

Sintering

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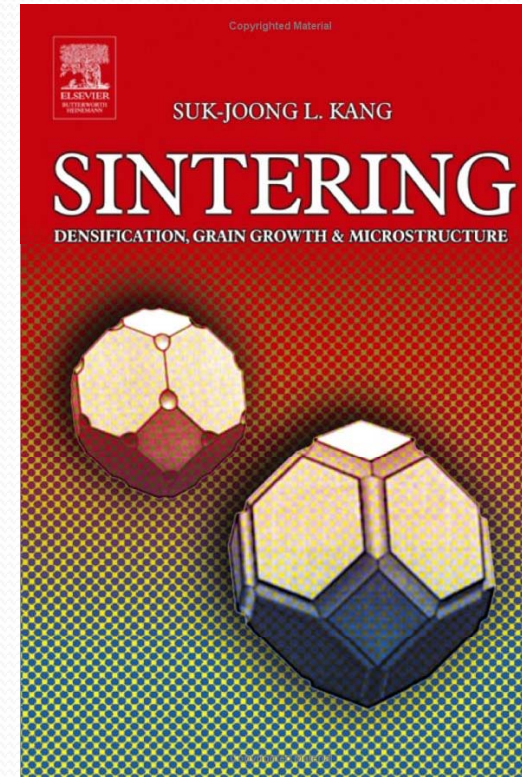
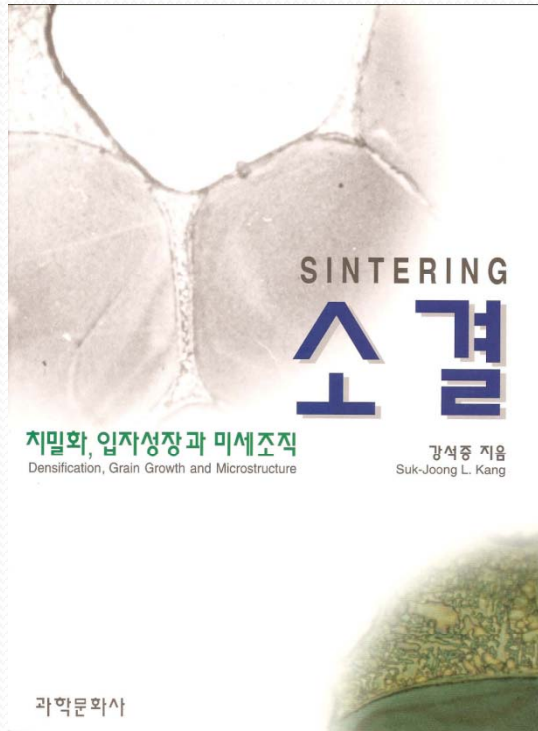
Lecture time: Tue, Thurs 4:30 pm (Room 107)

Discussion time (): Wed 11:00 am

Course Aims

- Explain the fundamentals of sintering: densification
grain growth
- Provide the basic principles of microstructure development during sintering

Course Text



Sintering: Densification, Grain Growth & Microstructure,
Suk-Joong L. Kang, Elsevier Butterworth-Heinemann (2005)

See also: Sintering Theory and Practice, Randall M. German, John Wiley & Sons (1996)

Course outline

Part I Basis of Sintering Science

Chapter 1 *Sintering Processes*

Chapter 2 *Thermodynamics of the Interface*

Chapter 3 *Polycrystalline Microstructures*

Part II Solid State Sintering Models and Densification

Chapter 4 *Initial Stage Sintering*

Chapter 5 *Intermediate and Final Stage Sintering*

Part III Grain Growth

Chapter 6 *Normal Grain Growth and Second-Phase Particles*

Chapter 7 *Grain Boundary Segregation and Grain Boundary Migration*

Chapter 8 *Interface Migration under Chemical Inequilibrium*

Chapter 9 *Abnormal grain growth*



Part IV Microstructure Development

Chapter 10 *Grain Boundary Energy and Sintering*

Chapter 11 *Grain Growth and Densification in Porous Materials*

Part V Sintering of Ionic Compounds

Chapter 12 *Sintering Additives and Defect Chemistry*

Chapter 13 *Densification and Grain Growth in Ionic Compounds*

Part VI Liquid Phase Sintering

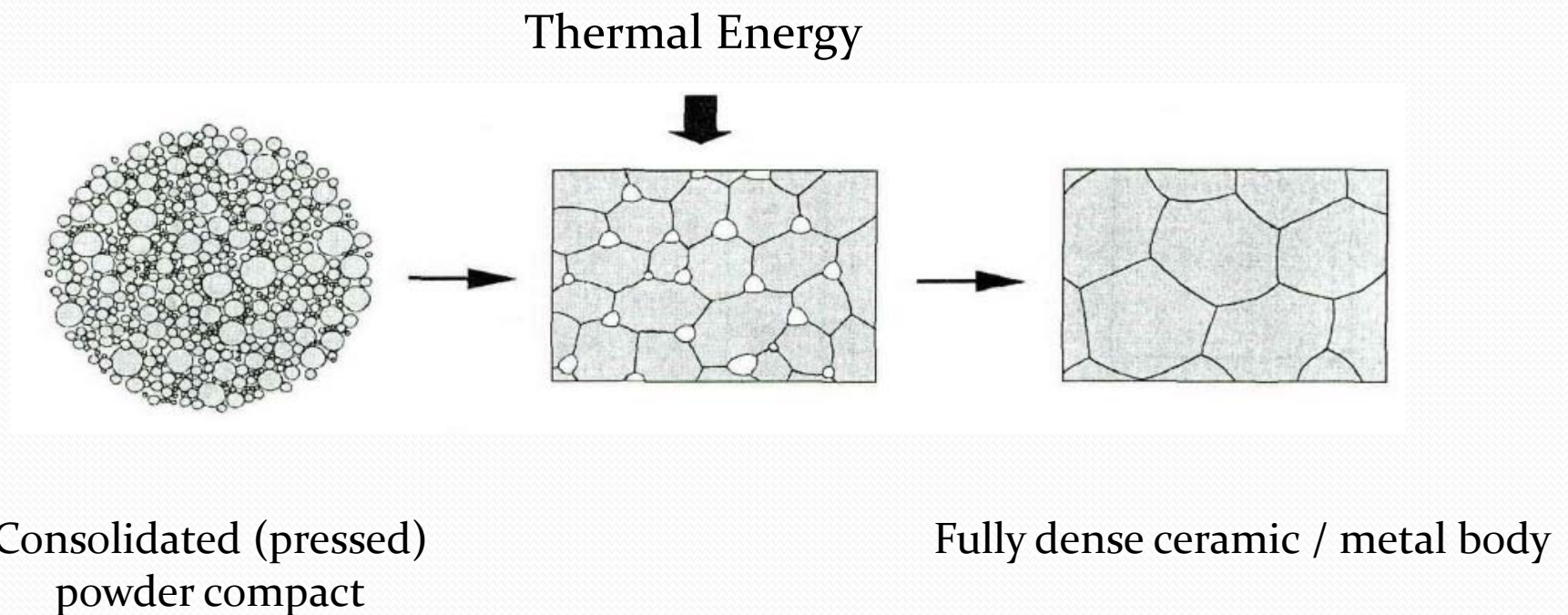
Chapter 14 *Basis of Liquid Phase Sintering*

Chapter 15 *Grain Shape and Grain Growth in a Liquid Matrix*

Chapter 16 *Densification Models and Theories*

What is sintering?

A processing technique used to produce controlled-density materials and components from ceramic or metal powders by applying thermal energy



A brief history of sintering

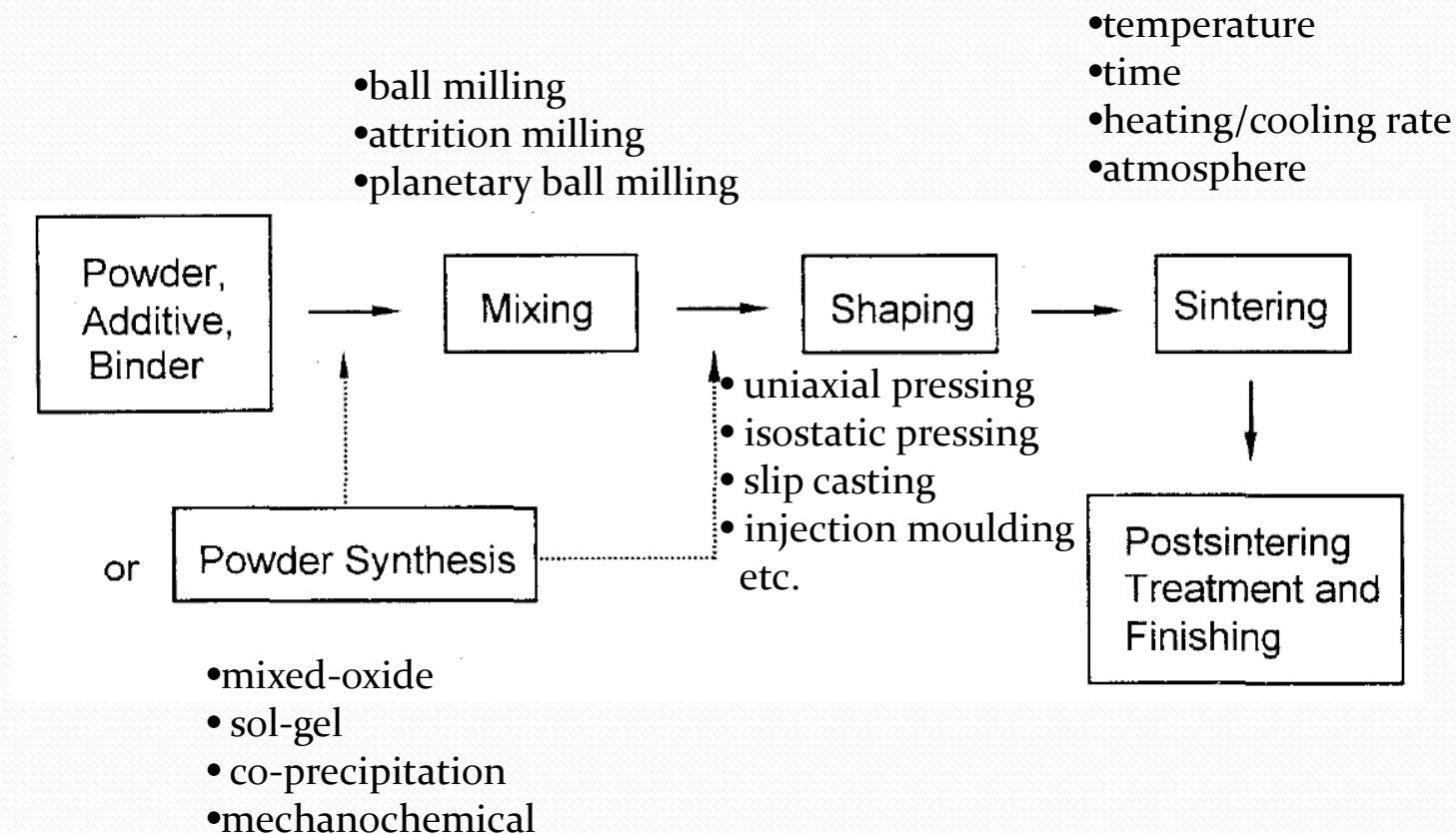
- One of the oldest human technologies.
- The modern era of sintering began in 1905 (William Coolidge, sintered W lightbulb filaments).
- 1940's – W alloys, UO_2 fuel elements, refractories
- First models of sintering emerged in the late 1940's.*
- Theory lags behind practice.



Jōmon pottery, 8,000-10,000 BC, Japan.

* G. C. Kuczynski, *Trans AIME*, **185**, 169-178 (1949)

General fabrication pattern of sintered parts



Even a slight variation in techniques and processing variables often results in big variations in sintered microstructure and properties

Aims of sintering

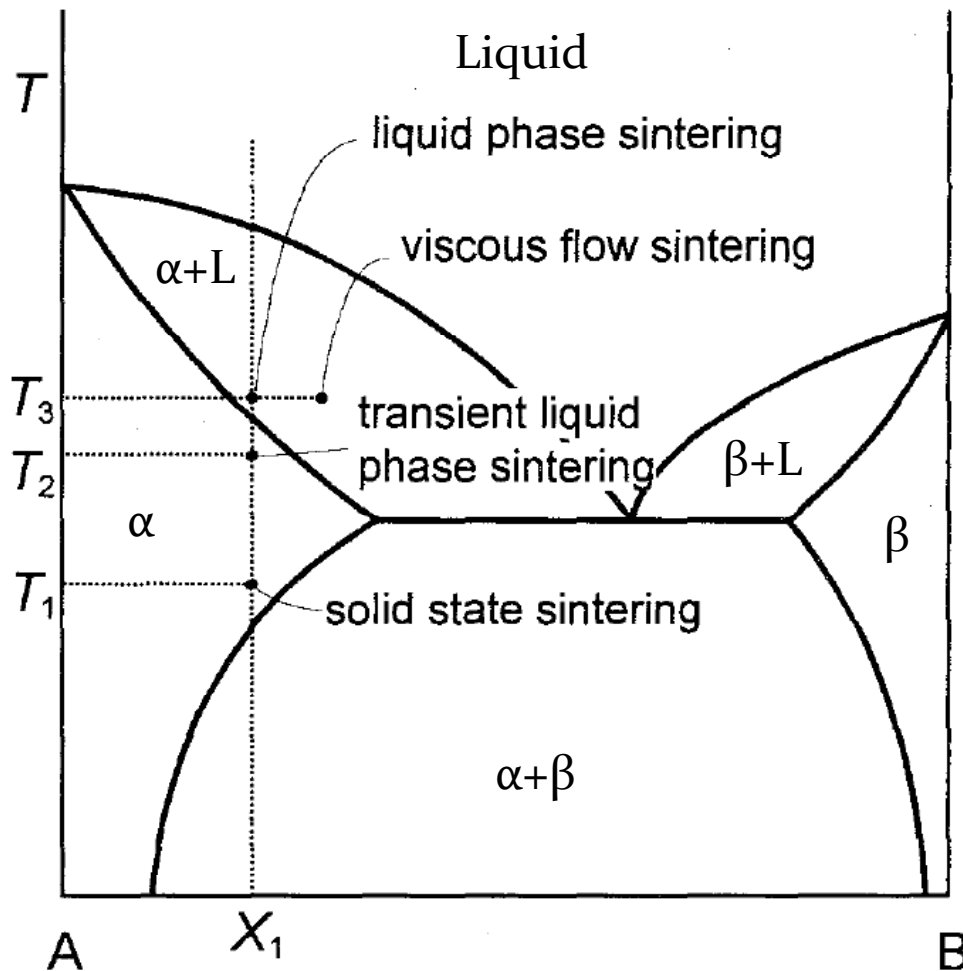
To produce sintered parts with controlled, reproducible and if possible, designed microstructures through control of sintering variables.

microstructure control

- grain size
- sintered density
- size and distribution of pores and other phases

Final goal → (usually) fully dense body with a fine grain structure

Categories of sintering techniques



- **solid state sintering:**

powder compact densified wholly in a solid state

- **transient liquid phase sintering**

liquid phase forms at an early stage of sintering

→ liquid disappears as sintering proceeds

→ densification completed in the solid state

- **liquid phase sintering**

a liquid phase present in a powder compact during sintering

- **viscous flow sintering:**

high liquid amount →

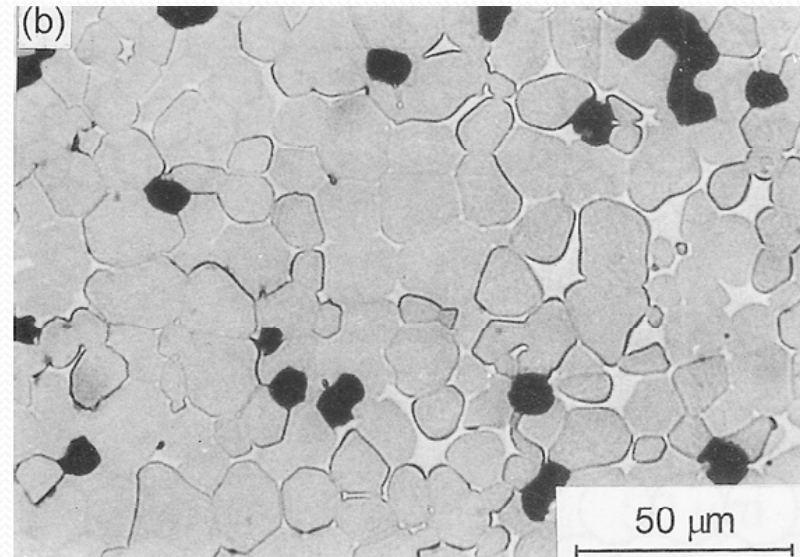
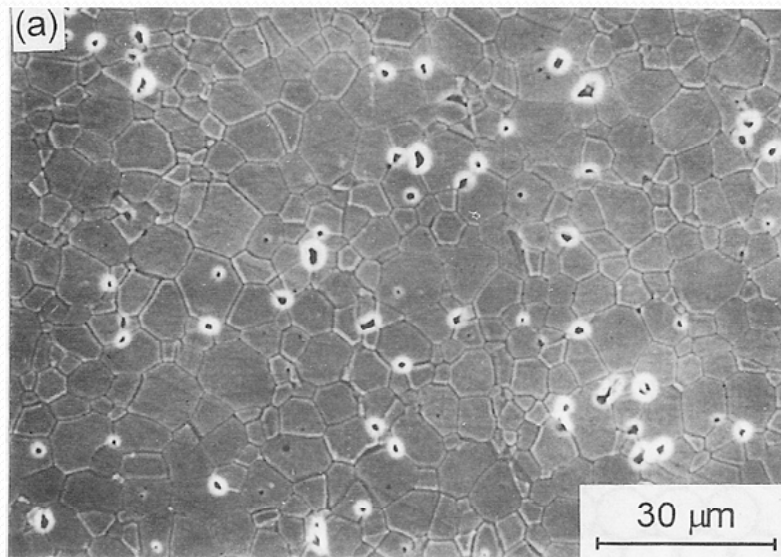
full densification of the compact by

viscous flow of grain-liquid mixture

without having any grain shape change

Liquid phase sintering vs. solid state sintering

- Liquid phase sintering allows: easy control of microstructure
low production cost
- degraded properties e.g. mechanical
- utilizing properties of g.b. phase
e.g. ZnO varistor (+Bi₂O₃ containing liquid phase), SrTiO₃ boundary layer capacitor



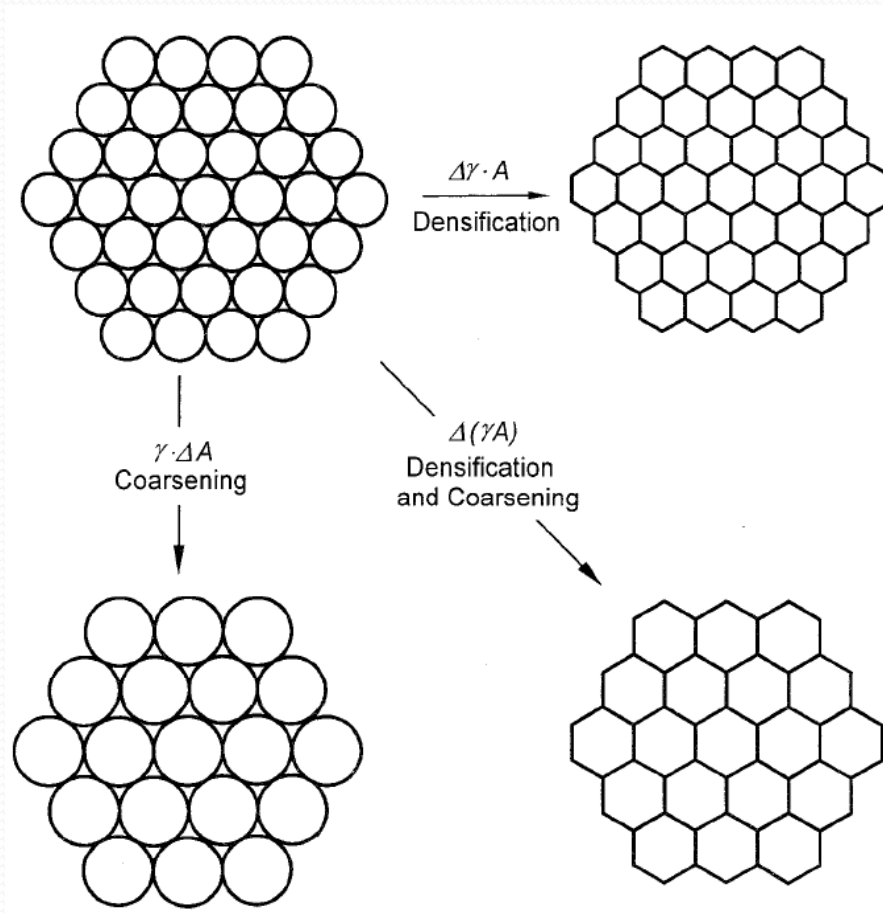
Typical microstructures during (a) solid state sintering (Al₂O₃) (b) liquid phase sintering (98W-1Ni-1Fe(wt%))

partially sintered powder compact with isolated pores : final stage of sintering

*Elimination of isolated pores utilizes almost all of the sintering time

Driving force and basic phenomena

Driving force = reduction in interfacial energy γA



γ = surface (interface) energy
 A = total surface (interface) area

γ : γ_{ss} (solid/solid), γ_{sl} (solid/liquid)
or γ_{sv} (solid/vapour)

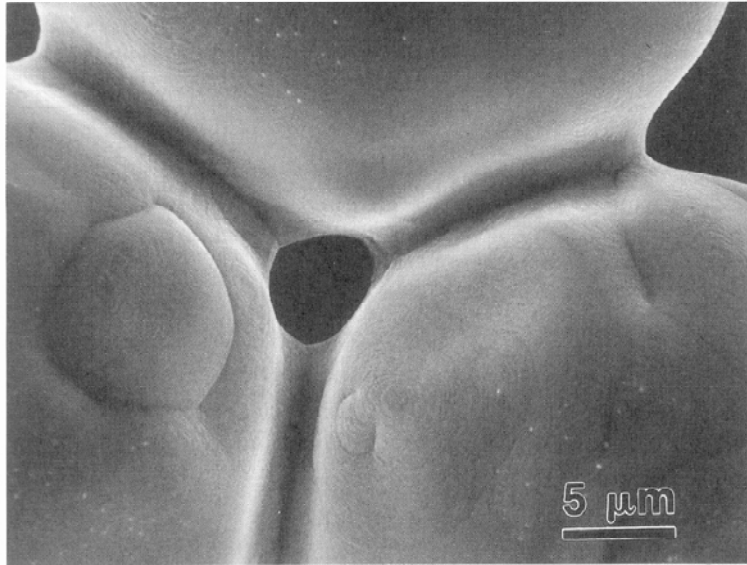
$$\Delta(\gamma A) = \Delta\gamma \cdot A + \gamma \cdot \Delta A$$

$\Delta\gamma \rightarrow$ densification

$\Delta A \rightarrow$ coarsening

Solid state sintering:

$$\gamma_{sv} > \gamma_{ss}$$



A reduction in interfacial energy ($\Delta\gamma$) takes place by the replacement of solid/vapour interfaces by solid/solid interfaces.

Necks grow at particle contacts.

For size 0.1 to 100 μm powders \rightarrow
Total surface energy (γ_{ss}) 500-0.5 J/mole

inconsiderably small compared with
the oxide formation energy (300~1500 kJ/mole)



necessary to understand and
control the variables in the sintering
processes

Sintering variables

Two groups of variable: material and process

Variables related with raw materials <u>(material variables)</u>	powder : shape, size, size distribution, agglomeration, mixedness, etc. chemistry : composition, impurity, nonstoichiometry, homogeneity, etc.
Variables related with sintering condition <u>(process variables)</u>	temperature, [*] time, pressure, atmosphere, heating and cooling rate, etc. ←Thermodynamic variables

Material variables ➡ powder compressibility and sinterability (densification, grain growth)

* improved by wet-chemistry routes (sol-gel, co-precipitation etc.)

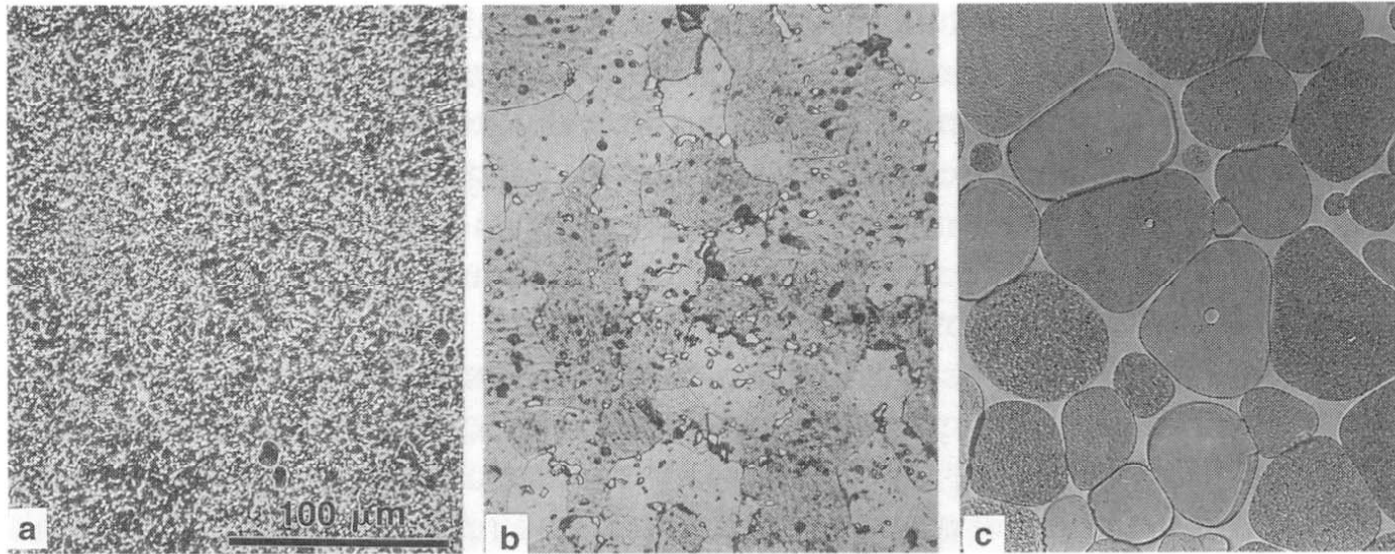
Unconventional processes controlling the process variables have been intensively studied and developed (Sec. 5.6, Sec. 11.6)

e.g.) pressure-assisted, microwave, rapid firing etc...

Overview of Sintering

All samples sintered at 1500°C for 1 hour in H₂.

Density ↑, Grain size ↑ 



Pure W powder

W + 0.3 wt % Ni

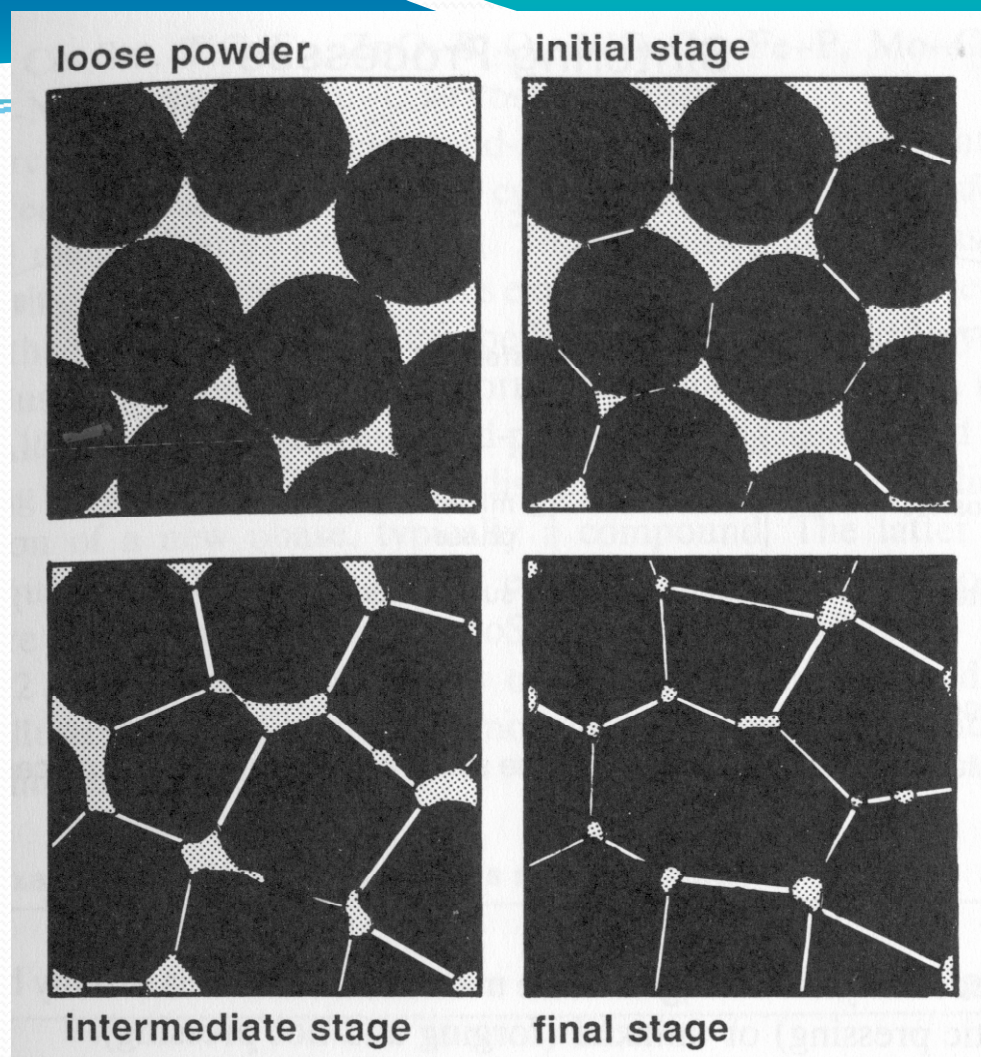
W + 5 wt % (Ni+Fe)

Strength and ductility increase 

Stages of sintering.

Table 1.1. Classic stages of sintering

Stage	Process	Surface Area Loss	Densification	Coarsening
Adhesion	Contact formation	Minimal unless compacted at high pressures	None	None
Initial	Neck growth	Significant, up to 50% loss	Small at first	Minimal
Intermediate	Pore rounding and elongation	Near total loss of open porosity	Significant	Increase in grain size and pore size
Final	Pore closure, final densification	Negligible further loss	Slow and relatively minimal	Extensive grain and pore growth



Starting compact: point bonds between particles.

Initial stage: contacts grow in size.

Intermediate stage: open pore structure, pores pin grain boundaries.

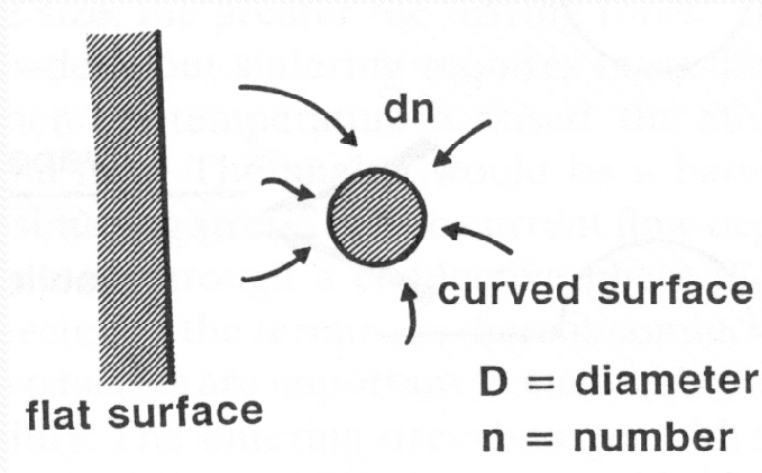
Final stage: closed pore structure, rapid grain growth.

Surface energy (solid/vapour energy) of a curved surface

Small particles: high surface area

high surface energy / unit volume

faster sintering



$$V = \frac{\pi}{6} D^3 \quad (1.1)$$

$D = \text{diameter}$
 $V = \text{volume}$

$$A = \pi D^2 \quad (1.2)$$

$A = \text{surface area}$

If n changes, then D and V change:

Or: $V = n\Omega$

$n = \text{no. of atoms}$

$\Omega = \text{atomic volume}$

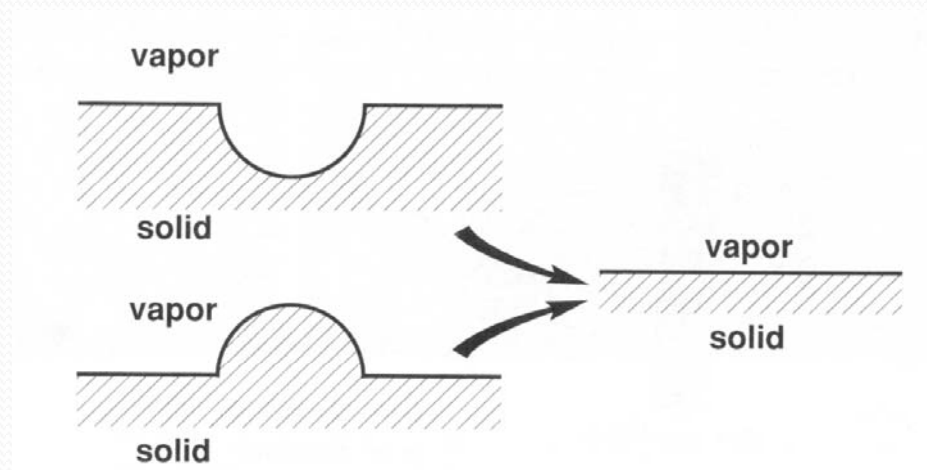
$$dV = \Omega dn = \frac{\pi D^2 dD}{2} \quad (1.3)$$

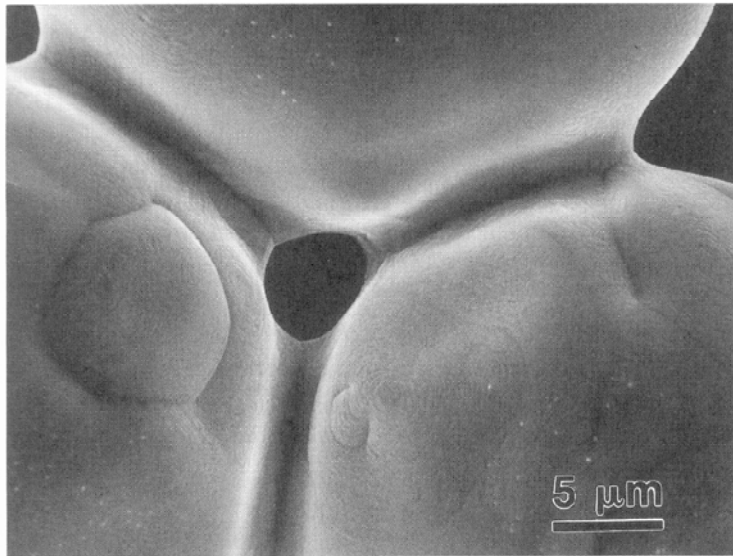
Due to higher surface area/unit volume of sphere, there is a chemical potential difference ΔU between flat surface and sphere:

$$\Delta U = \gamma_{sv} \frac{dA}{dn} = \gamma_{sv} \cdot 2\pi D \frac{dD}{dn} \quad (1.4) \quad \gamma_{sv} = \text{surface energy (solid/vapour)}$$

From equation (1.3), $dD/dn = 2\Omega/A$. Combining (1.3) and (1.4): $\Delta U = \frac{4\gamma_{sv}\Omega}{D}$

The excess energy per atom in the sphere \uparrow as $D \downarrow$





Spherical particle → convex surface → **mass source**

Pore → concave surface → **mass sink**

Add atoms to sphere → energy increase.

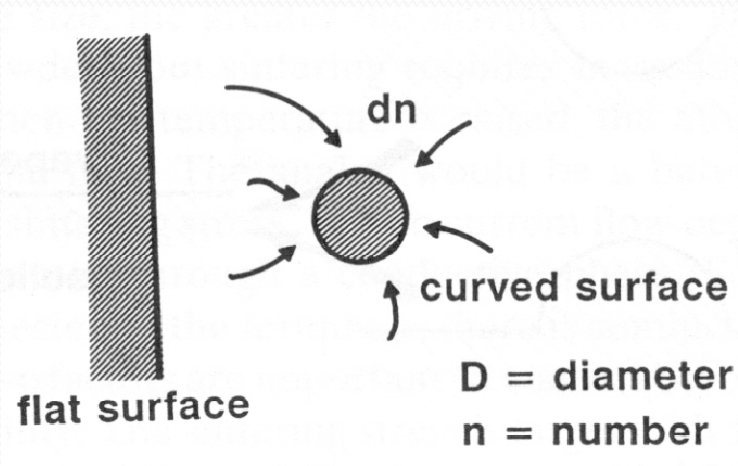
This is equivalent to a stress σ resisting the volume growth.

$$\sigma dV = \Delta U dn \quad (1.6)$$


Substituting from (1.3) and (1.5):

$$\sigma = \frac{4\gamma_{sv}}{D} \quad (1.7)$$

σ = **sintering stress** (stress due to curved surface)



Differences in stress lead to mass flow.

- 
- The driving force for sintering is the reduction of interfacial energy γA .
 - Small particles have higher sintering stress and driving force.
 - At room temp, atom mobility is too low.
 - Sinter at high temp to increase atom mobility e.g. for lattice diffusion:

$$\frac{N}{N_0} = \exp\left(-\frac{Q}{RT}\right) \quad (1.8)$$

N = no. of vacant sites or mobile atoms

N_0 = total no. of atoms

Q = activation energy for process (vacancy formation or atom diffusion)

R = gas constant

T = absolute temperature

Sintering stress controls direction of mass flow and temperature controls atom mobility.