Dekker 1997

Driving force for diffusion mechanisms

- Driving forces for diffusion are
  - **Vapor pressure** (Laplace law)
  - **Vacancy concentration**

  gradients between convex and concave surfaces
- Mass transport occurs from areas with « high » to areas with « low » potential energy

  ➔ Material flux **from convex to concave** surfaces
- **What happens at the triple points?**



Convex solid surface (r_1 et $r_2 > 0$)

Vapor pressure > equilibrium

Concave solid surface (r_1 et $r_2 < 0$)

Vapor pressure < equilibrium

$$P - P_\infty = \gamma_{sv}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

Laplace law

solid state sintering

Sintering states (Coble model)

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Three Coble sintering stages

#1_initial stage

- The powder compact is **consolidated** by rapid neck **formation and growth** between particles.
- **Curvature differences** between convex and concave surfaces are **rapidly reduced**.

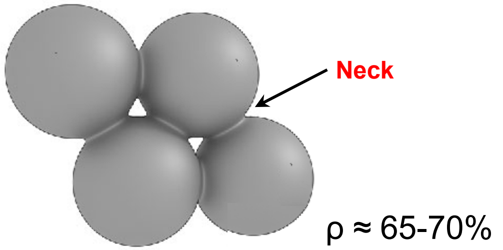
#2_intermediate stage

- There is a strong **densification** of the structure by **reduction of the porosity** located along the grain edges.
- **Grains** are **polyhedral**
- There is only **open porosity** (e.g. open pore channels)

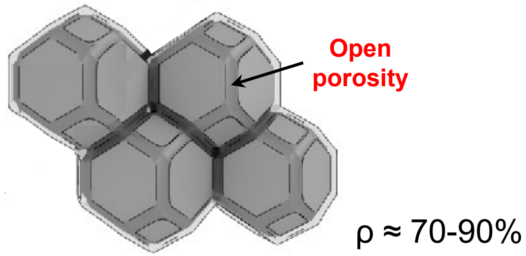
#3_final stage

- The **pores** are **closed** (isolated) and located mainly at the **corners** of the grains
- The **densification** is accompanied by more or less substantial **grain growth**.

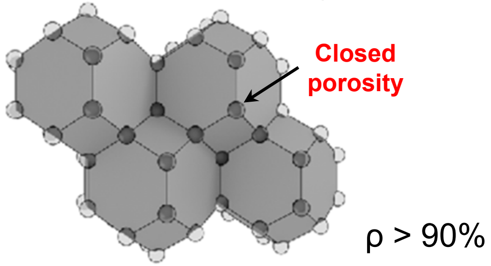
Initial stage



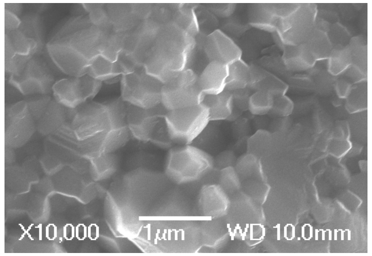
Intermediate stage



Final stage



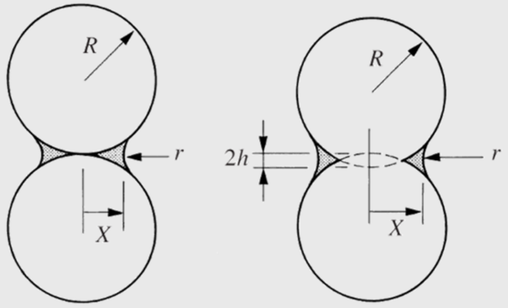
Typical fracture surface



Z. Diplomové Práce (2015), source d'origine: https://doi.org/10.1063/1.1702656

Models of the three Coble sintering stages

#1_initial stage



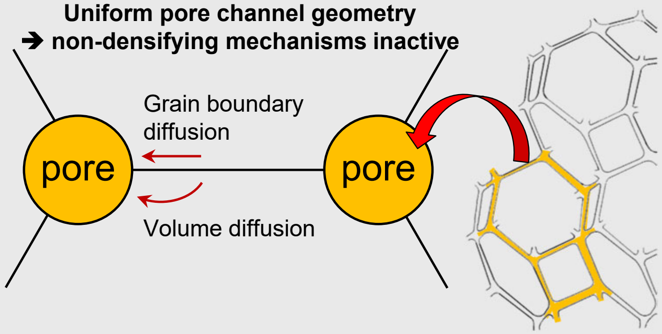
Phenomenon: Bridge formation between particles

- **Grains:** spheres with radius R
- **Pores:** not considered
- **End state:** r = ~0.5 R

Mechanisms

- **Densifying:** active
- **Non-densifying:** active

#2_intermediate stage



Uniform pore channel geometry
➔ non-densifying mechanisms inactive

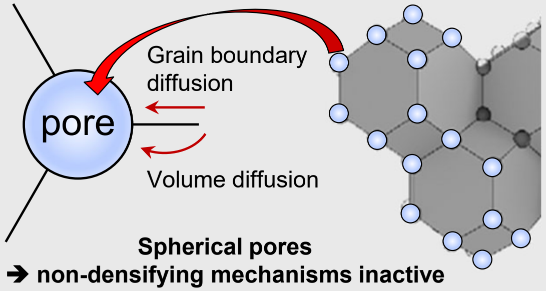
Phenomenon: Densification by reduction of the cross-section of the porous network

- **Grains:** tetrakaidecahedral
- **Pores:** channels at edges
- **End state:** pore closure

Mechanisms

- **Densifying:** active
- **Non-densifying:** inactive

#3_final stage



Spherical pores
➔ non-densifying mechanisms inactive

Phenomenon: Densification by reduction of the pore radius (note: grain growth not taken into account, as regular arrangement of uniform grains)

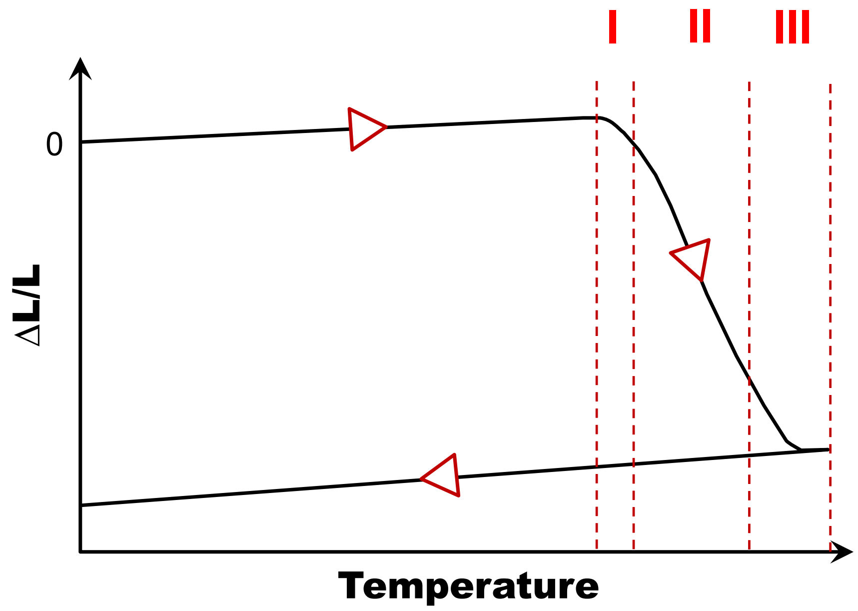
- **Grains:** tetrakaidecahedral
- **Pores:** spherical at the grain tips

Mechanisms

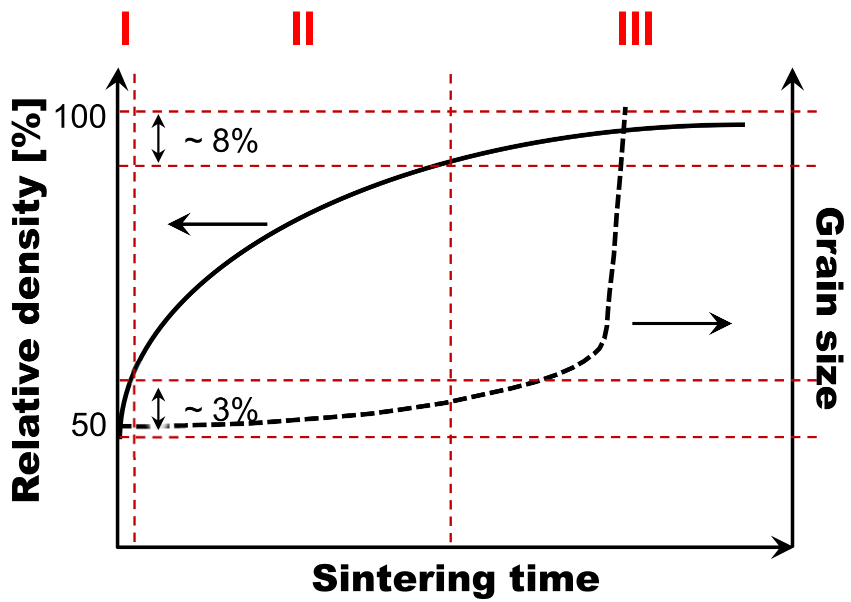
- **Densifying:** active
- **Non-densifying:** inactive

source: https://doi.org/10.1063/1.1702656

Shrinkage and grain growth at different sintering stages



Dilatometry curve of a green body during **constant heating rate**



Isothermal dilatometry and grain size curves

Significant densification occurs at stage II

Significant grain growth occurs at stage III

Dilatometry =measurement of dimensional change as a function of temperature and/or time

solid state sintering

Grain growth

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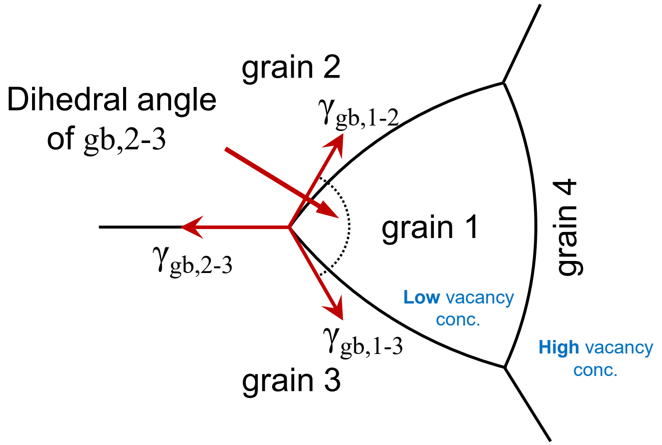
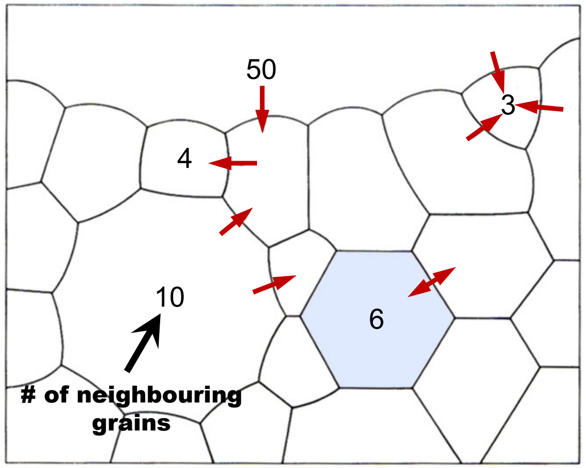
Local driving force for grain growth

- **Balance** of **interfacial tensions** at triple junctions **imposes/defines** grain boundary **curvature**
- **Consequences**:
  - **Centre of curvature** of grain boundaries is located on the side of the **smaller grain**
  - Following the **Laplace law**, diffusion occurs across the grain boundaries from the small towards the large grains.
    ➔ **Grain boundaries move towards their center of curvature !**

Small grains disappear in favor of larger grains





Grain boundary migration (e.g. microstructure evolution) based on # of neighboring grains (**assuming** that the **grain boundary energy** is **independent of the orientation**)

Von Neumann-Mullins law (e.g. n-6 rule)

- Assuming **isotropic** grain boundary energies and **uniform** grain boundary curvature, n-6 rule states that:

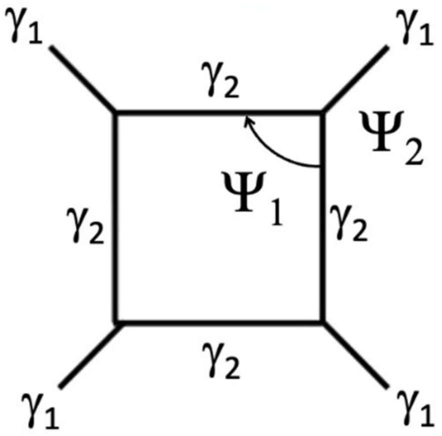
$$\frac{dA}{dt} = \frac{\pi k}{6(n-6)}, k = M\gamma$$

- M: grain boundary mobility
- γ: grain boundary energy
- n: number of triple junctions
- A: grain surface area
- t: time

- If the number of triple junctions is
  - < 6, center of curvature inside grain ➔ it shrinks
  - = 6, grain boundary is flat ➔ stable grain
  - > 6, center of curvature outside grain ➔ it grows

➔**GBs move towards center of curvature**

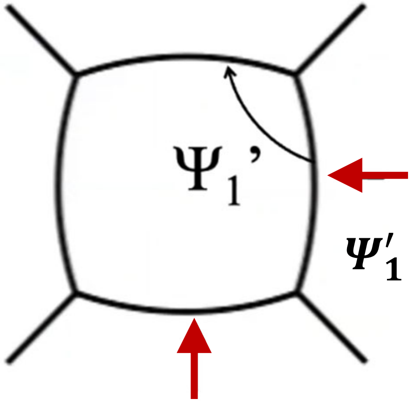
➔**GB mobility and curvature are correlated**



$\Psi_1 = 90°$
$\Psi_2 = 135°$

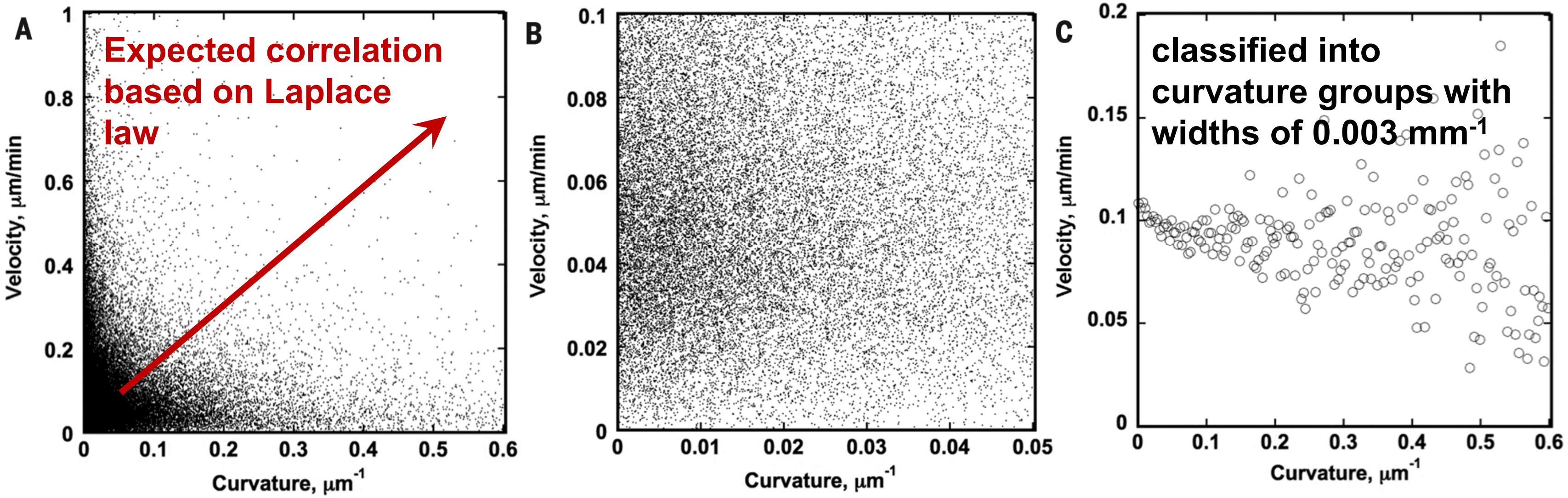
$\gamma_1 = \gamma_2$

$$\rightarrow \frac{\gamma_1}{\sin \Psi_1} = \frac{\gamma_2}{\sin \Psi_2}$$



$\Psi'_1 = 120°$

No correlation between GB velocity and curvature

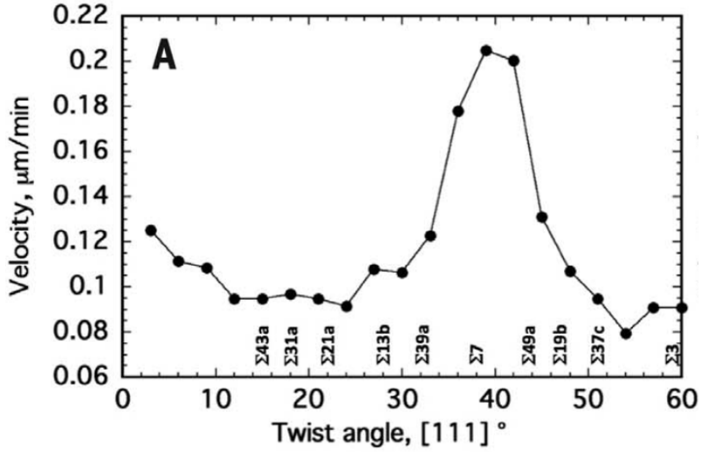


Expected correlation based on Laplace law

classified into curvature groups with widths of 0.003 mm^{-1}

- **No correlation** can be observed **between GB curvature and GB velocity!**
- But, GB velocity significantly changes depending on GB type.

➔ **Other mechanisms affect GB mobility**



source: https://doi.org/10.1126/science.abj3210

Anisotropic grain boundary energies

- **Boundary energies do not have to be isotropic**, nor must they have a uniform curvature !
- Under which condition can a 4-sided grain grow?
  - For simplicity assume the grain boundary energy of the 4-sided grain with its neighbors is γ_2 and between the neighboring grains γ_1
  - Grain boundary energy of a square grain:

$$4L\gamma_2$$

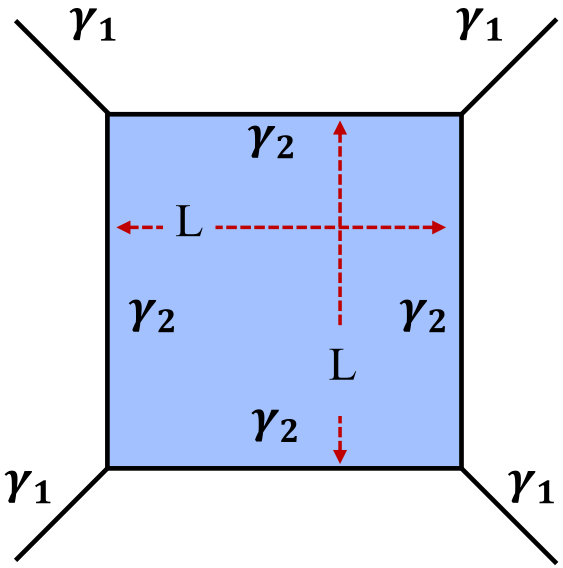
  - If grain disappears this grain boundary energy is replaced by:

$$\frac{4\sqrt{2}}{2}L\gamma_1$$

  - Square grain grows when

$$4L\gamma_2 < \frac{4\sqrt{2}}{2}L\gamma_1 \rightarrow \frac{\gamma_1}{\gamma_2} > \sqrt{2}$$

➔ **Grains can grow, independently of the grain boundary curvature!**



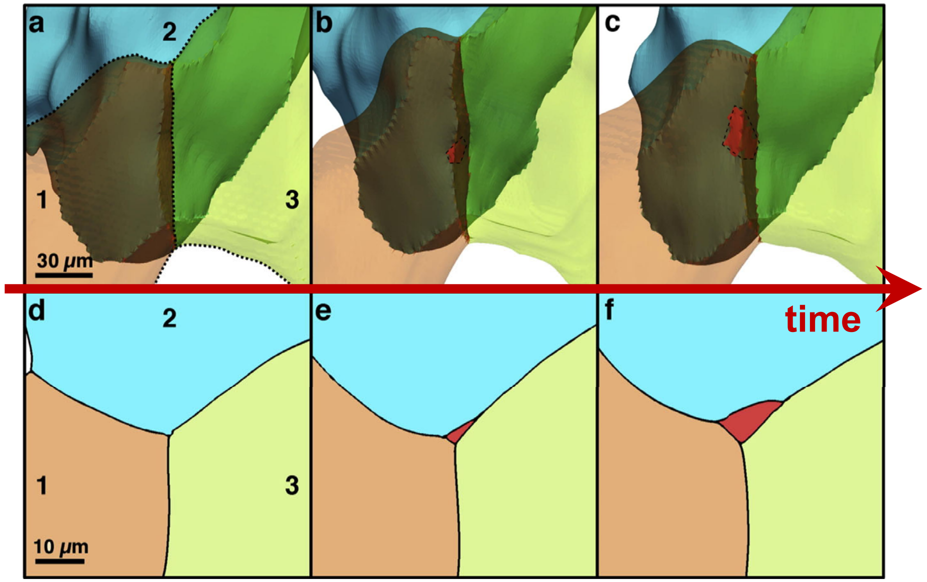
Nucleation of new grains at grain boundary

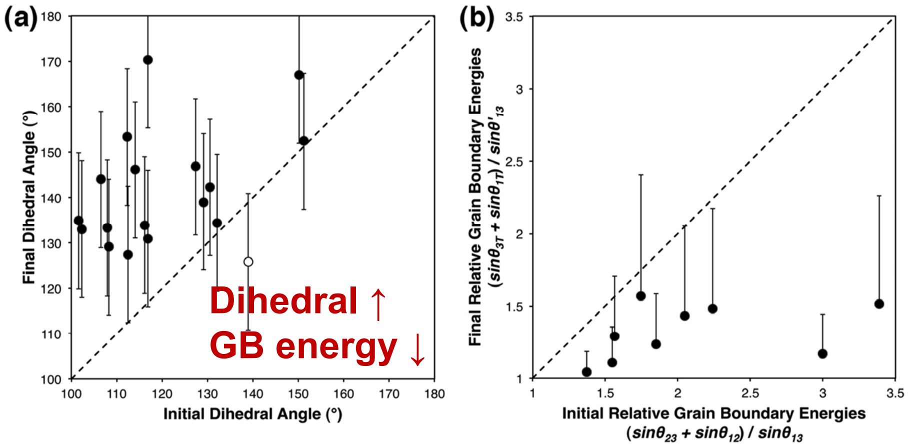
- ♦ **New grains can nucleate** at grain boundaries, despite associated **increase of the total grain boundary area**!

- ♦ **How can this occur?**
  When the nucleation and growth of a new grain reduces the total **grain boundary energy**.

➔ **It is all about the lowering of the system free energy!**

➔ **Left to answer: Why can some grain boundaries move faster ?**





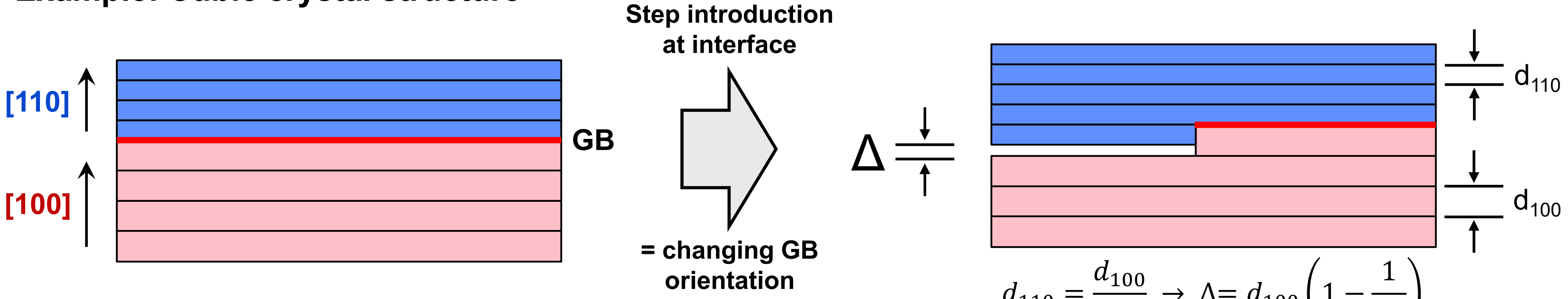
source: 10.1016/j.actamat.2015.07.041

Grain growth

Disconnections

- **One approach to explain different GB velocities in coincident site lattice (CSL) GBs refers to disconnections**

Example: Cubic crystal structure

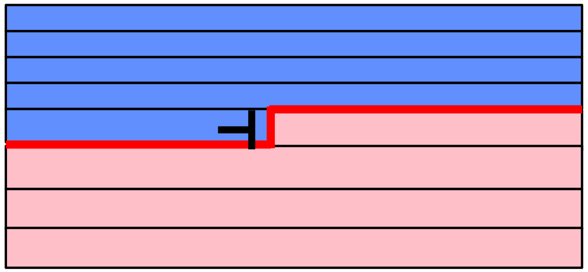


$$d_{110} = \frac{d_{100}}{\sqrt{2}} \rightarrow \Delta = d_{100}\left(1-\frac{1}{\sqrt{2}}\right)$$

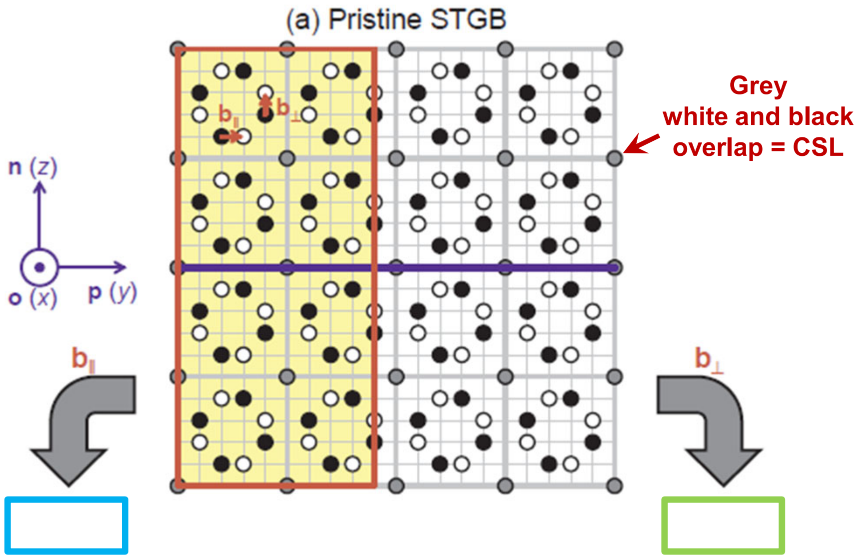
- To **close the gap** Δ a lattice distortion, i.e. a **dislocation** with Burgers vector Δ, has to be introduced. This is a disconnection with:

  Step height: $h = (d_{100} + d_{110})/2$

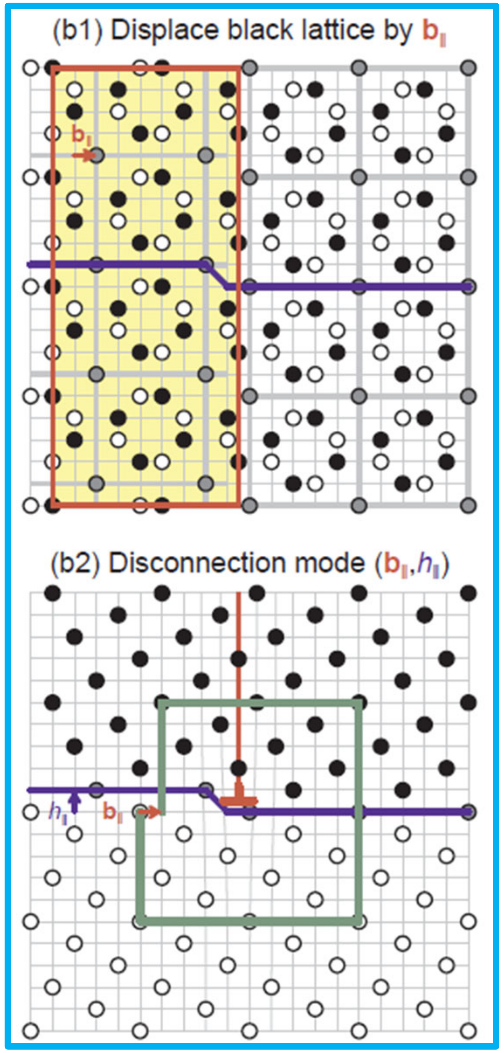
  Burgers vector: $\boldsymbol{b} = d_{100}\left(1-\frac{1}{\sqrt{2}}\right)[100]$

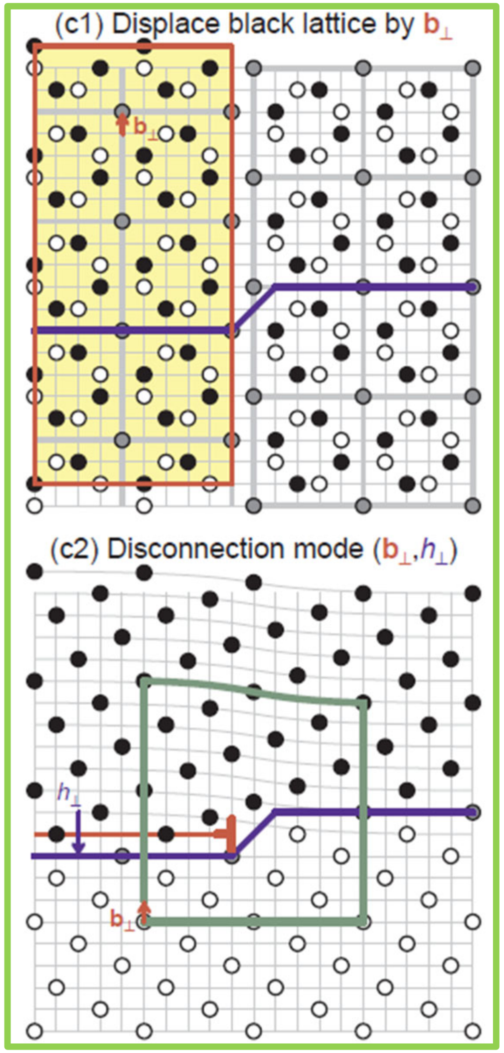


Disconnection modes



**Grey
white and black
overlap = CSL**





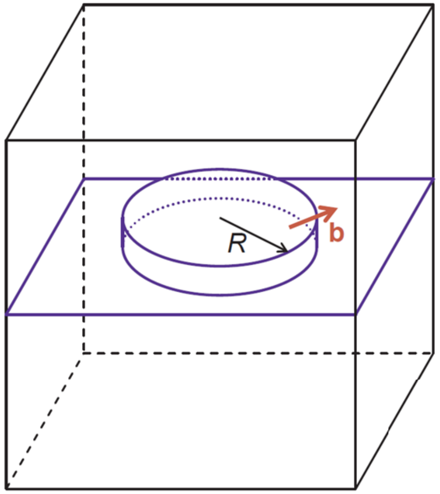
Disconnections in a Σ5 [100] simple tilt GB (STGB) by the operation of translational symmetry related to the DSC (displacement shift complete) lattice.

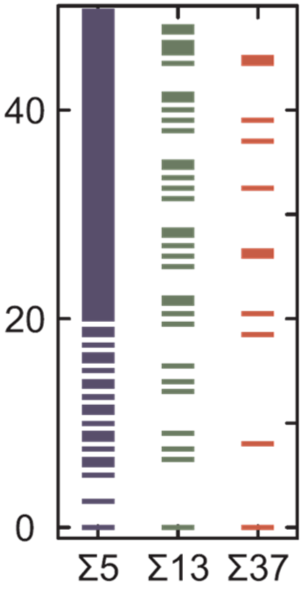
Example: (b1) Based on (a), displace the black lattice in the yellow region with respect to the white lattice by the red vector parallel to the GB plane $b_{||}$; the blue line is the new GB plane after such displacement. (b2) A disconnection $b_{||}$,$h_{||}$) is formed by removing the black lattice below the GB plane and the white lattice above the GB plane in (b1).

source: 10.1016/j.pmatsci.2018.05.004

Disconnection model for grain boundary migration

- **Migration** of GBs controlled by **nucleation and expansion of disconnections** across the grain boundary
- For a given GB there are different disconnection modes associated with different **nucleation energies** which primarily depend on h and ***b***
- Multiple modes are needed for a GB to move continuously
- The **more disconnection modes** there are and the **lower** their **nucleation energies**, the higher (in principle) the associated GB mobility
  (shear stresses and GB stiffness may play a significant role as well! ==> ongoing debate in literature)



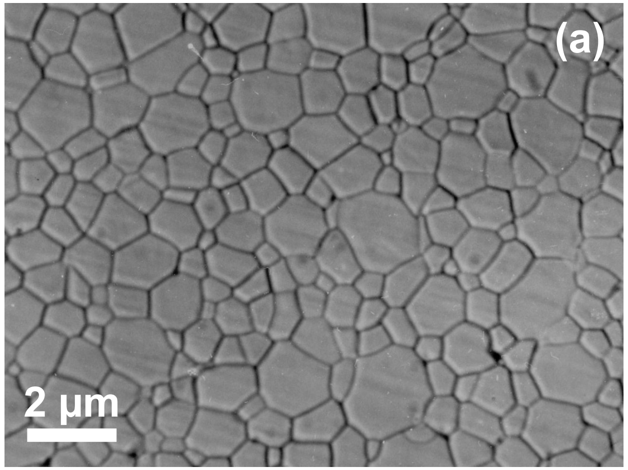


Example:
Disconnection energy spectra of selected simple tilt grain boundaries in cubic crystal

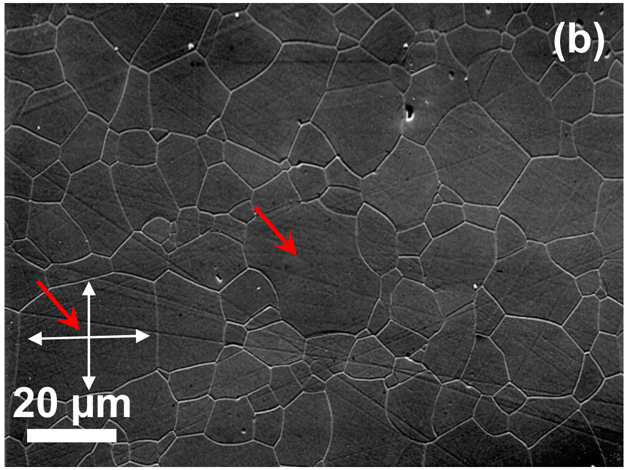
source: 10.1016/j.pmatsci.2018.05.004

Normal and abnormal grain growth

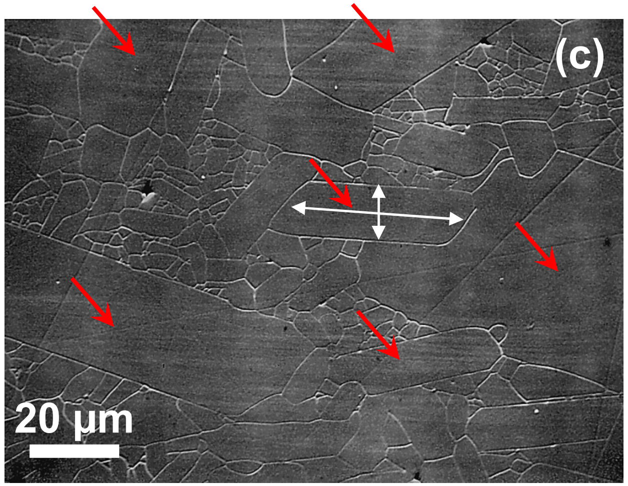
- Examples of microstructures after different grain growth modes
  - a) **Normal** grain growth
  - b) **Isotropic abnormal** grain growth ($d_{F_{max}} \approx d_{F_{min}}$)
  - c) **Anisotropic abnormal** grain growth ($d_{F_{max}} \gg d_{F_{min}}$)



Normal isotropic



Abnormal isotropic



Abormal anisotropic

The grain growth and thus microstructural development can be modified through the **sintering cycle** (time, temperature, pressure, …) and **doping strategy**

solid state sintering

Microstructural development control

- Basic concepts -

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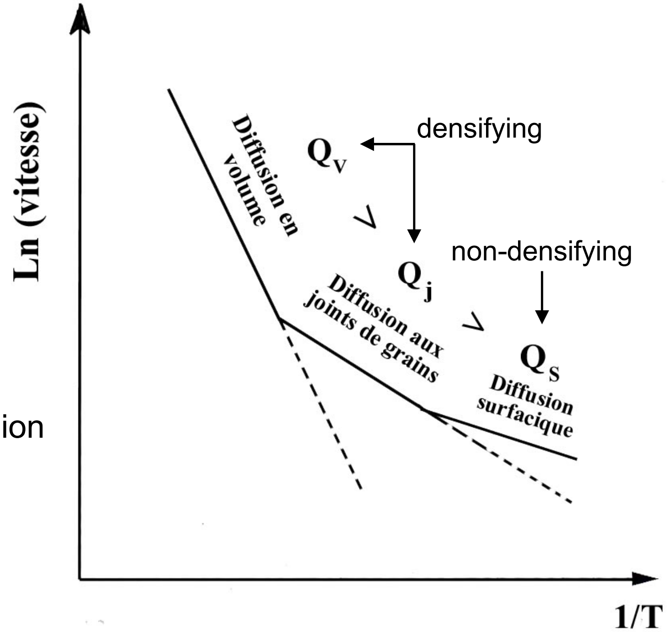
Influence of temperature on active diffusion mechanisms

- **Temperature** has a major **influence** on **diffusion kinetics** and thus on sintering
- Each diffusion mechanism is:
  - Thermally activated → **Arrhenius law:**

$$D_i = D_{0,i} e^{-Q_i/RT}$$

- Q_i: activation energy of mechanism ***i***
- $D_{0,i}$: Diffusion constant of mechanism ***i*** (~Diffusion at infinite ***T***)
- i: ***s*** surface, ***v*** volume and ***j*** grain boundary diffusion

  - Has its specific **activation energy**



The **thermal cycle** has a direct influence on the **microstructural development** controlling the predominant diffusion mechanisms

Influence of particle size on sintering speed

Herring’s scaling law

- The **ratio of sintering times** t_1 et t_2 to achieve the **same sintering advancement** from powders with **particle sizes** R_1 et R_2 respectively is given by:

$$\boxed{\frac{t_1}{t_2} = \left(\frac{R_1}{R_2}\right)^m \quad \Rightarrow \text{ if } R\uparrow \text{ then } t\uparrow}$$

m depends on the predominant mass transport mechanism
- m = 1: viscous flow
- m = 2: evaporation and condensation
- m = 3: volume diffusion
- m = 4: surface or grain boundary diffusion

- Herring’s scaling law is **only valid if** **dominant sintering mechanism remains the same** for the particle size range considered!

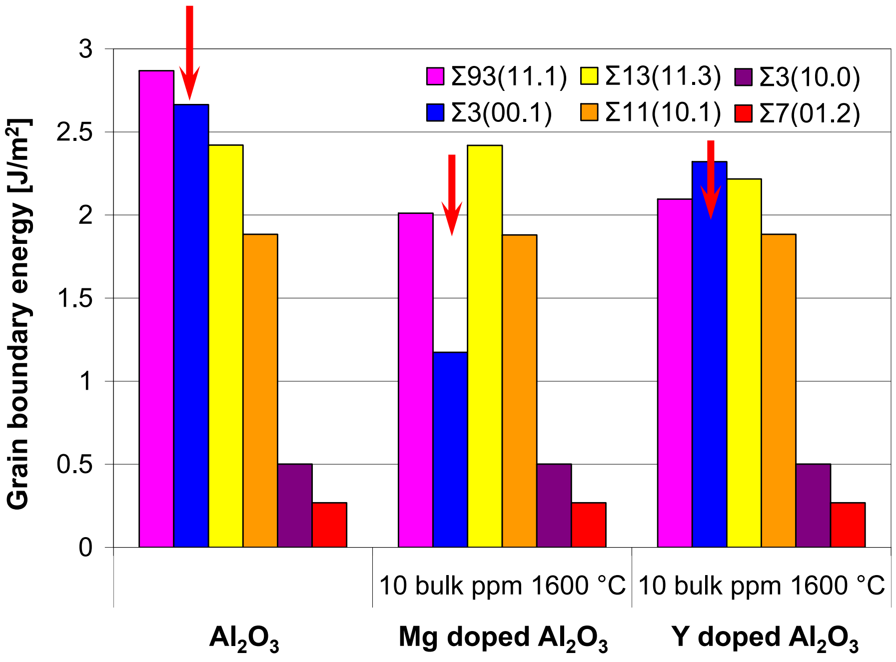
(the dominant mechanism could change, for example, if the size ratio is high enough to significantly change the ratio between volume diffusion and surface/grain boundary diffusion)

Effects of dopants on sintering

Dopants

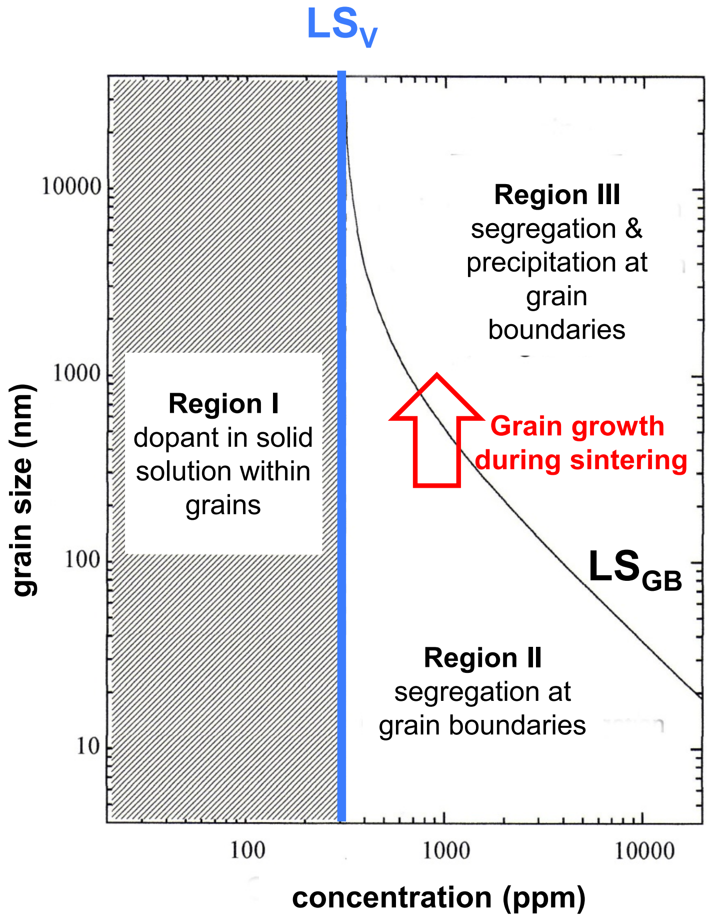
- Modify **interface energies** and thus:
  - Change the **driving forces** for sintering and grain growth
  - Change **grain morphology** by modifying the energy ratios between interfaces (e.g. system aims for energy minimization)
- Modify **activation energies and diffusion kinetics** and thus:
  - Change **sintering kinetics**
  - Change **ratios between consolidation, densification and grain growth**
  - May reduce the grain boundary mobility via the so-called solute drag effect

Examples of dopant effects on selected grain boundary energies following doping with Mg and Y



Segregation and precipitation of dopants at grain boundaries

- ♦ **Doping** used to modify the **microstructural development** during sintering
- ♦ **Doping level**, i.e. dopant concentration, chosen based on **segregation/precipitation diagrams**
  - – If the **overall dopant concentration** is above the **volume solubility limit** (LS_V), then **grain growth** during sintering can lead to **second phase precipitation** at the grain boundaries.
- ♦ **Upon appearance of precipitates**, grain growth is impinged by **Zener pinning**

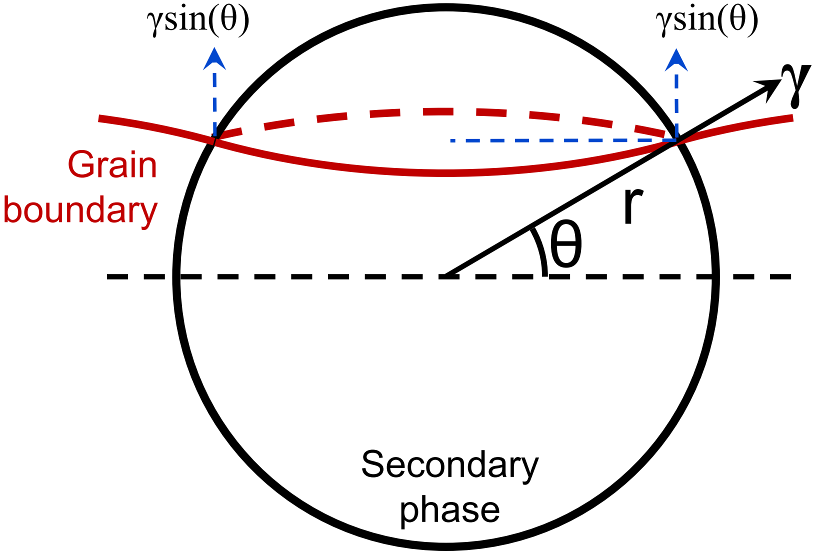


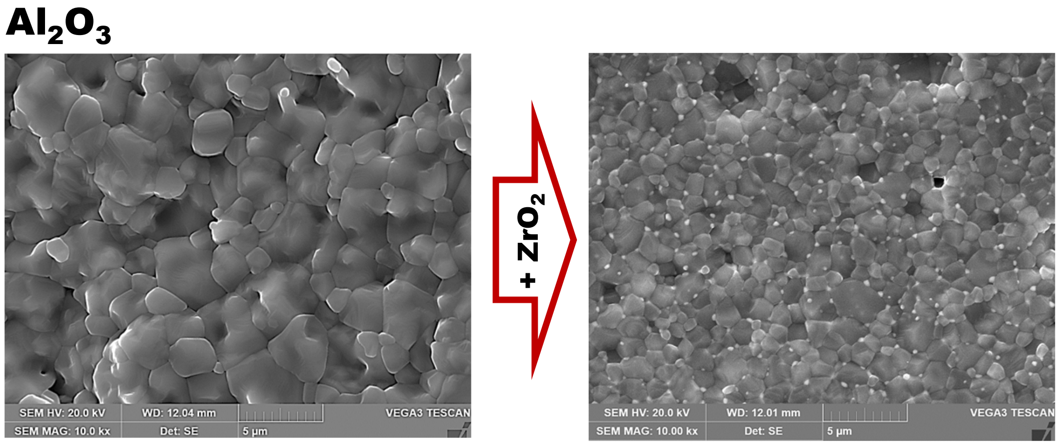
Zener pinning

- Small **secondary phases impair grain boundary migration** by exerting a counteracting pinning pressure.
- The **Zener pinning pressure** is maximum at an angle of 45° and given by:

$$P_{zener} = \frac{3\gamma f}{3r}$$

  - γ: grain boundary energy
  - f: volume fraction of secondary phase
  - r: secondary phase radius





solid state sintering

Apparent activation energy for densification and Master sintering curve

M. Stuer

Apparent activation energy from iso-density analysis

- Assuming no mass loss during sintering

$$\rho_{(T)} = \frac{\rho_0}{\xi^2\left[1+\frac{\Delta L_{(T)}}{L_0}\right]^3}$$

- $\rho_{(T)}$: volume mass at temperature T
- ρ_0: green body volume mass at starting temperature T_0
- ξ : shrinkage anisotropy
- $\Delta L_{(T)}$: $L_{(T)} - L_0$ the sample height variation at T compared to T_0

- For precise density analysis, sample thermal expansion α has to be considered

$$\alpha = \frac{1}{L_{(T)}}\frac{\partial L_{(T)}}{\partial T} \rightarrow L_{(T)} = L_0 e^{\alpha(T-T_0)}$$

- The relative density D at T is defined as

$$D_{(T)} = 100\,\frac{\rho_{(T)}}{\rho^{th}_{(T)}}$$

- $\rho_{(T)}$: actual density at T
- $\rho^{th}_{(T)}$: theoretical density at T

- Assuming no mass loss during sintering $\rho^{th}_{(T)}$ can be written as a function of ρ^{th}_0

$$\rho_0^{th} = \frac{m}{L_0^3} \xrightarrow{at\ T} \rho_T^{th} = \frac{m}{L_{(T)}^3} = \frac{m}{L_0^3}e^{-3\alpha(T-T_0)}$$

- Thus, the instant relative density at T can be written as a function of the densities at T_0:

$$D_{(T)} = 100\,\frac{\rho_0}{\rho_0^{th}}\frac{1}{\xi^2\left[1+\frac{\Delta L_{(T)}}{L_0}\right]^3}e^{3\alpha(T-T_0)}$$

source: 10.1111/j.1551-2916.2006.01415.x

Apparent activation energy from iso-density analysis

- The instantaneous densification rate can be separated into temperature, grain size and density dependent quantities

$$\frac{dD_{(T)}}{dt} = \frac{dD_{(T)}}{dT}\,\frac{dT}{dt} = A\,\frac{f\left(D_{(T)}\right)}{G^n}\,\frac{e^{-Q_d/RT}}{T}$$

- A: constant
- $f\left(D_{(T)}\right)$: function of density
- Q_d: apparent activation energy for densification
- R: perfect gas constant
- G: grain size
- n: grain size exponent function of diffusion mechanism

- Applying $\ln$ and multiplying by T one finally obtains

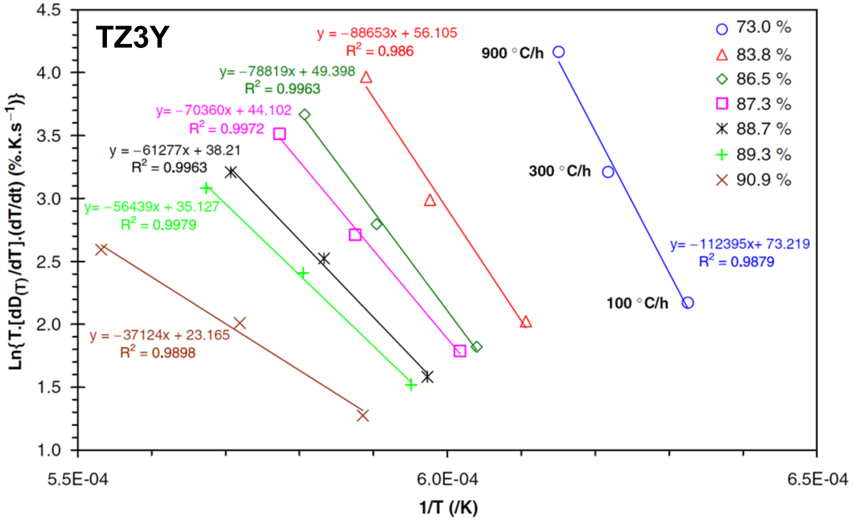
$$\ln\left[T\,\frac{dD_{(T)}}{dT}\,\frac{dT}{dt}\right] = -\frac{Q_d}{RT} + \ln\left[f\left(D_{(T)}\right)\right] + \ln A - n\ln G$$

- A plot of the left-hand side versus $1/T$ for different heating rates ($\frac{dT}{dt}$) allows obtaining Q_d
  - if taken at constant $D_{(T)}$
  - grain size G is only dependent on the density (may not always be the case!)

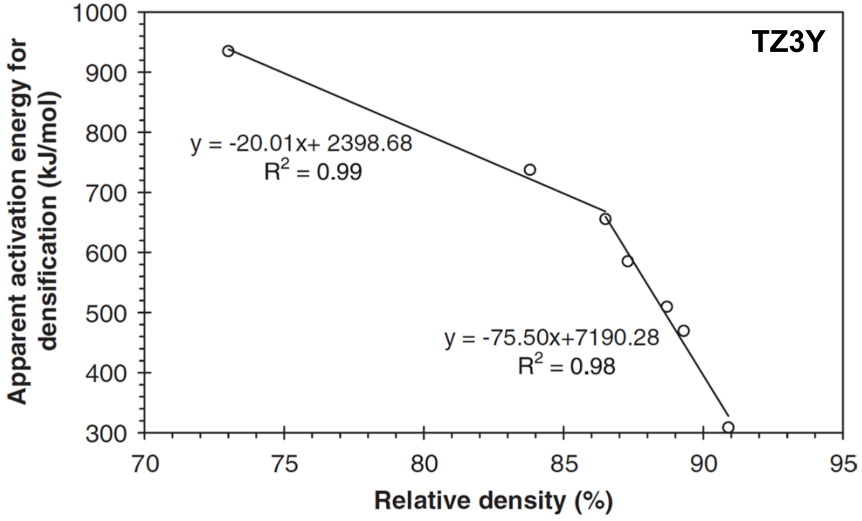
source: 10.1111/j.1551-2916.2006.01415.x

Apparent activation energy from iso-density analysis

- Find Q_d at different densities $D_{(T)}$



- Plot Q_d as a function of density $D_{(T)}$



- Changes in the apparent activation energy Q_d as a function of $D_{(T)}$ may be indicative of:
  - Changes in the mass transport mechanisms or their individual contribution to densification
  - Changes in point defect generation energies
  - Breakdown of $G = f\left(D_{(T)}\right)$ hypothesis

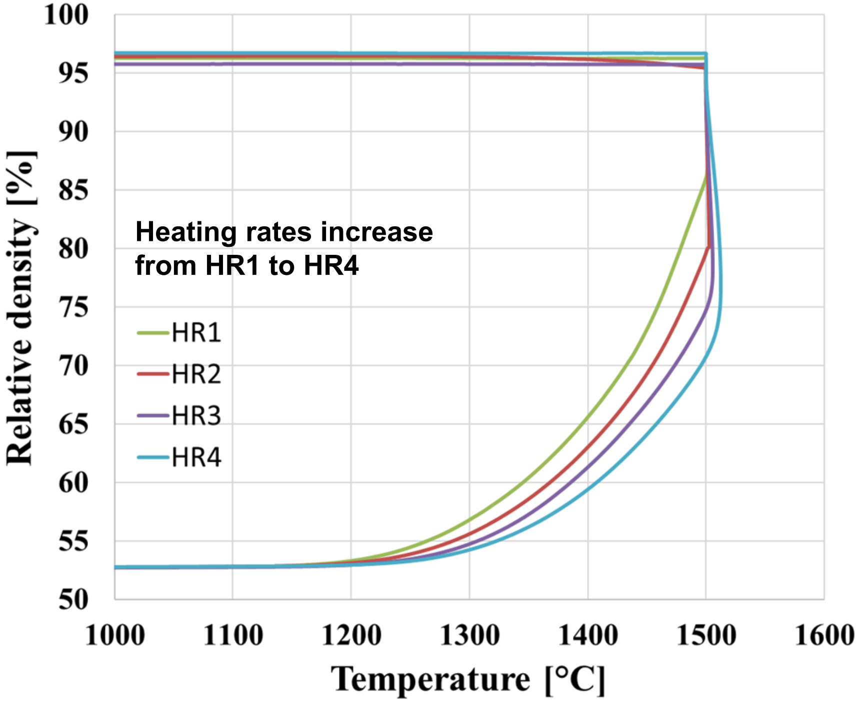
➔ **Do not determine Q_d at a single $D_{(T)}$ only**

source: 10.1111/j.1551-2916.2006.01415.x

Iso-density analysis vs Master sintering curve analysis

- **Iso-density analysis** method
  - **Only densities** reached during **constant heating rate** regime can be investigated
  - To analyze full density range
    - Use dilatometer with (very) high temperature limit
    - Use heating series with **slow heating rates** (i.e. higher densities at dwell start)
- **Master sintering curve** analysis is an alternative method which (theoretically) allows the full density range considering **time-temperature dependence** to be covered

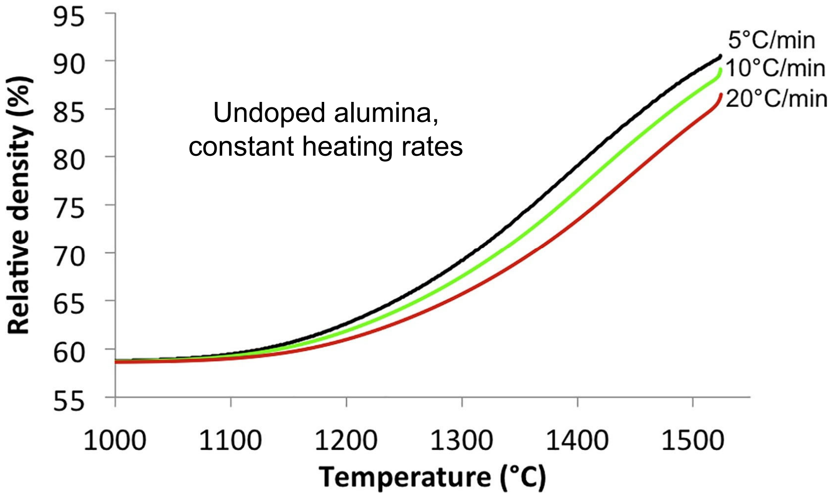
Example of dilatometry curves with different heating rates



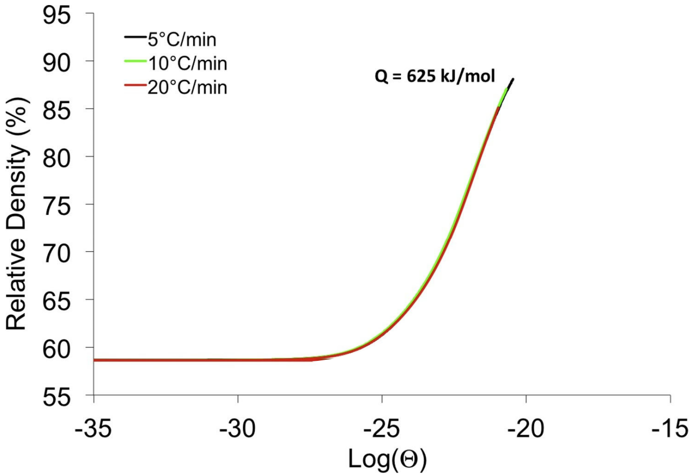
Activation energy

Master sintering curve: Big picture

- **Master Sintering Curve (MSC)**
  describes densification during sintering as a **universal function of temperature and time**, **independent of the heating profile**.
  It enables prediction and optimization of densification by combining sintering kinetics into a single curve



MSC formulation



source: 10.1016/j.jeurceramsoc.2017.12.025

Activation energy

Master sintering curve analysis

◆ The normalized $\left(\frac{1}{\rho}\right)$ densification rate $\left(\frac{d\rho}{dt}\right)$ can be written as:

$$\frac{1}{\rho}\frac{d\rho}{dt} = \frac{3\gamma\Omega}{k_B T}\left(\underset{\substack{\uparrow\\ \text{term for}\\ \text{volume}\\ \text{diffusion}}}{\frac{\Gamma_v D_v}{G^3}} + \underset{\substack{\uparrow\\ \text{term for grain}\\ \text{boundary}\\ \text{diffusion}}}{\frac{\Gamma_{gb} D_{gb}}{G^4}}\right)$$

- ρ: instantaneous density
- γ: surface energy
- Ω: atomic volume
- k_B: Boltzmann constant
- T: absolute temperature
- D_v: volume diffusion coefficient
- D_{gb}: grain boundary diffusion coefficient
- G: mean grain size diameter
- Γ_v: scaling parameter (ρ and G dependent)
- Γ_{gb}: scaling parameter (ρ and G dependent)

◆ **If there is:** Single dominant diffusion mechanism
Grain size is only density dependent $G(\rho, T, t) \approx G(\rho)$ ➔ $\Gamma_i(\rho, G) = \Gamma_i(\rho)$

then, using $D(T) = D_0 \exp\left(-\frac{Q}{RT}\right)$, the above expression simplifies to:

$$\frac{1}{\rho}\frac{d\rho}{dt} = \frac{3\gamma\Omega}{k_B T}\left(\frac{\big(\Gamma(\rho)\big)D}{G(\rho)^m}\right) = \frac{3\gamma\Omega}{k_B T}\frac{\big(\Gamma(\rho)\big)D_0 \exp(-Q/RT)}{G(\rho)^m} = \frac{3\gamma\Omega}{k_B T}\frac{\big(\Gamma(\rho)\big)D_0}{G(\rho)^m}\exp\left(-\frac{Q}{RT}\right)$$


Activation energy

Master sintering curve analysis

- Rearranging the terms to separate density ρ from $T(t)$ terms:

$$\frac{1}{\rho}\frac{d\rho}{dt} = \frac{3\gamma\Omega}{k_B T}\frac{\big(\Gamma(\rho)\big)D_0}{G(\rho)^m}\exp\left(-\frac{\boldsymbol{Q}}{RT}\right)$$

$$\Rightarrow \frac{k_B}{3\gamma\Omega D_0}\frac{1}{\rho}\frac{G(\rho)^m}{\Gamma(\rho)}d\rho = \underbrace{\frac{1}{T}\exp\left(-\frac{Q}{RT}\right)dt}_{\text{Entire time-temperature dependence is contained here!}}$$

- Integrating over *t* defines the *master sintering variable* $\varTheta\big(t, T(t)\big)$:

$$\boldsymbol{\varTheta\big(t, T(t)\big) \equiv \int_0^t \frac{1}{T}\exp\left(-\frac{Q}{RT}\right)dt}$$

This function combines the effects of time and temperature into a single master variable

- $\boldsymbol{Q}$: apparent activation energy for densification
- ρ: instantaneous density
- γ: surface energy
- Ω: atomic volume
- k_B: Boltzmann constant
- T: absolute temperature
- D_0: diffusion coefficient for dominant mechanism
- G: mean grain size diameter
- Γ : scaling parameter (depends on ρ)
- m: 3, grain volume and 4, grain boundary diffusion

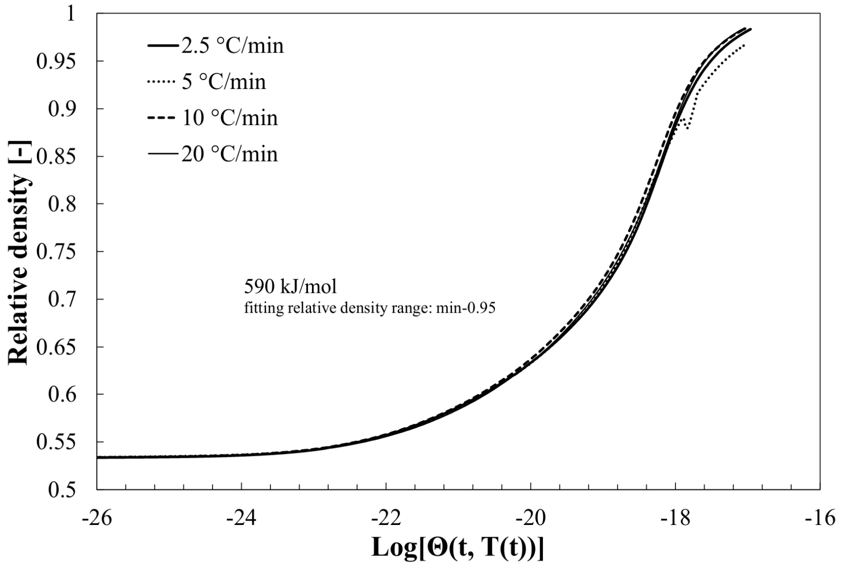
Master sintering curve analysis

- Integrating the density side of the equation from previous slide:

$$\underbrace{\frac{k_B}{3\gamma\Omega D_0}\int_{\rho_0}^{\rho}\frac{1}{\rho}\frac{G(\rho)^n}{\Gamma(\rho)}d\rho}_{\textit{master sintering curve}} = \int_0^t \frac{1}{T}\exp\left(-\frac{Q}{RT}\right)dt \equiv \Theta\big(t,T(t)\big)$$

- ρ_0: green body volume mass
- ρ: density at time t

- **Master sintering curve** (MSC) contains all microstructure and material properties (e.g. grain size); lower integration limit starts at green density ρ_0
- From dilatometry, relative density, time and temperature are known
- Q has to be determined via a fitting procedure!



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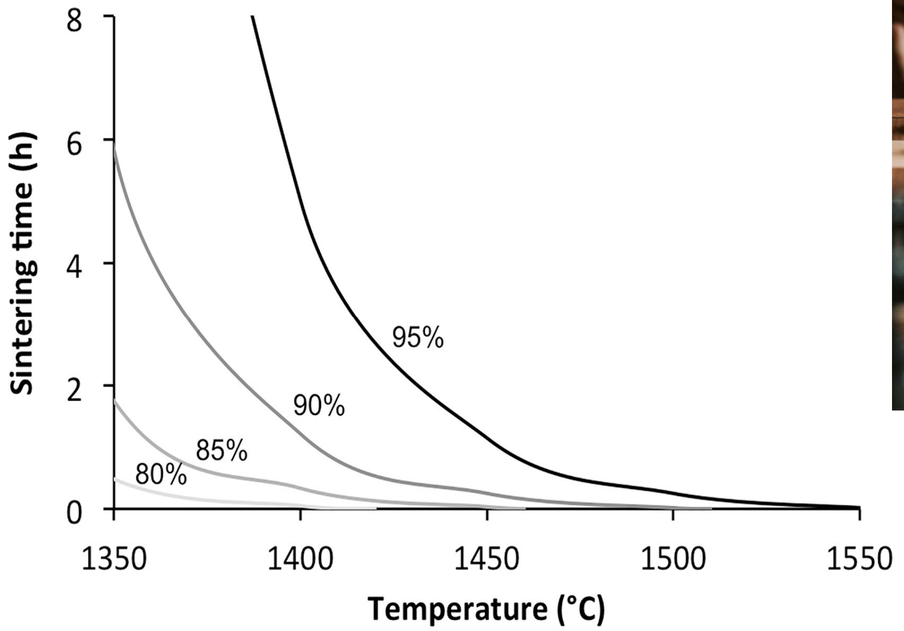
Master sintering curve analysis: time-temperature curves

- MSC $\rho(\Theta)$ is **unique** for a **given powder and given (reproducible!) green body forming technique**
- Allows density prediction based on the combined time-temperature variable $\Theta = \Theta(t, T)$, which can be considered as an accumulated thermal load
  - ➔ Density $\rho(\Theta)$ is **independent of the sintering path**
  - ➔ Given density can be reached for any sintering path t, T giving the same
- **Iso-density t-T curves** can be calculated for a given powder and green body preparation method



source: 10.1016/j.jeurceramsoc.2017.12.025

Master sintering curve analysis: Practical approach

- How to obtain apparent activation energy for densification Q?
  - Run a **series of sintering dilatometry measurements** with different temperature profiles
  - Calculate the sintering curves for each measurement as a function of $\log(\Theta(t, T))$
  - **Vary Q over expected value range** and determine residual between the set of sintering curves
  - Q value corresponding to minimum residual:
    - allows overlaying all individual $\rho(\log(\Theta(t, T)))$ sintering curves into a single master sintering curve
    - corresponds to the apparent activation energy for densification

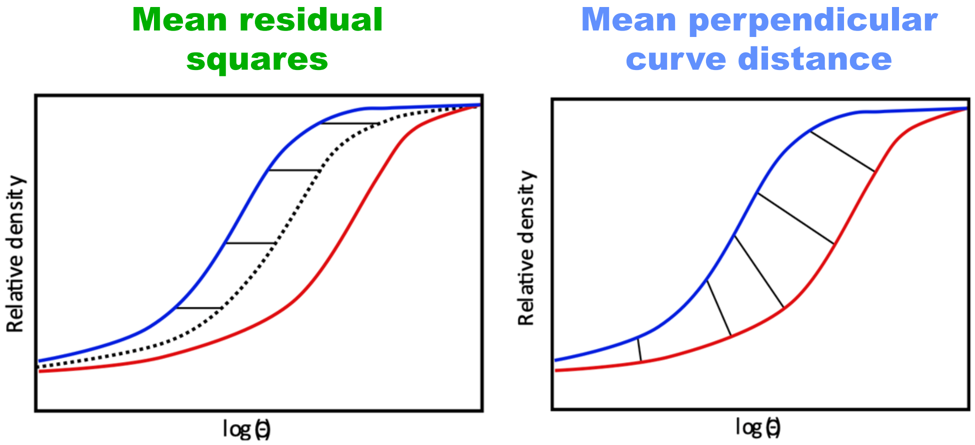
Master sintering curve analysis: Error minimization

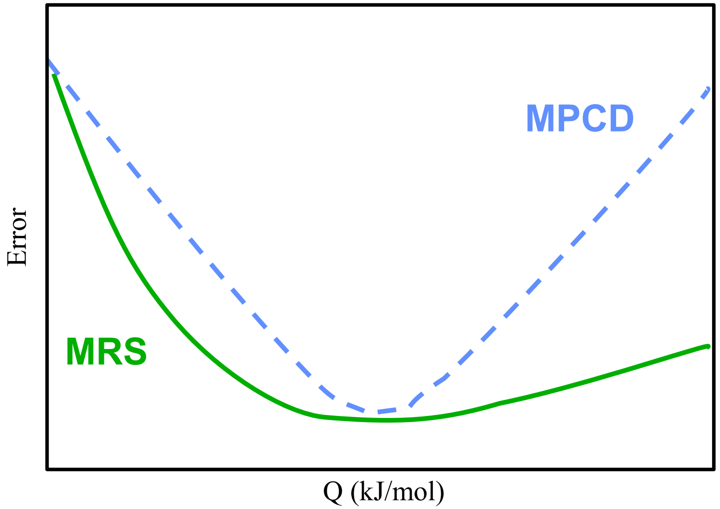
- Two error minimization methods for Q optimization are used

$$MRS = \sqrt{\frac{1}{\rho_f-\rho_0}\int_{\rho_0}^{\rho_f}\frac{1}{N}\sum_{i=1}^{N}\left(\frac{\Theta_i}{\Theta_{avg}}-1\right)^2 d\rho}$$

$$MPCD = \sqrt{\frac{1}{\rho_f-\rho_0}\int_{\rho_0}^{\rho_f} PD(\rho)d\rho}$$

- $MPCD$ gives sharper minimum and may improve MSC convergence on extremities
- **Note:**
  At extremities requirements for MSC approach are sometimes not respected
  (see next slide)

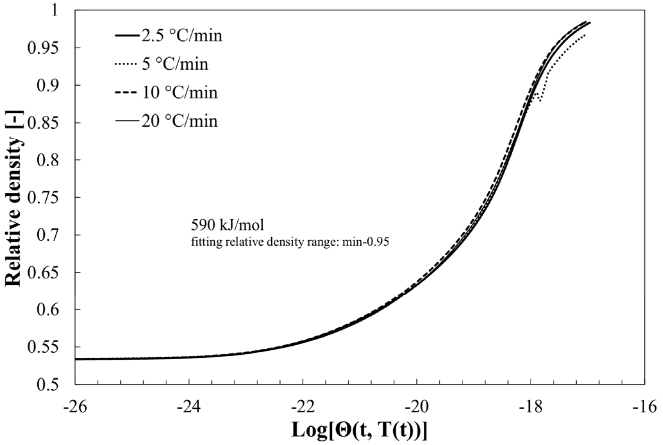




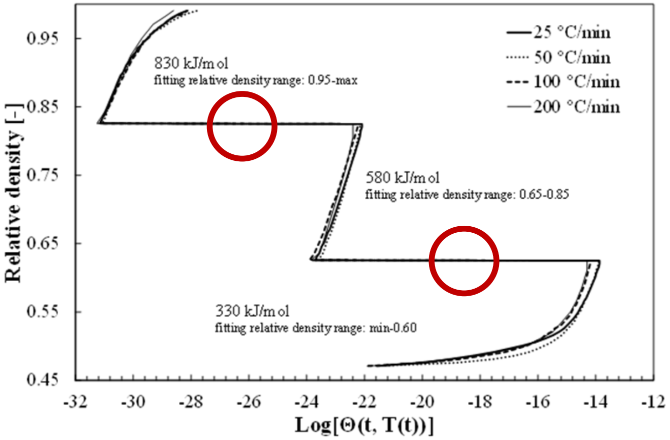
source: 10.25103/jestr.166.15

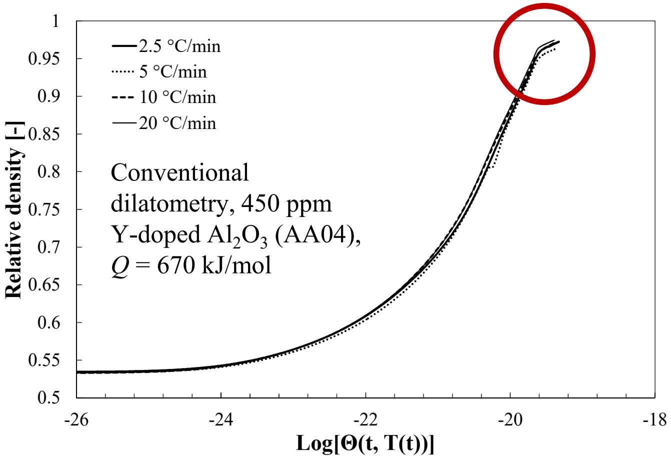
Master sintering curve analysis: Limitations

- Essential to the MSC approach are the assumptions that allow for a separation of ρ- and (T, t)-dependent variables
  - ➔ Q can be reasonably interpreted as apparent activation energy when the data are well-collapsed onto single MSC
  - ➔ otherwise, it implicitly includes other unmodeled contributions (e.g. dominant mechanism change, abnormal grain growth, plastic deformation)



- Changes of dominant mechanisms may be accounted for by splitting the MSC
- Construction of iso-density t-T curves does not account for nucleation-growth dependent processes (e.g. complexion transitions)





Conventional dilatometry, 450 ppm Y-doped Al_2O_3 (AA04), Q = 670 kJ/mol

The end

What was on the
- MENU -
today ?

- **Summary**
  - Sintering classes
  - Driving forces for sintering
  - Mass flow mechanisms
  - Sintering stages and grain growth dynamics
  - Analysis of sintering process by dilatometry

- **Questions?**

Sintering driving force – Surface energy calculation example

- **Example:**
  Green body Al_2O_3
  - r = $1 \cdot 10^{-6}$ m (particle radius)
  - M = 101.6 g/mole (molar mass)
  - ρ = 3.987 g/cm^3 (density)
  - V_m = $25.6 \cdot 10^{-6}$ m^3/mol (molar volume)
  - γ_{sv} = 0.7 J/m^2 (solid-vapor surface energy)

  ➔ **$E_{s,\ green}$ = 53.8 J/mol**

- If the surface is reduced by sintering a dense cube without pores or grain boundaries, the surface energy becomes **$E_{s,\ sintered}$ = 0.02 J/mol**