Part VI: Liquid Phase Sintering

- Up till now, we've looked at solid-state sintering.
- But most ceramics are sintered in the presence of a liquid - *liquid phase sintering*.
- During liquid phase sintering, densification and grain growth take place simultaneously.
- Two theories for densification: contact flattening theory
  pore filling theory
- One theory for grain growth - Ostwald Ripening

Chapter 14: Basis of Liquid Phase Sintering
Chapter 15: Grain Shape and Grain Growth in a Liquid Matrix
Chapter 16: Densification Models and Theories

Chapter 14 - Basis of Liquid Phase Sintering

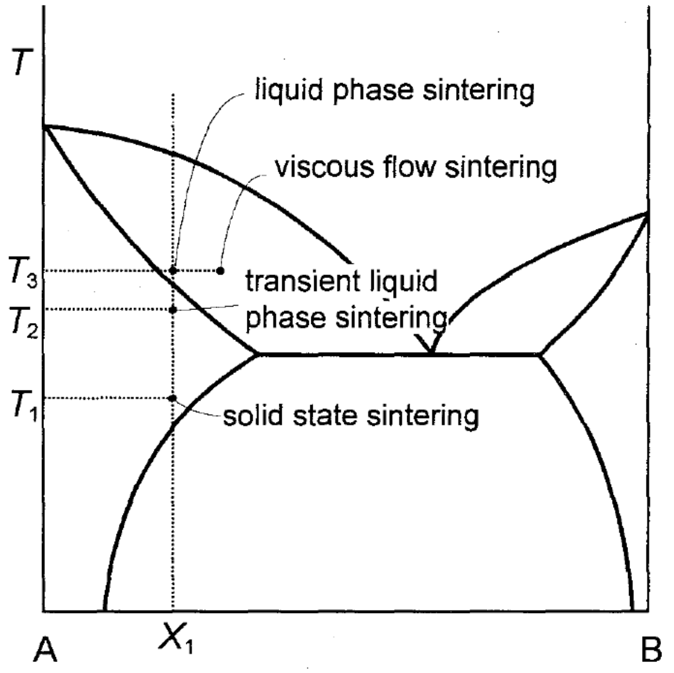
Liquid phase sintering: A sintering technique of powder compacts containing more than one component at a temperature above the solidus line of the components i.e. in the presence of a liquid.

- liquid phase sintering

a liquid phase present in a powder compact during sintering

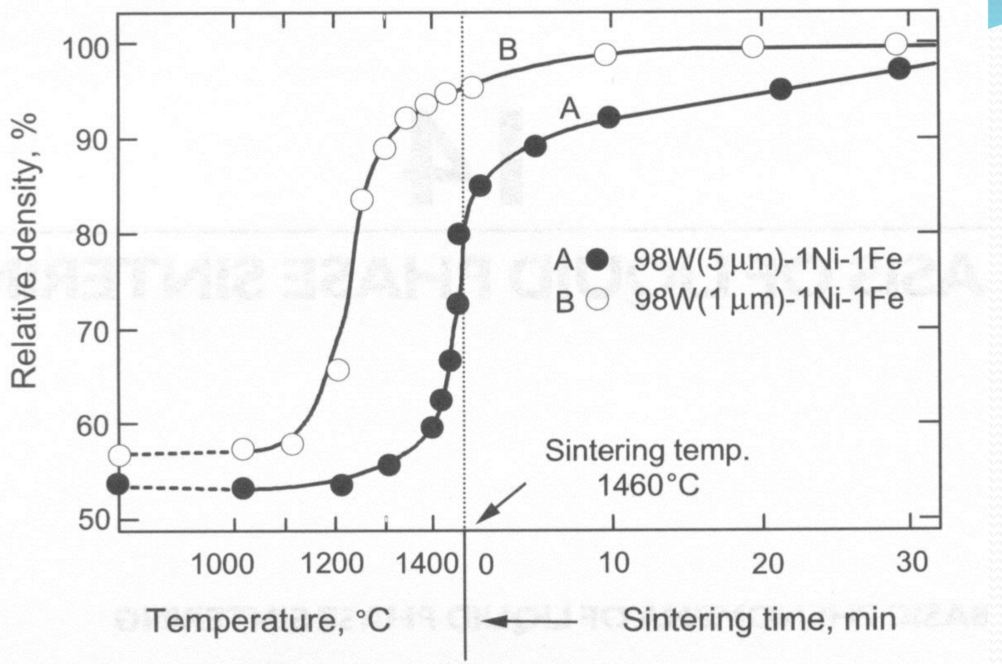
- transient liquid phase sintering

liquid phase forms at an early stage of sintering
→ liquid disappears as sintering proceeds
→ densification completed in the solid state



Three concerns: solid solubility in the liquid
wetting of the liquid on the solid grains
solid phase diffusion in the liquid

- Microstructure change is fast due to fast material transport through liquid.
- Densification also occurs in the solid state during heating to the liquid phase sintering temperature e.g. up to 90 % in the example.
- Initial microstructure of liquid phase sintering is affected by the solid state sintering stage.

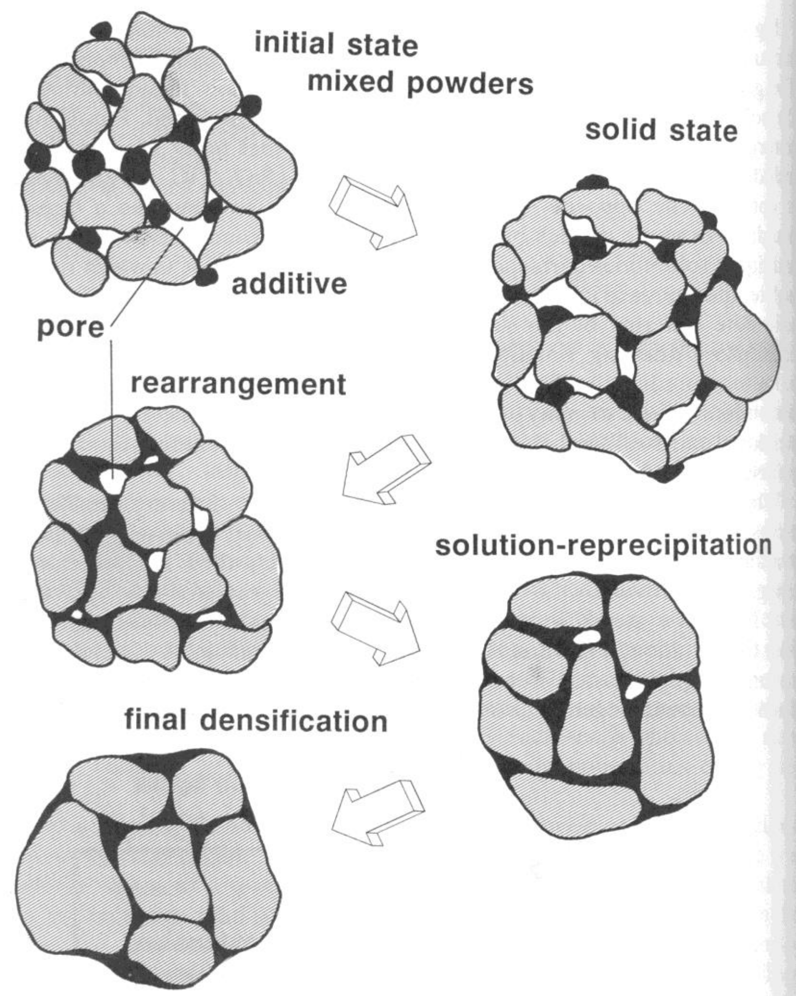


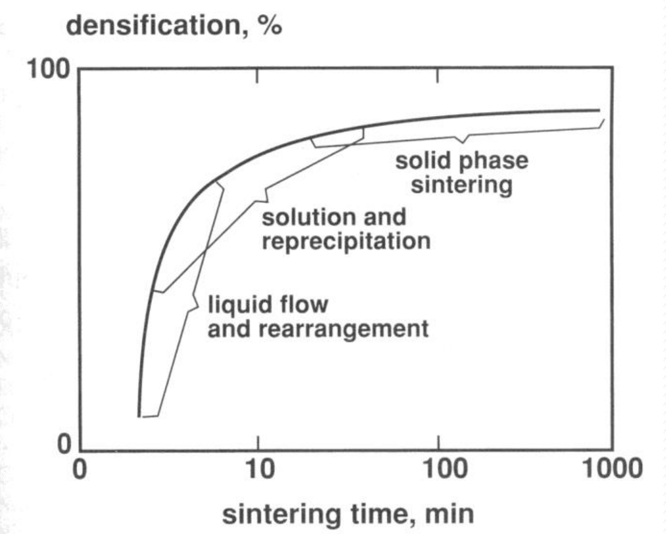
Densification curves of 98W-1ni-1Fe (wt%) alloys during heating to and isothermal liquid phase sintering at 1460°C

- When the liquid phase forms, liquid flows into fine capillaries due to the difference in capillary pressure between fine and coarse channels between solid particles.
- Most of the sites of the particles that have melted become pores because the liquid flows away into the capillaries. The removal of these pores governs densification.

Classic Model of Liquid Phase Sintering

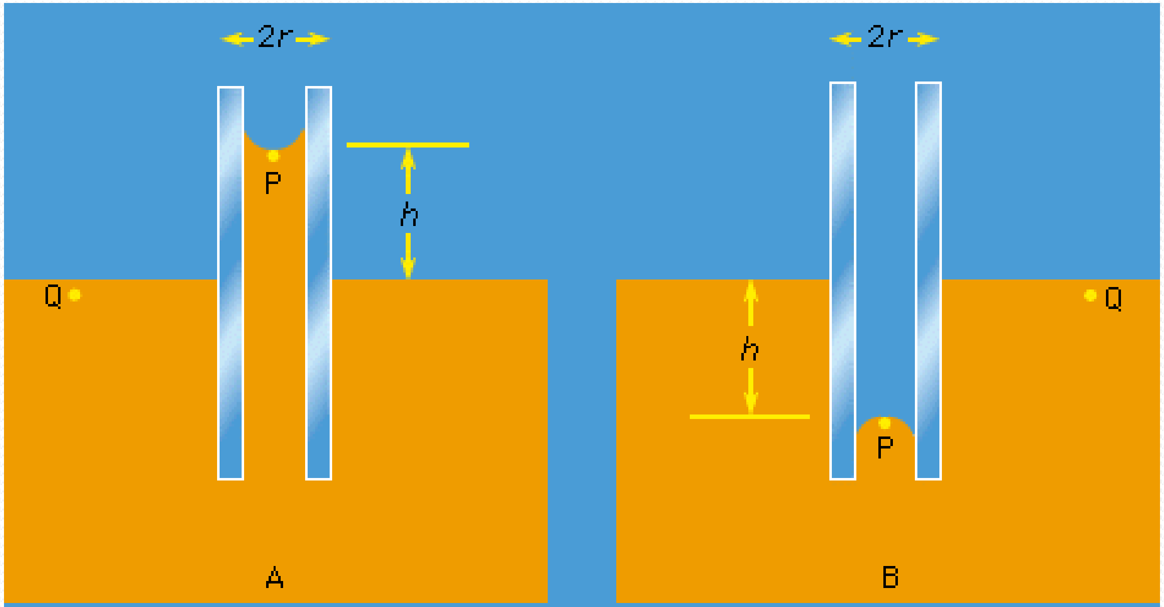
- Solid state sintering during heating
- When the additive melts, liquid flows into capillaries.
- Solid particles can be moved about (rearranged) by the liquid flow (particle rearrangement).
- During solution-reprecipitation, grains grow and change shape (contact flattening). Pores are removed by liquid flow during this stage.
- Final densification is governed by solid-state sintering.





Capillarity in Liquid Phase Sintering

$\theta < 90°$



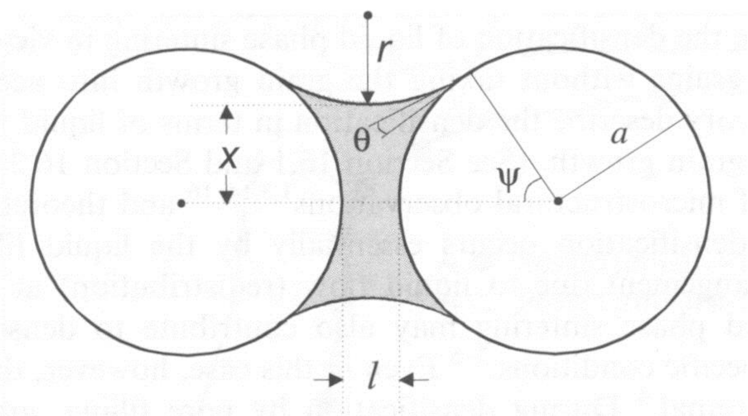
(A) The liquid wets the tube and rises up in it. (B) The liquid does not wet the tube and is depressed.

$\theta > 90°$

$$h = \frac{2\gamma\cos\theta}{\rho g r}$$

- γ is the liquid-air surface tension (J/m² or N/m)
- θ is the contact angle
- ρ is the density of liquid (kg/m^3)
- g is acceleration due to gravity (m/s²)
- r is radius of tube (m).

Compressive pressure *F* between two particles due to presence of liquid.



$$F = F_1 + F_2$$
$$= \gamma_l \left(\frac{1}{r} - \frac{1}{x}\right) \pi a^2 \sin^2 \psi + \gamma_l 2\pi a \sin \psi \sin(\psi + \theta)$$
$$= \gamma_l \left[\pi a^2 \sin^2 \psi \left(\frac{1}{r} - \frac{1}{x}\right) + 2\pi a \sin \psi \sin(\psi + \theta)\right]$$

F_1 = pressure difference between liquid and external atmosphere

F_2 = surface tension of liquid

γ_l = liquid-vapour interfacial energy

r = radius of curvature of liquid

a = particle radius

x = meniscus radius

l = interparticle distance

f_l = liquid volume fraction

θ = wetting angle

Ψ = contact angle

If the liquid surface shape is a fraction of a circle:

$$x = a \sin \psi - \left[a(1 - \cos \psi) + \frac{l}{2}\right] \frac{1 - \sin(\psi + \theta)}{\cos(\psi + \theta)}$$

and

$$r = \frac{a(1 - \cos \psi) + l/2}{\cos(\psi + \theta)}$$

F increases as Ψ and θ decrease.

As $f_l \rightarrow 0$ ($\Psi \rightarrow 0$):

$F = 2\pi a \gamma_l \cos\theta$

For $l = 0$, the critical wetting angle θ_{cr} for $F = 0$ is:

$$\theta_{cr} = 90 - \frac{\psi}{2}$$

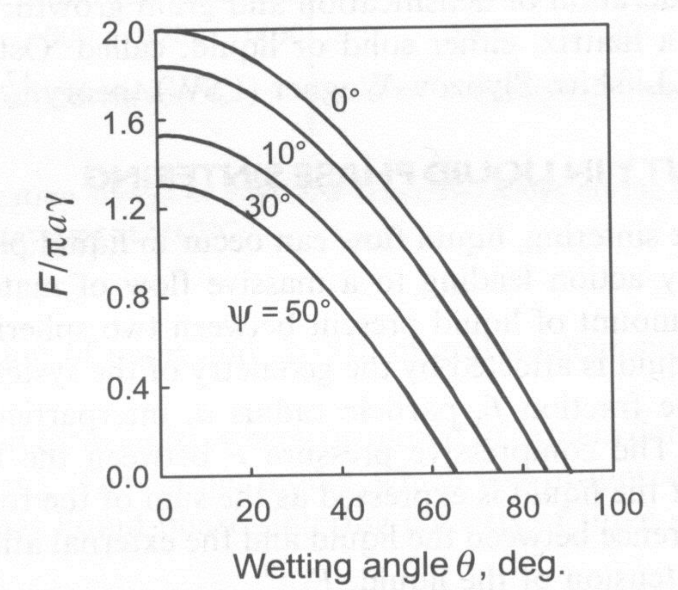
For $\theta > \theta_{cr}$ F is repulsive and l becomes > 0.

For a case where $l \neq 0$, F can also be calculated using the above eqn.

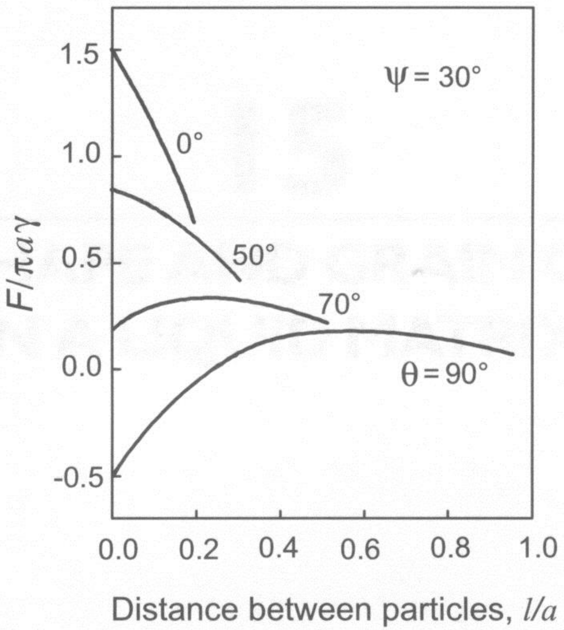
F increases as θ decreases.

For low θ, equilibrium is at $l = 0$

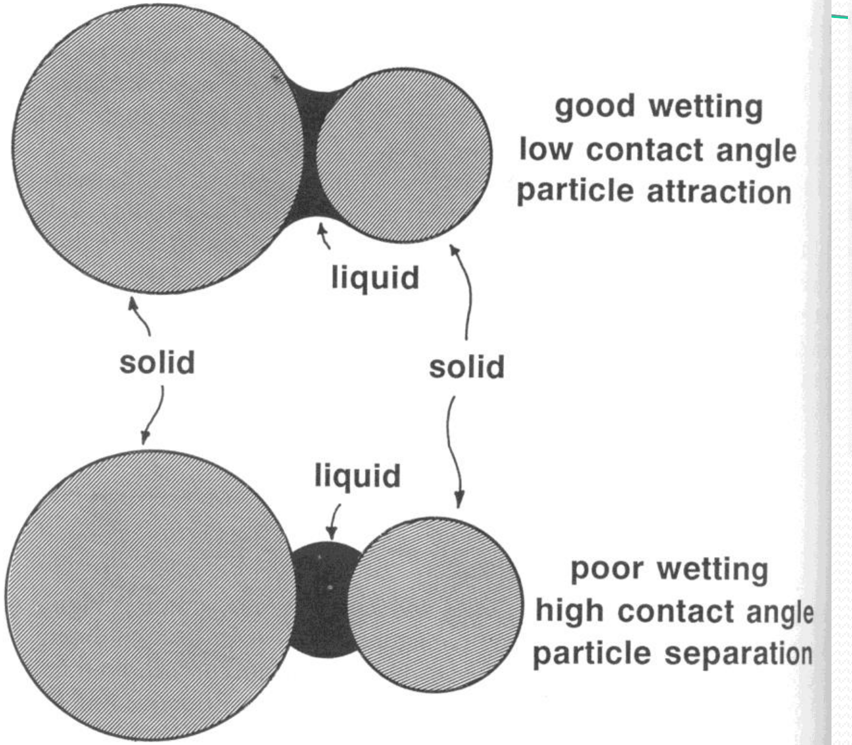
For high θ, an equilibrium distance exists.

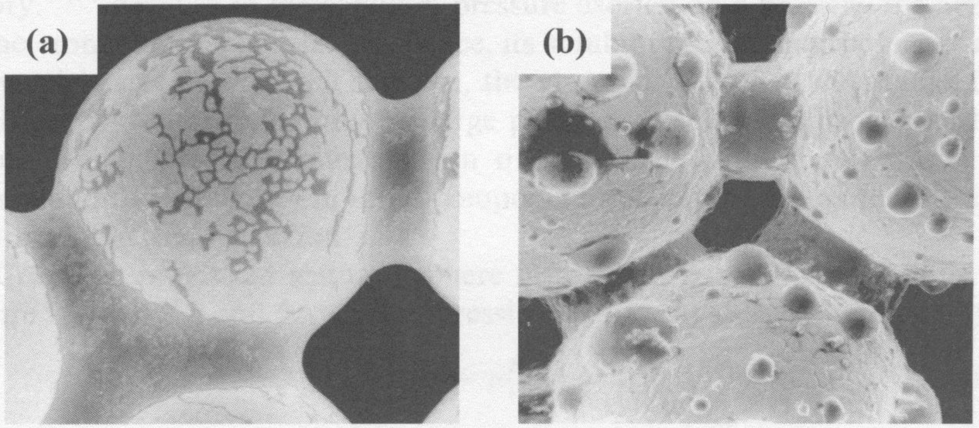


Variation of F with θ for $l = 0$

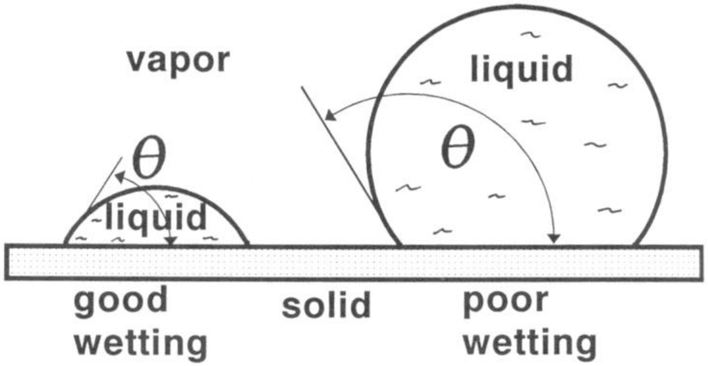


Variation of F with l





Distribution of liquid Cu between W spheres (~200 μm diameter) for (a) θ = 8° and (b) θ = 85°

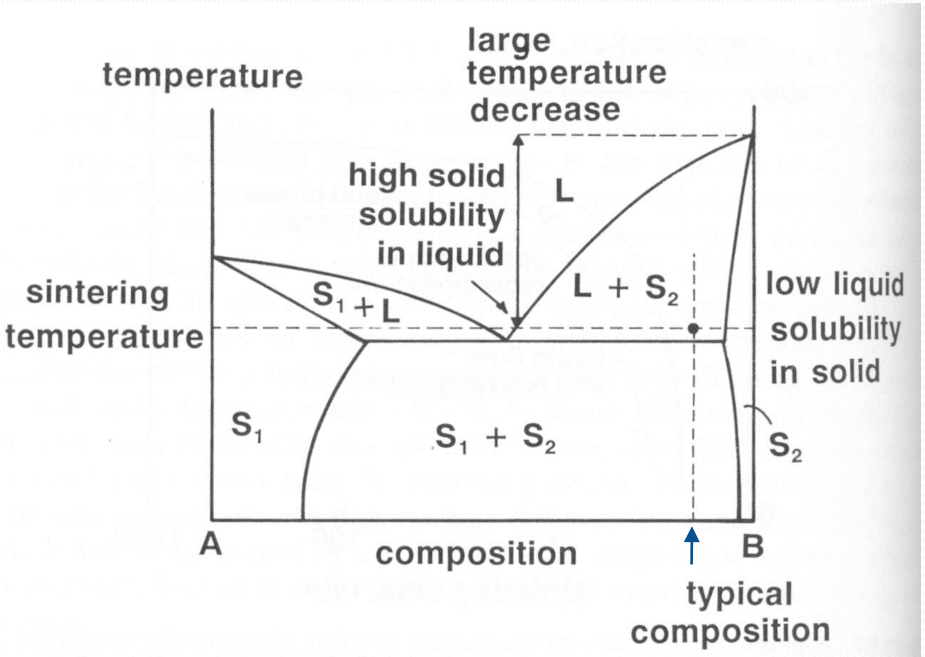


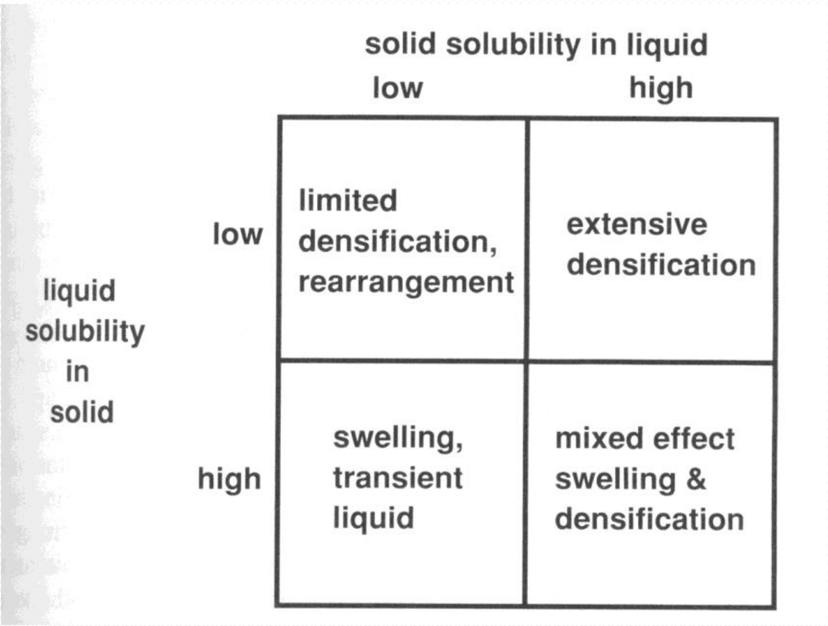
If θ is high, liquid agglomerates locally and densification does not occur.

What Makes a Good Liquid Phase Sintering Aid?

A liquid phase sintering aid should have the following characteristics:

1. The solid phase should have a high solubility in the liquid.
2. The liquid phase should have a low solubility in the solid.
3. The liquid phase should wet the solid grains.
4. The solid phase should have a high diffusion rate in the liquid.





		solid solubility in liquid	
		low	high
liquid solubility in solid	low	limited densification, rearrangement	extensive densification
	high	swelling, transient liquid	mixed effect swelling & densification