2017 Fall

"Calculation and Applications Phase Equilibria"

Principles *of* Solidification

06.07.2017

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Q: Thermodynamics and Kinetics of eutectic solidification ($L \rightarrow \alpha + \beta$) ?

Undercooling ΔT_0

$$\Delta T_0 = \boxed{\Delta T_r} + \boxed{\Delta T_D}$$

Curvature **Composition gradient**

$$\rightarrow \quad \Delta G_{total} = \boxed{\Delta G_r} + \boxed{\Delta G_D} \quad \rightarrow \quad \boxed{v = k_2 D \frac{\Delta T_0}{\lambda}(1 - \frac{\lambda^*}{\lambda})}$$

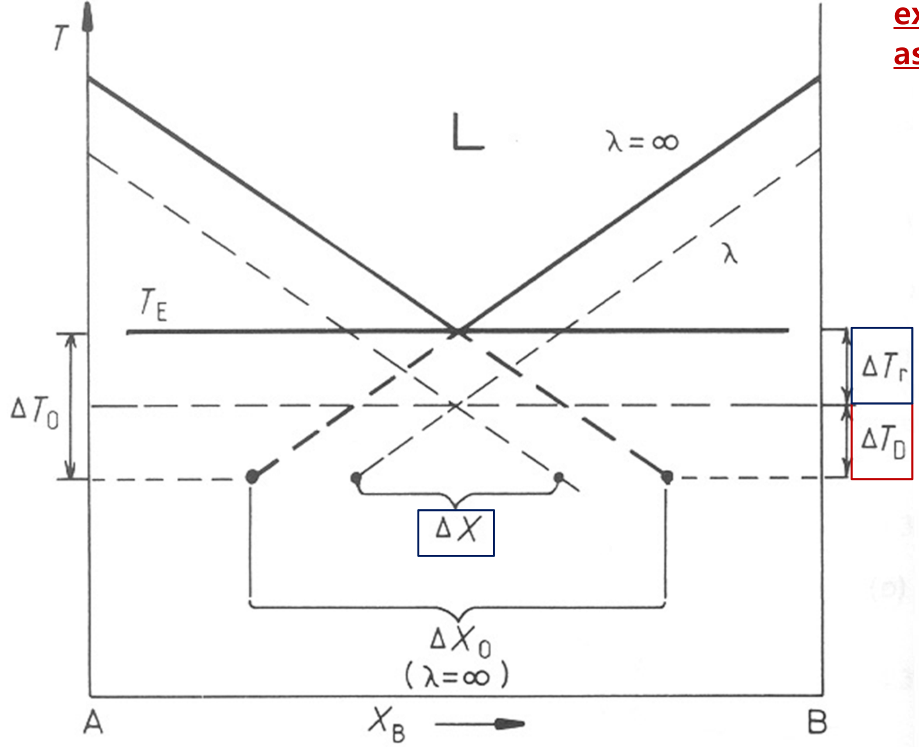
$$\Delta G_r = \frac{2\gamma_{\alpha\gamma} V_m}{\lambda}$$

$\rightarrow$ *free energy dissipated in forming α / β interfaces*

$\Delta G_D \rightarrow$ *free energy dissipated in diffusion*

By varying the interface undercooling (ΔT_0) it is possible to vary the growth rate (v) and spacing (λ) independently.

Therefore, it is impossible to predict the spacing that will be observed for a given growth rate. However, controlled growth experiments show that a specific value of λ Is always associated with a given growth rate.



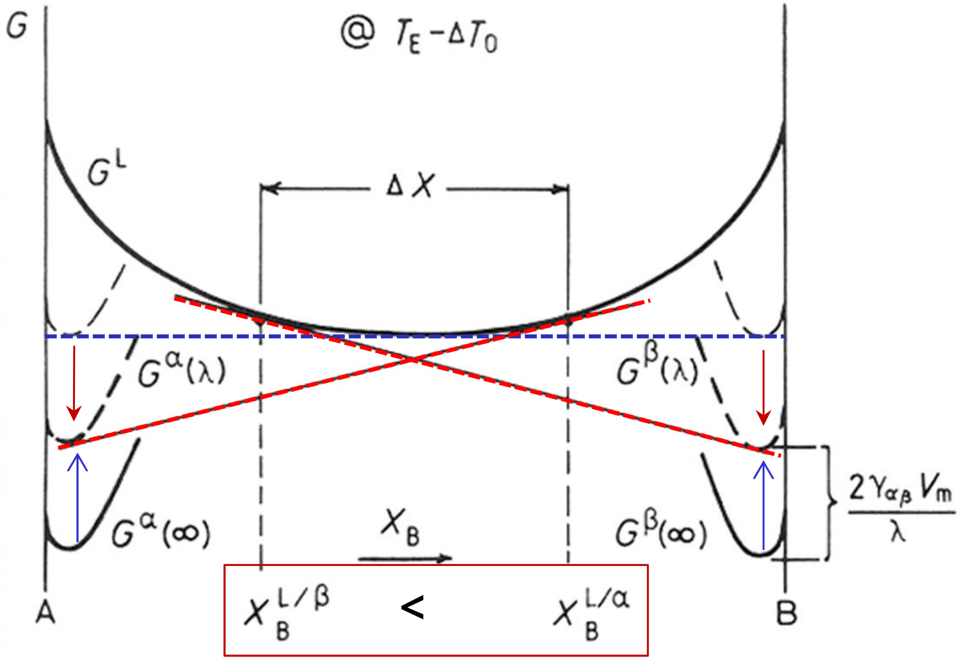


Fig. 4.34 Eutectic phase diagram showing the relationship between ΔX and ΔX_0 (exaggerated for clarity)

Undercooling ΔT_0

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Therefore, it is impossible to predict the spacing that will be observed for a given growth rate. However, controlled growth experiments show that a specific value of λ Is always associated with a given growth rate.

*** For example,**

Maximum growth rate at a fixed ΔT_0 $\rightarrow \boxed{\lambda_0 = 2\lambda^*}$

(4) $$v = k_2 D \frac{\Delta T_0}{\lambda}(1 - \frac{\lambda^*}{\lambda}) \rightarrow \boxed{v_0 = k_2 D \Delta T_0 / 4\lambda^*} \quad \textbf{(5)}$$

From Eq. 4.39

$$\lambda^* = + \frac{2T_E \gamma V_m}{\Delta H \Delta T_0} \rightarrow \boxed{\Delta T_0 \propto 1/\lambda^*} \quad \textbf{(6)}$$

So that the following relationships are predicted:

(5) + (6) $\rightarrow$

$$v_0 \lambda_0^2 = k_3 \ \textbf{(constant)}$$

$$\frac{v_0}{(\Delta T_0)^2} = k_4$$

Ex) Lamellar eutectic in the Pb-Sn system

k_3~ 33 μm³/s and k_4~ 1 μm/s·K²

$\rightarrow$ v = 1 μm/s, λ_0 = 5 μm and ΔT_0 = 1 K

5) Lamellar growth: experimental

Al-Zn, Al-Cu, Al-Zn, Pb-Sn, Pb-Cd
good agreement

$$v_0 \lambda_0^2 = k_3 \text{ (constant)}$$

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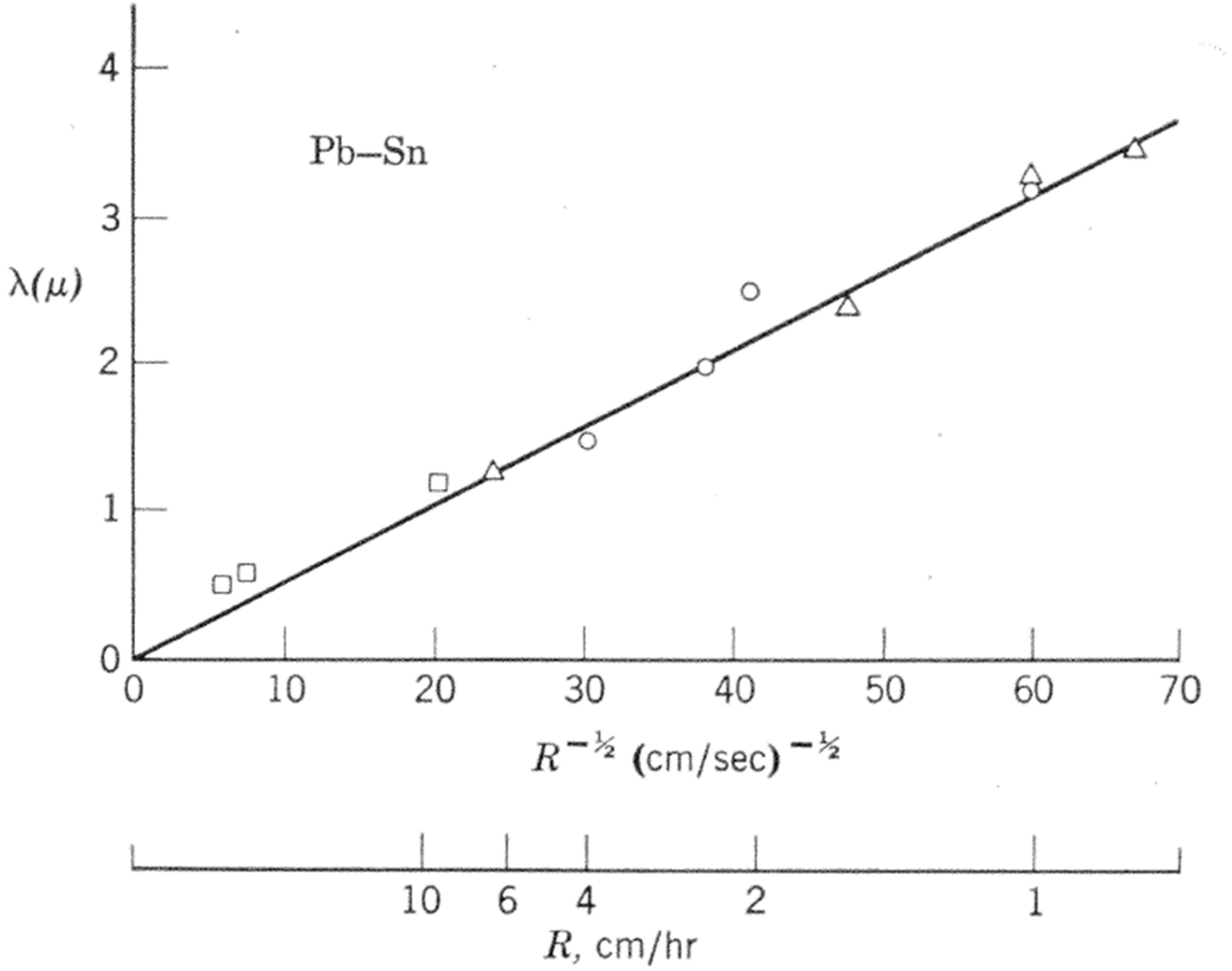

Fig. 6.18. Relationship between interlamellar spacing and growth rate for the lead-tin eutectic.

5) Lamellar growth: experimental

Al-Zn, Al-Cu, Al-Zn, Pb-Sn, Pb-Cd
good agreement

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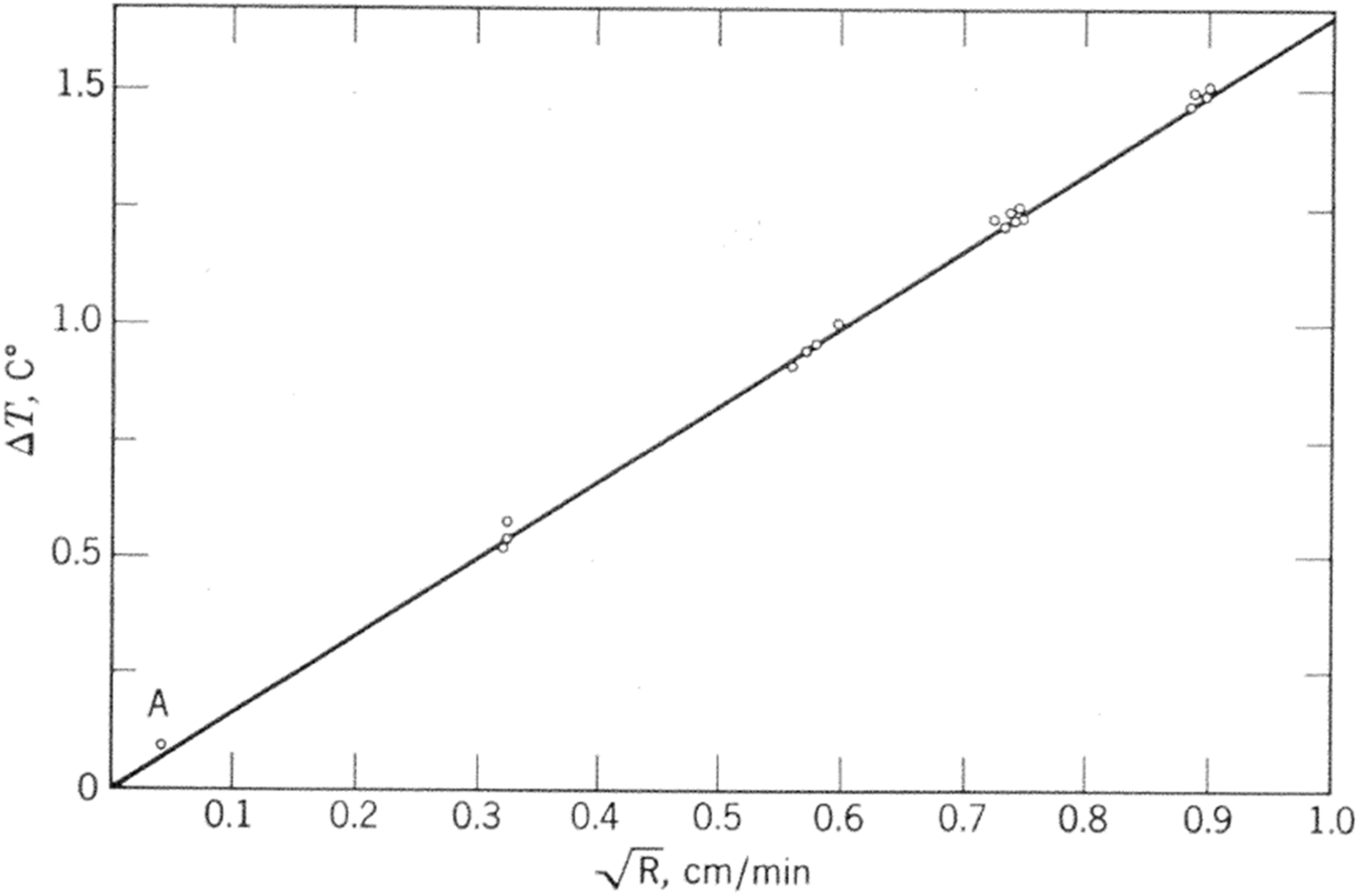


Fig. 6.19. Supercooling of eutectic interface as a function of growth rate (lead-tin).

* Total Undercooling

$$\Delta T_0 = \Delta T_r + \Delta T_D$$

Undercooling required to overcome the interfacial curvature effects

Undercooling required to give a sufficient composition difference to drive the diffusion

Strictly speaking,

ΔT_i term should be added but, negligible for high mobility interfaces

Driving force for atom migration across the interfaces

$\Delta T_D \rightarrow$ Vary continuously from the middle of the α to the middle of the β lamellae

$\Delta T_0 = const$ ← Interface is essentially isothermal.

$\Delta T_D \rightarrow \boxed{\Delta T_r}$ The interface curvature will change across the interface.

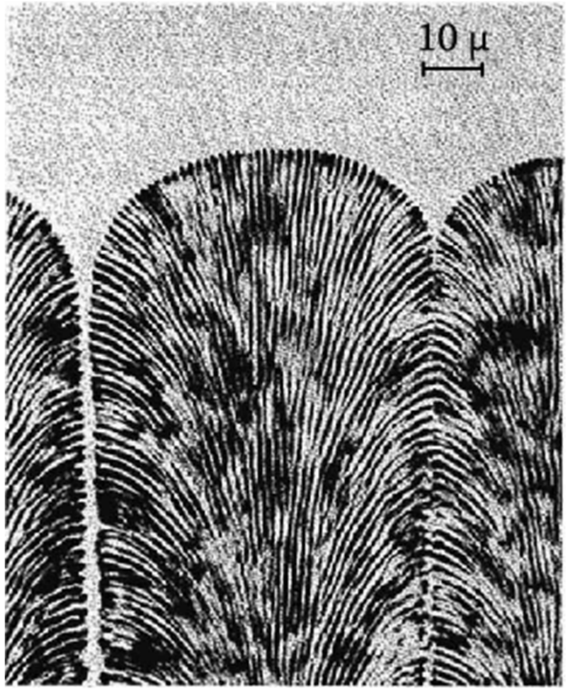
Should be compensated

* A planar eutectic front is not always stable.

Binary eutectic alloys contains impurities or other alloying elements ➡ "Form a cellular morphology" analogous to single phase solidification restrict in a sufficiently high temp. gradient.

➡ The solidification direction changes as the cell walls are approached and the lamellar or rod structure fans out and may even change to an irregular structure.

➡ Impurity elements (here, mainly copper) concentrate at the cell walls.



(d) Discontinuous eutectic structure

: required renucleate repeatedly due to "strong anisotropy" of growth characteristics

a) Case I: both phases renucleate repeatedly due to the termination of growth of crystals

* Typical discontinuous eutectic type growth mechanism (Figure 6.26)

- Random nucleation and growth independent with growth interface

- I_1: three Si phases (A, B, C) growth
  B= block of growth of C
  A & B distance increase
  I_2 : Nucleation and growth of D

- Chinese script (Fig. 6.25) type has not been investigated sufficiently.

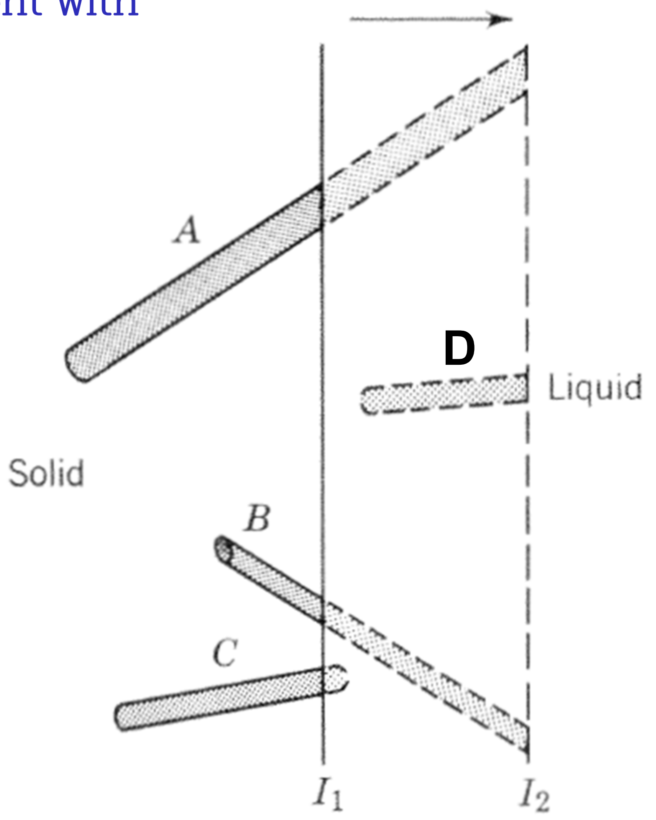


Fig. 6.27. Growth of a discontinuous eutectic (schematic), showing two positions of the interface (I_1 and I_2).

(d) Discontinuous eutectic structure

b) "Spiral type의 discontinuous eutectic" - Al-Th & Zn-Mg alloys

: one or both of the phases → anisotropic in growth rate

→ α phase grows faster than the β phase in one direction and more slowly in the other (unusual structure in Fig. 6.30).

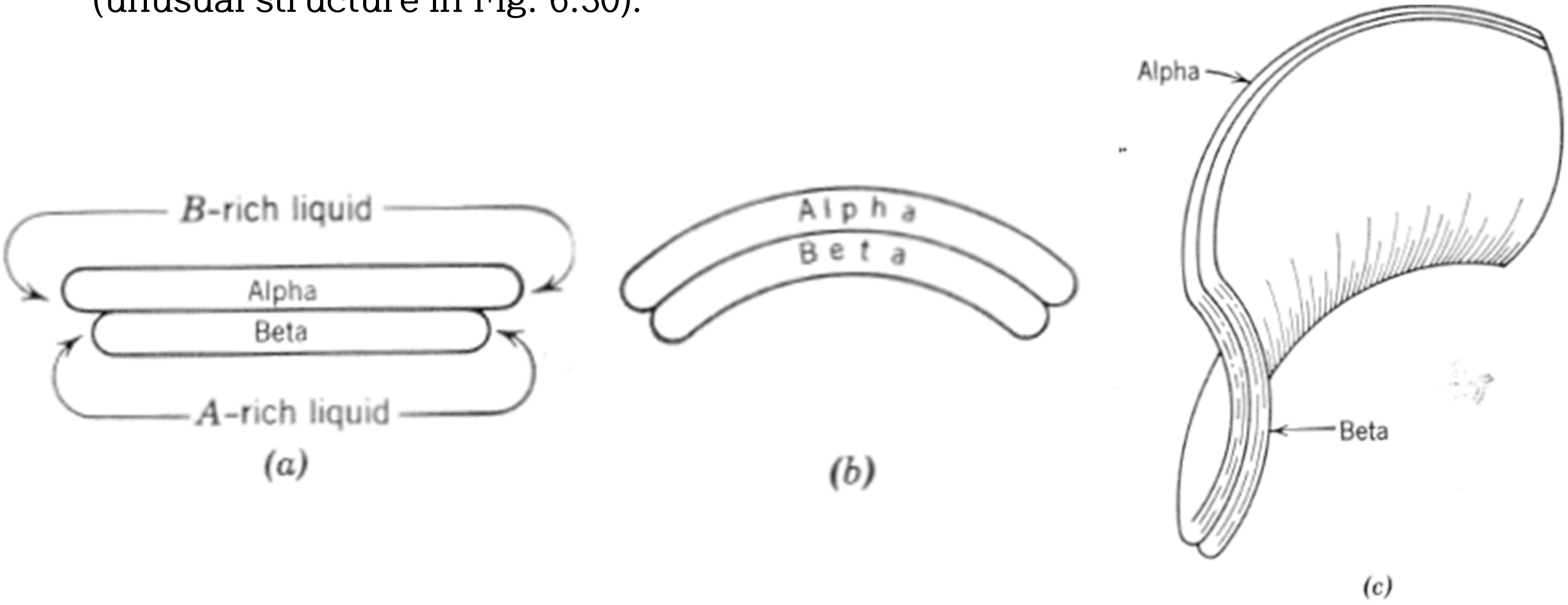


Fig. 6.30. Origin of spiral eutectic (schematic).

(d) Discontinuous eutectic structure

b) "Spiral type의 discontinuous eutectic" - Al-Th & Zn-Mg alloys

: one or both of the phases → anisotropic in growth rate

* If the two edges of the β phase do not form a closed ring, but overlap, then a spiral will be formed in that plane, and the complete structure will develop into a double conical spiral as shown in Fig. 6.29.

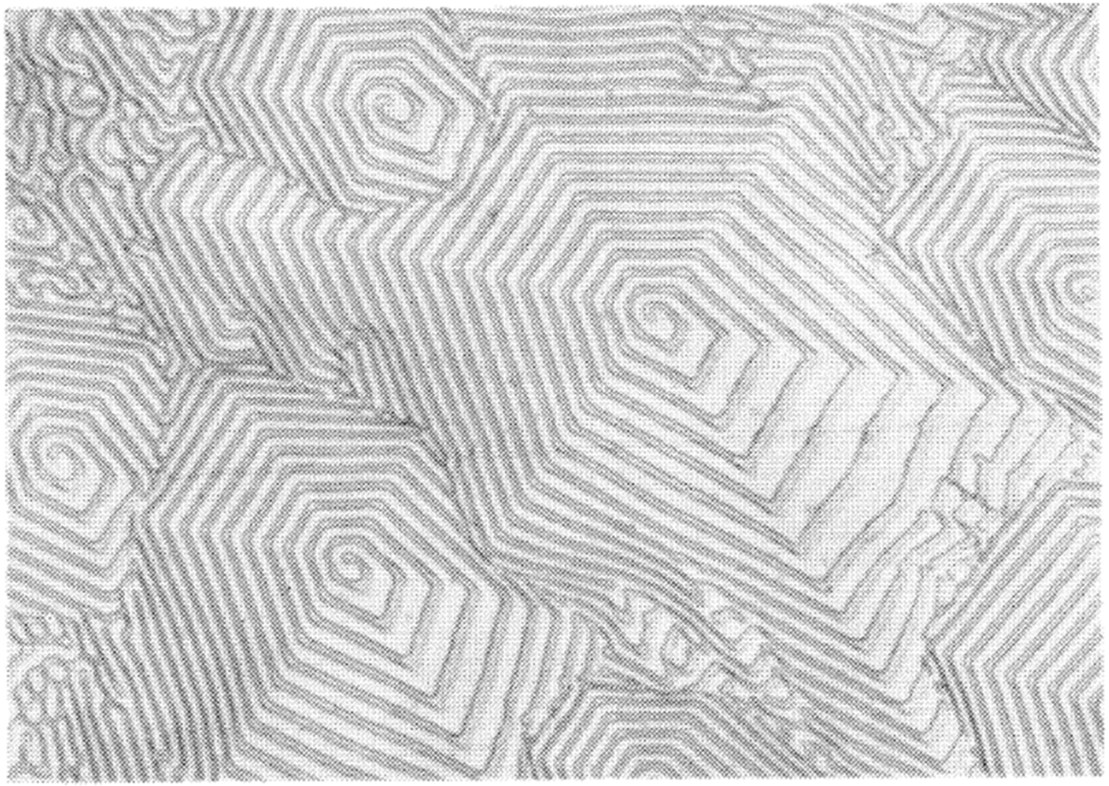


Fig. 6.28. Spiral eutectic structure in Zn-Mg alloy.

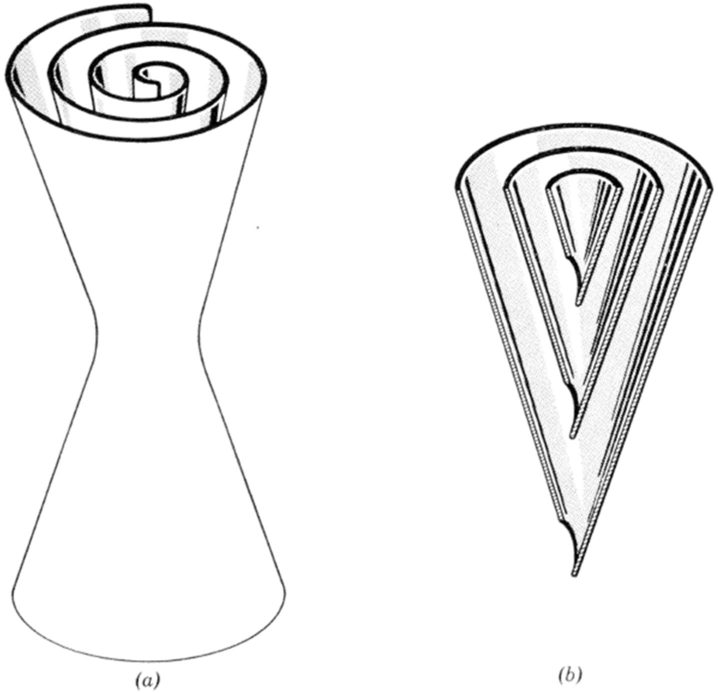


Fig. 6.29. Detailed structure of the spiral eutectic (schematic).

10) Divorced eutectic

- The primary phase continues to solidify past the eutectic point (along the line EA) of Fig. 6.31 until either the whole of the liqud has solidified or the other phase nucleated and forms a layer, which is some times dendritic, separating the two layers of the primary phase.

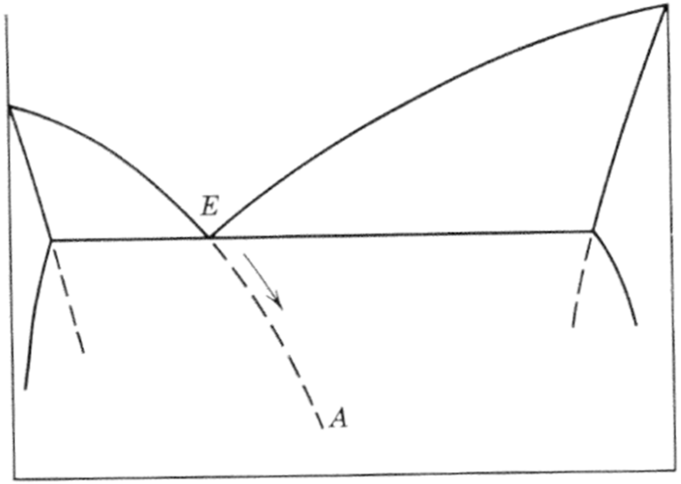
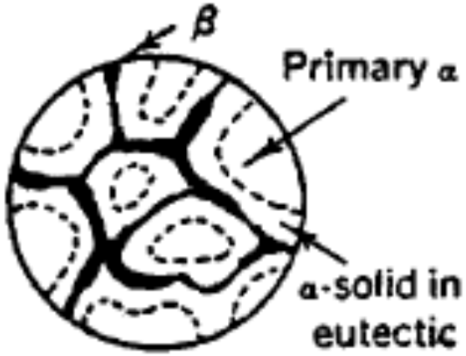


Fig. 6.31. Supercooling of eutectic in the absence of the second phase.

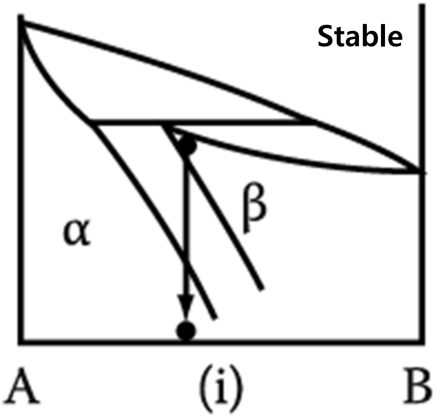
- One of the phases requires considerable supercooling for nucleation.

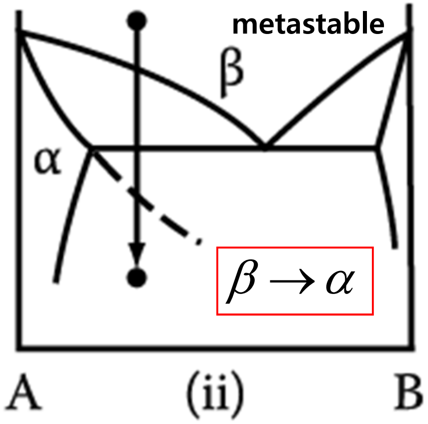


- "Divorced eutectic" is used to denote eutectic structures in which one phase is either absent or present in massive form.

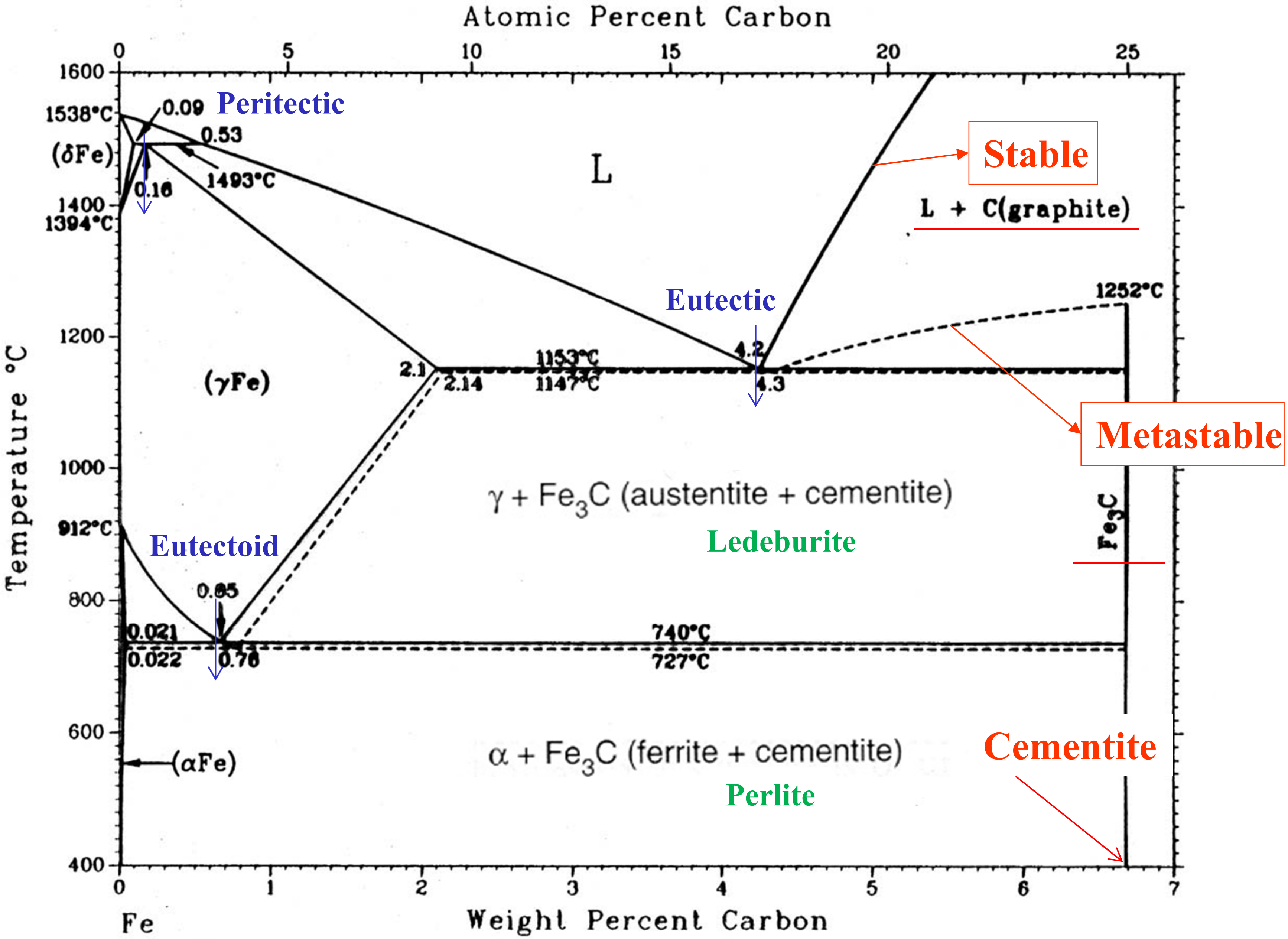
- **Massive Transformation**

: The original phase decomposes into one or more new phases which have the same composition as the parent phase, but different crystal structures.





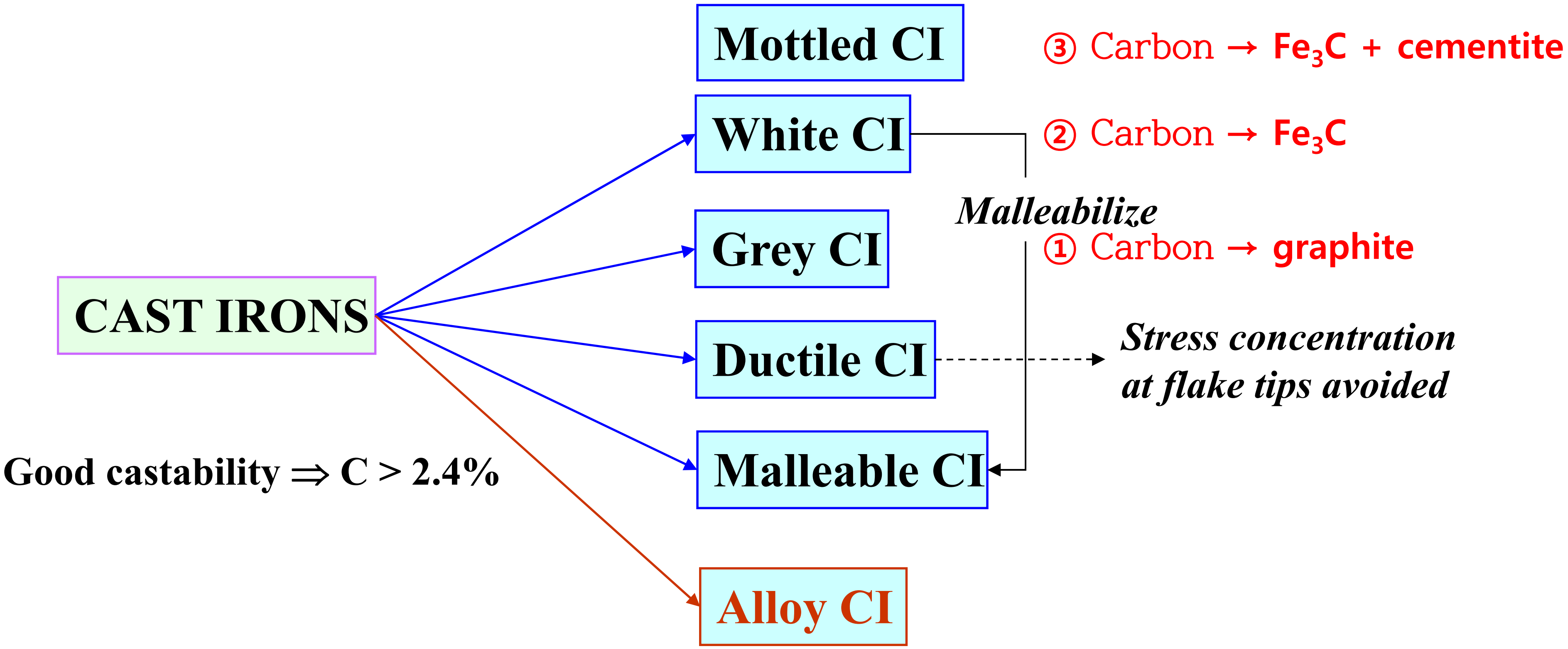
12) Cast Iron: Fe-C alloy (1.7 ≦ c ≦ 4.5%)



∗ Two eutectic system: Fe-graphite & Fe-Fe_3C

: If there is no other additive element, the Fe-graphite system is stable & Fe-Fe_3C (cementite) eutectic is formed by rapid cooling of liquid phase

∗ Classification of Cast Iron is possible depending on the type of Carbon.



Mottled CI

③ Carbon → **Fe_3C + cementite**

White CI

② Carbon → **Fe_3C**

Malleabilize

Grey CI

① Carbon → **graphite**

CAST IRONS

Ductile CI

Stress concentration at flake tips avoided

Malleable CI

Good castability ⇒ C > 2.4%

Alloy CI

∗ Fe−Fe$_3$C eutectic temp $\overset{6°C}{<}$ Fe−graphite eutectic temp.

*** If solidification proceeds at interface temperature above the cementite eutectic temperature,**

Graphite eutectic formation

→ Gray cast Iron

∗ If the solidification proceed below Cementite eutectic temperature due to lower the liquidus temperature through fast quenching and a suitable nucleation agent to form an over-solute layer,

→ White cast Iron

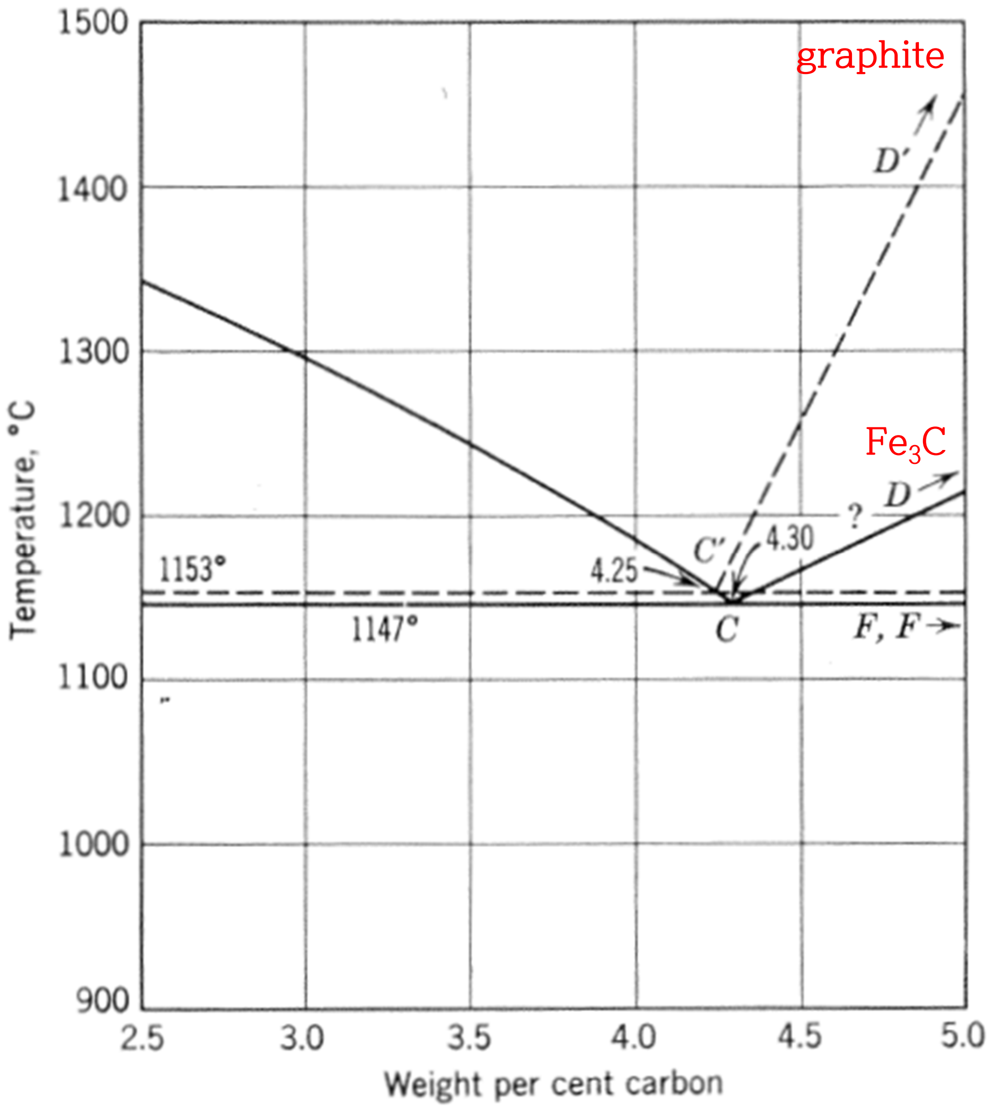
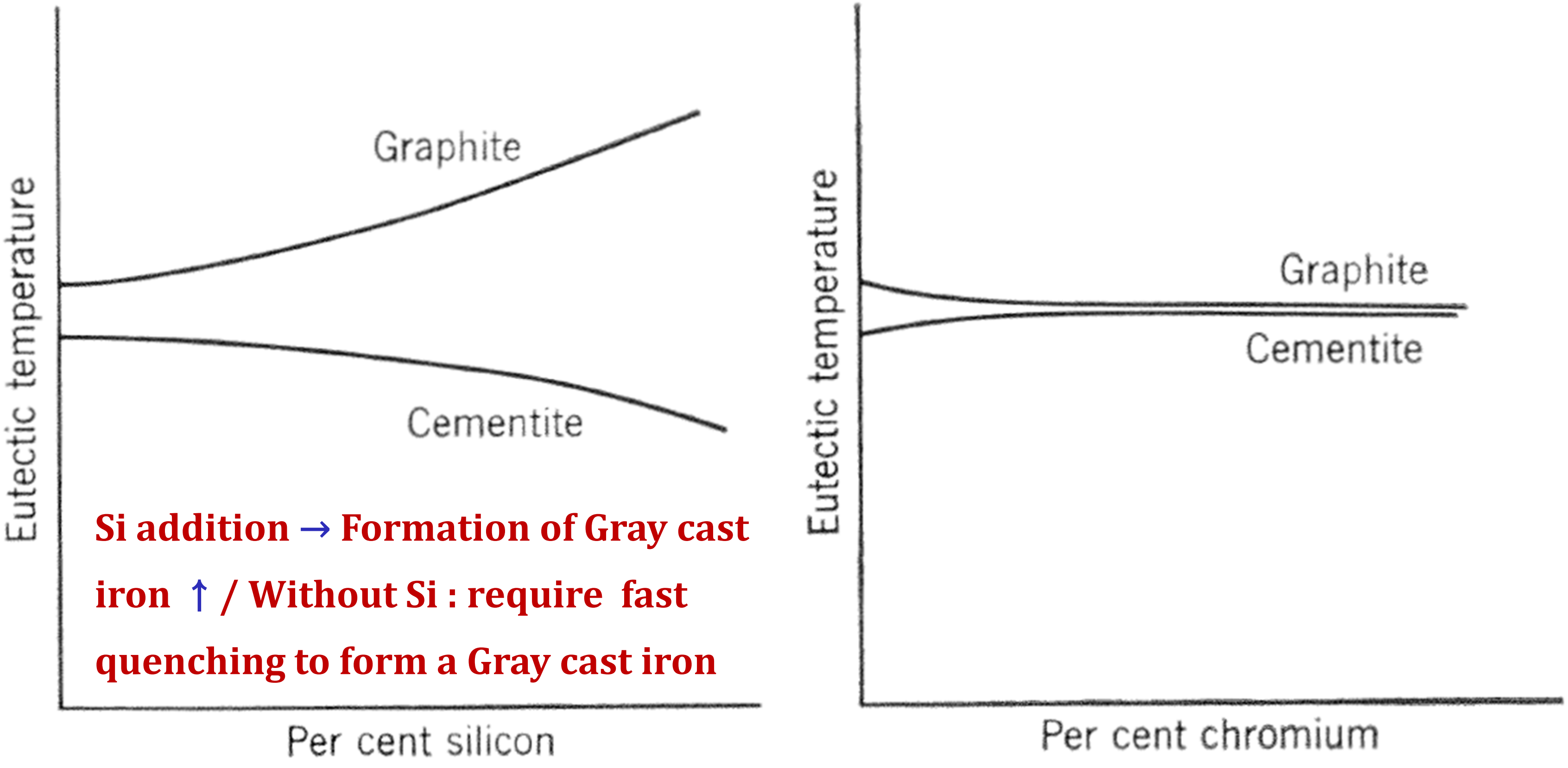


Fig. 6.35. Eutectic region of the iron carbon system.

* Addition effects of other elements

① **Si → $T_E^{graphite}$ ↑ / $T_E^{Cementite}$ ↓**

② Cr: decreasing the temperature rage where graphite is formed



Si addition → Formation of Gray cast iron ↑ / Without Si : require fast quenching to form a Gray cast iron

Fig. 6.36. Effect of third component on the eutectic temperatures (schematic). (a) Silicon type, (b) chromium type.

* Graphite morphology

2D: separated flake shape

3D: Continuous flake shape after dissolving out the iron

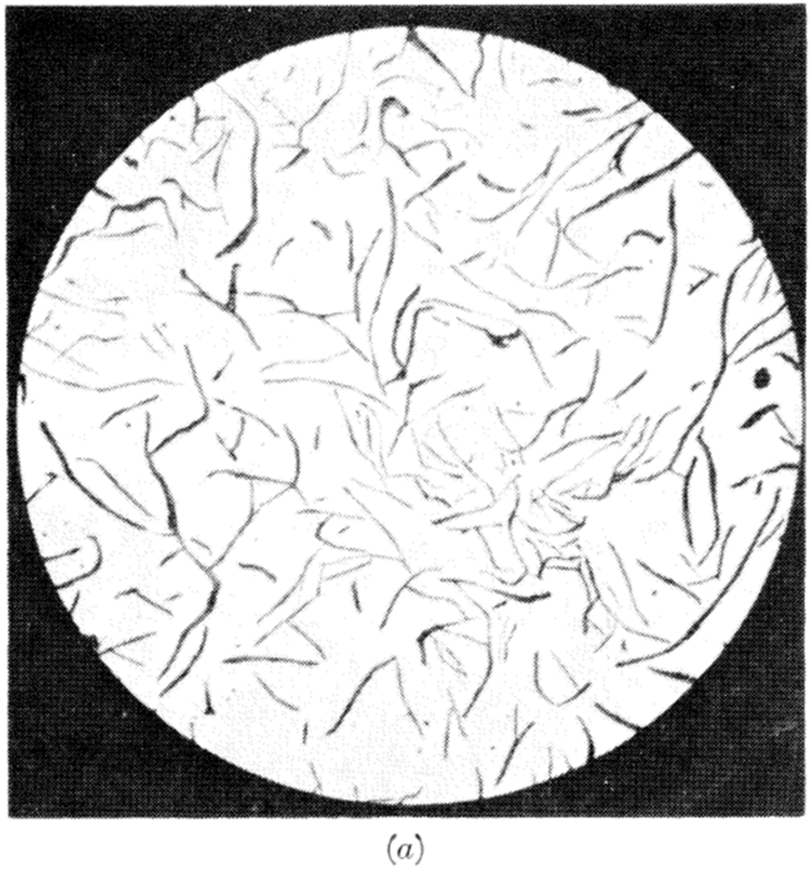


Fig. 6.37. Graphite in cast iron. (a) Nodular,

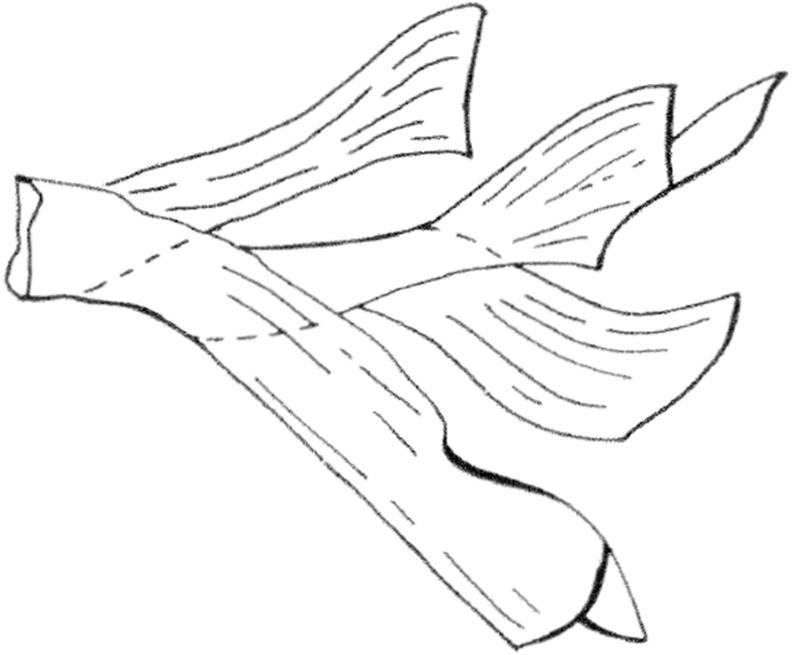


Fig. 6.38. Continuous graphite flake (schematic).

- **Spheroidal graphite: Similar to the Si shape control method used for Al-Si for improving mechanical properties, a small amount of Cerium was added to gray cast iron**

Continuous flake → formation of discrete spherulet

* Spherulitic graphite morphology

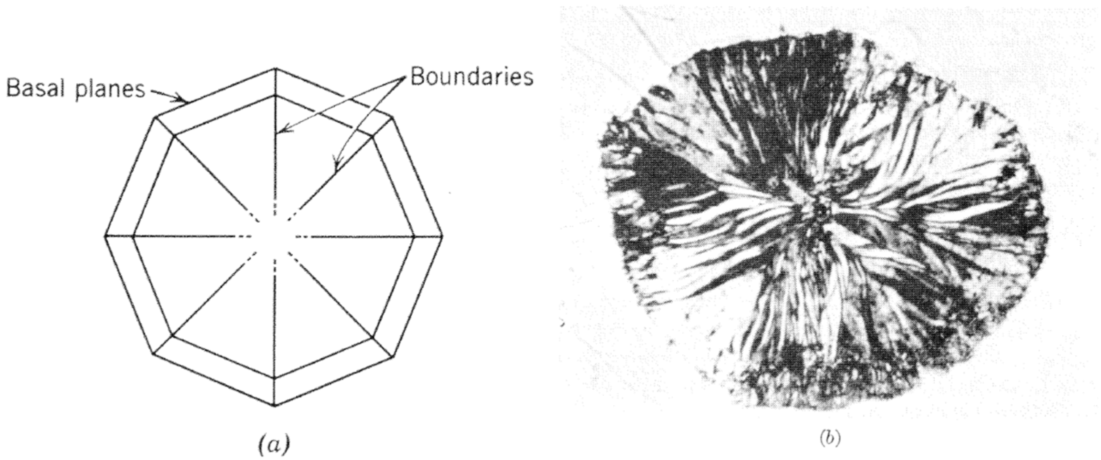
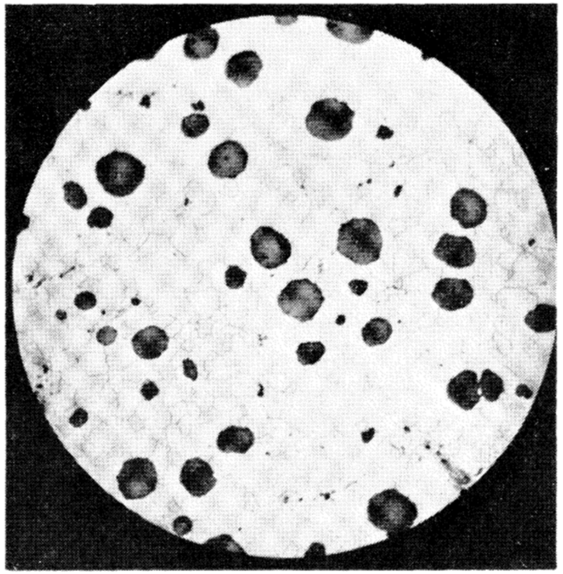


Fig. 6.39. Spherulet of graphite. (a) Schematic, (b) photomicrograph.



(b)

Fig. 6.37. Graphite in cast iron. (b) spherioidal.

- Orientation: everywhere such that the basal plane of the structure (which is the low E surface) faces the melt.→ highly polyhedral structure
- Probably most stable form, energetically (combine a low surface area → **spherical shape)**
- appears during long-term heat treatment of cast iron (malleableizing) : most stable configuration will be approached.
- Development of Spherulitic form = very low contents of sulfur in Iron melt/ Addition of spherodizing agent (Ce or Mg) → **combining with sulfur /** Addition of inoculant (Si) → produce graphite rather than cementite

13) Peritectic Solidification

: Occurs when two liquidus lines intersect with a slope of the same direction

∗ Eutectic reaction: One liquid is balanced with two solid phases at a fixed composition and temperature

∗ Peritectic reaction l+**α→β**

→ complete equilibrium

: Only possible under equilibrium solidification conditions.

→ at peritectic temperature

during cooling, Liquid composition P / α composition S

① C_0 → l+**α→β**

② C_1 or C_2 → Primary α or liquid + β

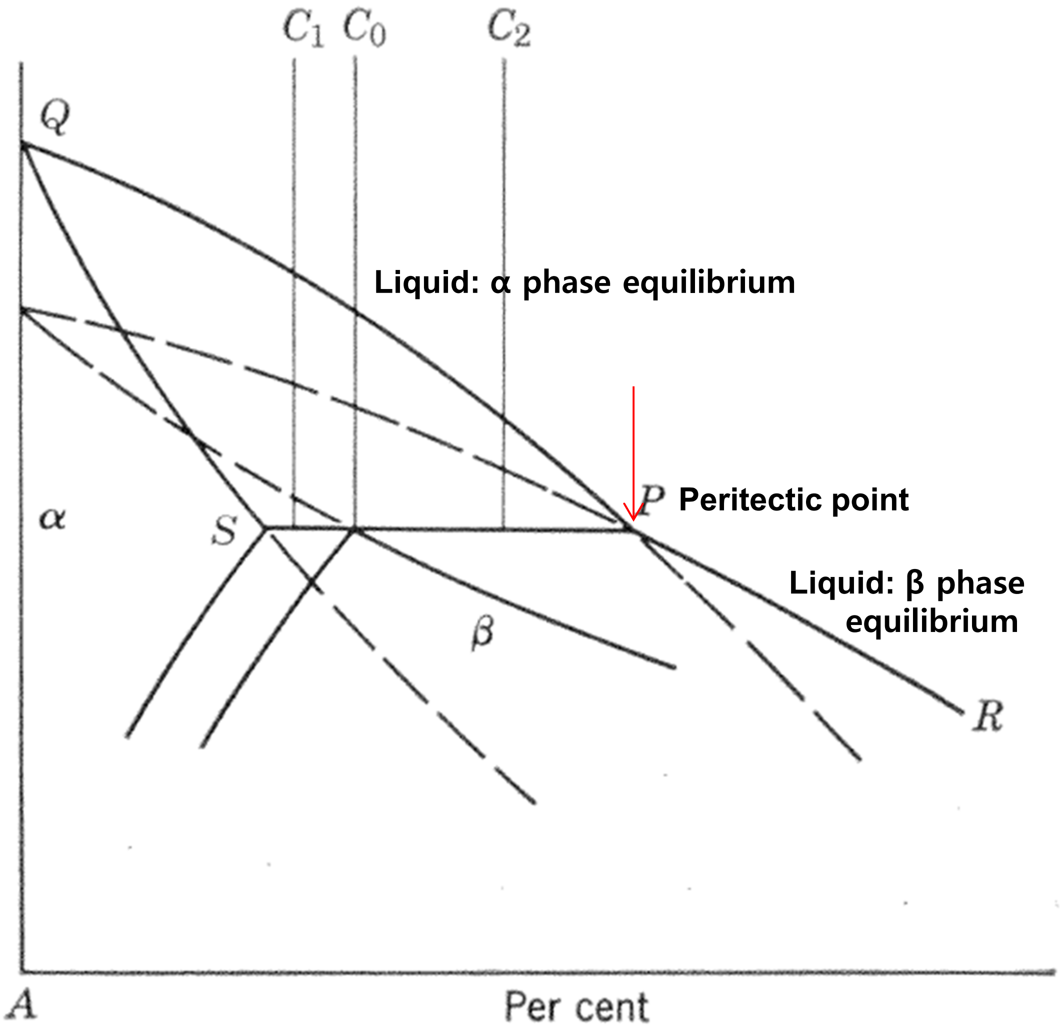


Fig. 6.40. Peritectic system, showing equilibrium phase boundaries —— and nonequilibrium phase boundaries ---.

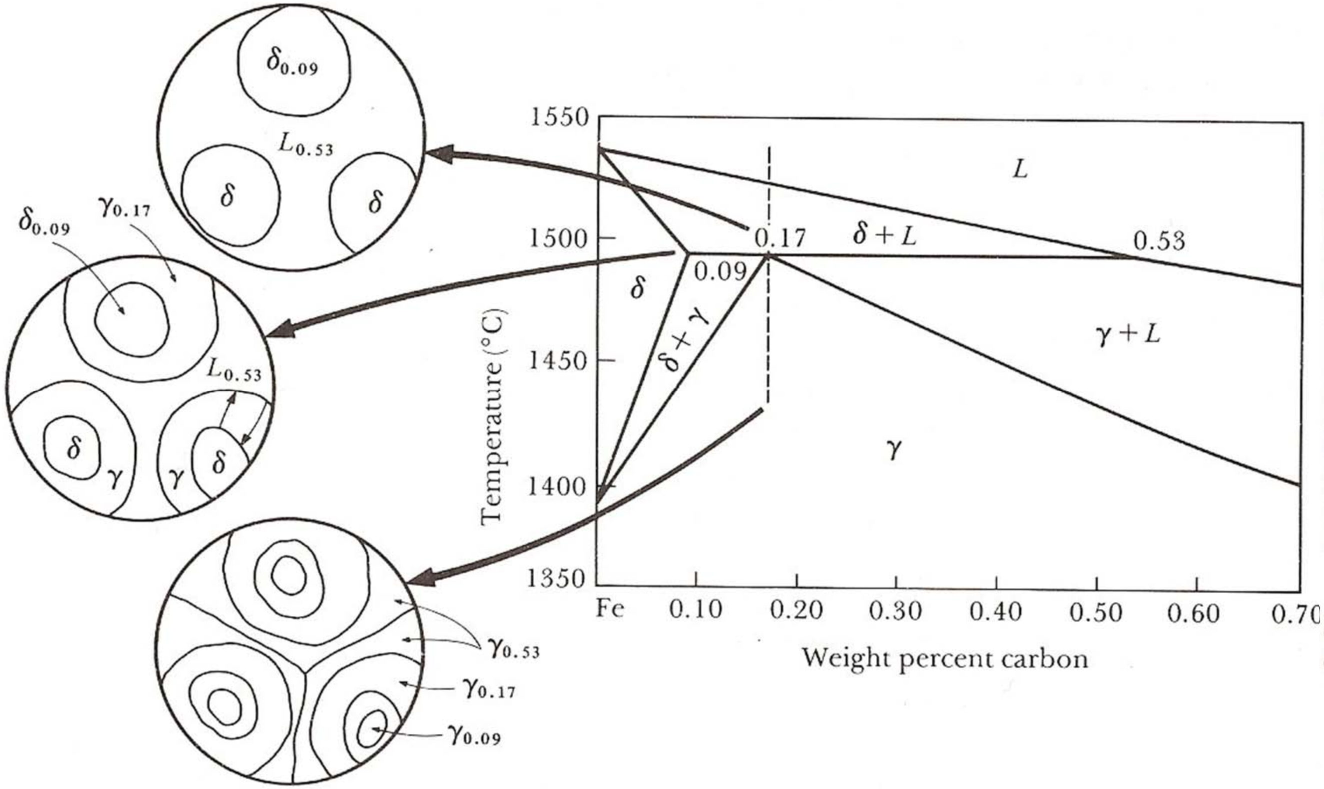
- $L + \alpha \rightarrow \beta$ is a very slow reaction except for the initial state, because liquid and α are separated by β

→ Diffusion must always occur for reaction to continue

→ When β is thickened (diffusion distance increases), the reaction slows down.

- Solidification and microstructure that develop as a result of the peritectic reaction

→ Unlike eutectic, peritectic does not grow into lamellar structure.



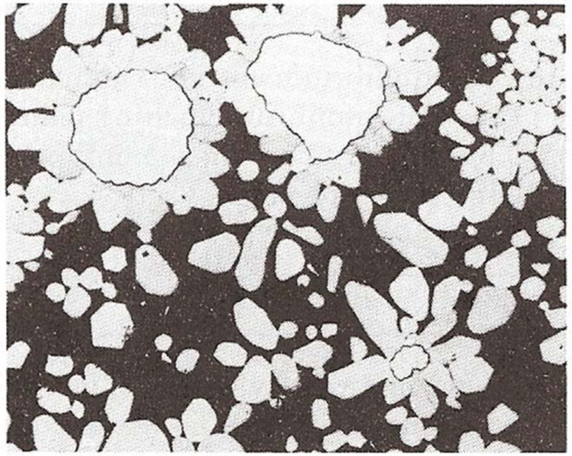


FIGURE 10-24 The peritectic reaction in a Cd-10% Cu alloy begins when rounded

- $L + \alpha \rightarrow \beta$ is a very slow reaction except for the initial state, because liquid and α are separated by β
- Uhlmann and Chadwick: Ag-Zn peritectic experiment

→ Peritectic melt of composition M_1 :

→ below T_3, β matrix + massive α dendrites

→ Dendrite α phase remaining at wide composition range and growth speed

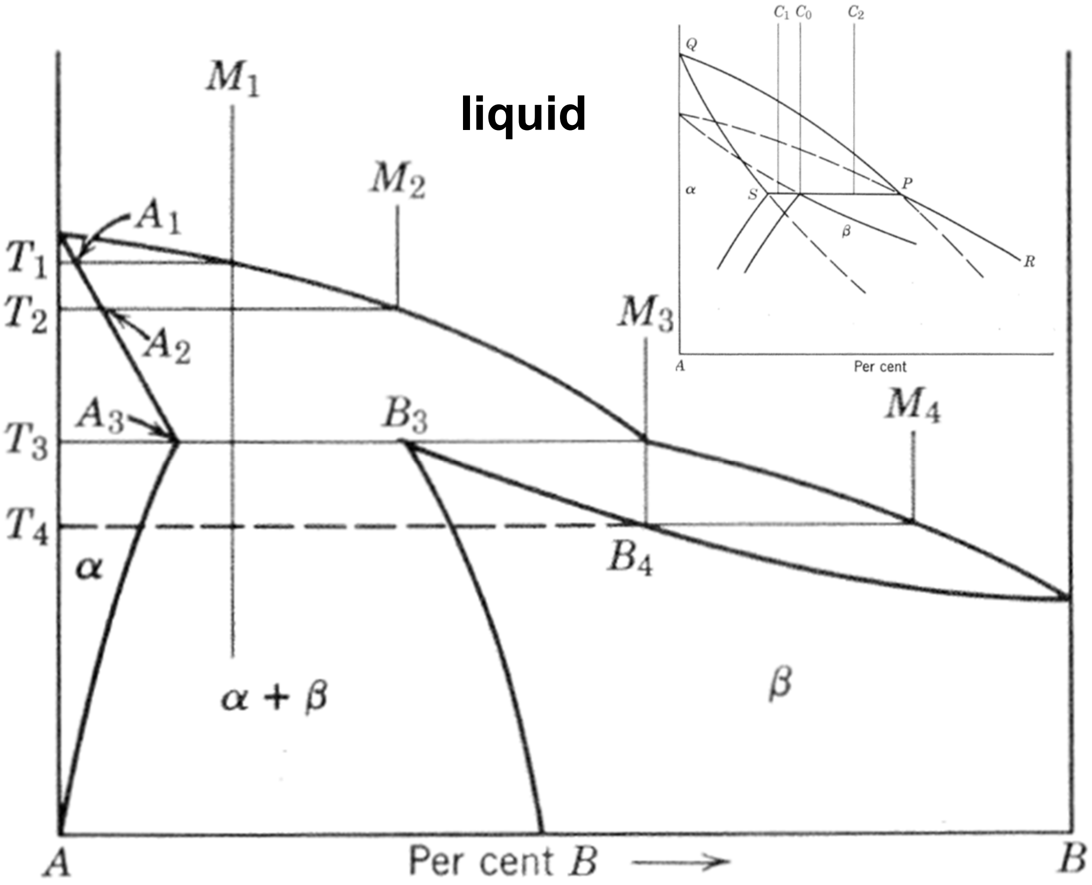


Fig. 6.41. Peritectic system.

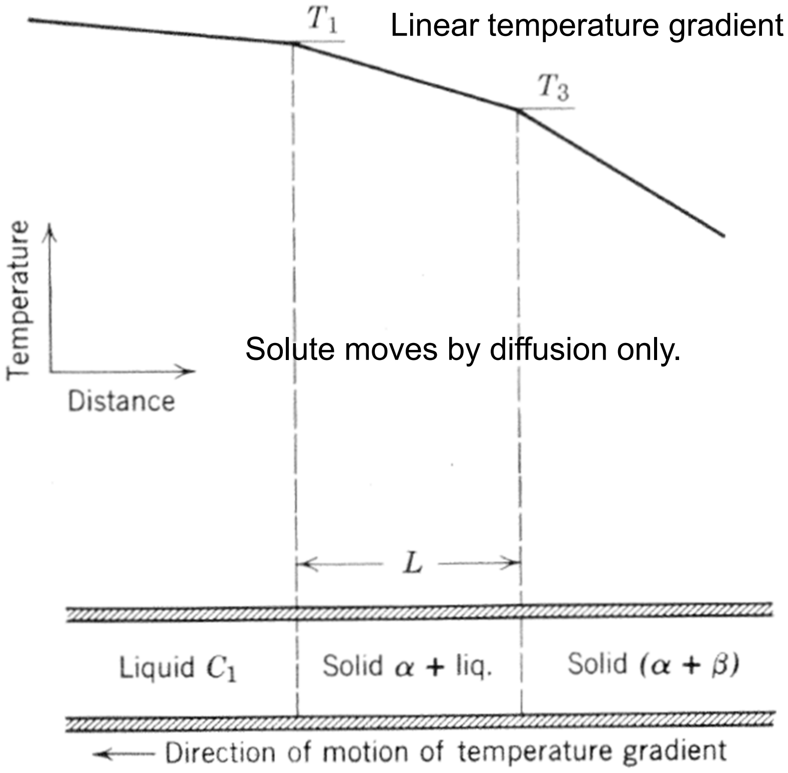
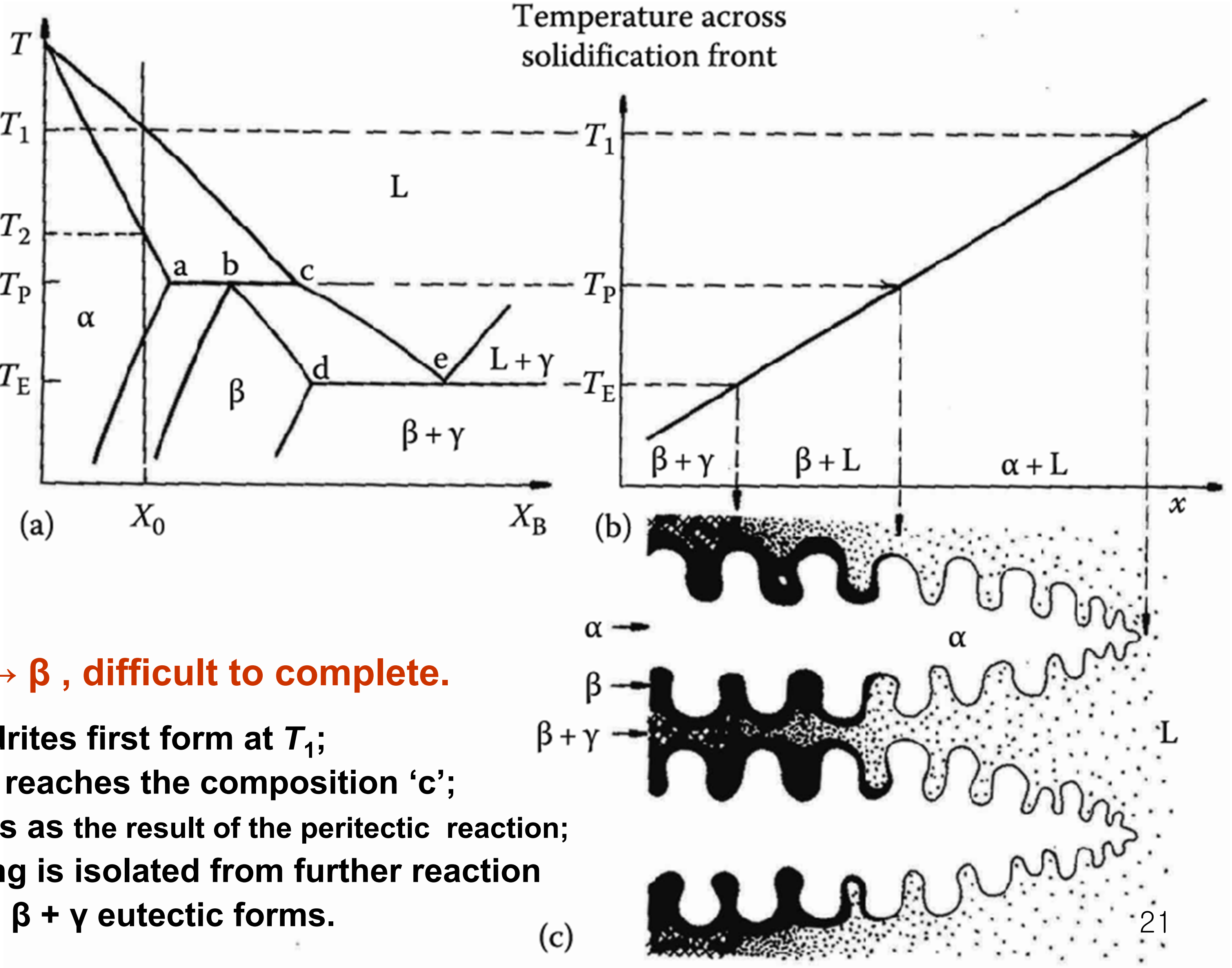


Fig. 6.42. Solidification of a peritectic in a temperature gradient.

* L + α → β is a very slow reaction except for the initial state, because liquid and α are separated by β



- **L + α → β , difficult to complete.**

- **α dendrites first form at T_1;**
  Liquid reaches the composition ‘c’;
  β forms as the result of the peritectic reaction;
  α coring is isolated from further reaction
  finally β + γ eutectic forms.

6.4. Solidification in the presence of a solid phase

- If liquid metals contain particles of solid in suspension; their distribution in the resulting solid influence dislocation content (page 58) or directly the mechanical properties. → **relevant to consider the interaction btw an advancing S-L interface and solid particles in the liquid.**
- Three factors that may influence the final location of a particle

(1) If "density" of particle is different from that of liquid: particle ~ float or sink

- Particle behavior dominated by its buoyancy (positive or negative)

: depends on density difference and the size and shape of the particle

Ex) A particle (sufficiently small) will remain in suspension indefinately as a result of its Brownian motion even if its density is substantially different from that of the liquid. The actual size for effective Brownian motion depends on the density difference, but in general is of the order of 0.1 **μm**.

* Rate (B) of ascent or descent for large particle: by Stokes formula

① Sphere,

$$B = \frac{2}{9}\frac{gr^2(D_1 - D_2)}{\eta}$$

r = 1 **μm particle/ Density difference, Δd=2gm/cm^3**

→ B = order of 10^{-4} cm/sec

② For nonspherical shapes, the value of B is smaller because a particle always tends to orient itself so that it offers the max. resistance to its own motion through the liquid.

(2) Second factor = "Fluid motion"_ generated as the liquid enters the mold

large enough to maintain in suspension particles that would sink or float in a stationary liquid

: persist for a considerable time before it gives way to convection caused by thermal and composition gradient.

(3) Third factor = "Interface speed" : Although there may be some vertical separation due to flotation or sedimentation, and some radial separation resulting from centrifugal forces, the smaller particles may remain suspended with a nearly random distribution.

→ ∴ The final distribution in the solid depends on whether a particle is "trapped" in situ by the advancing S-L interface or whether it is pushed ahead as the interface moves forward.

→ Experiments (Uhlmann & Chalmers) : some nonmetallic system

1) Fast rate of advancing interface (>critical velocity, CV) : particles are "trapped".

(ex) Mgo particle in Orthoterphenyl: critical velocity_about 0.5 um/sec

2) Although the CV varies from 0 to 2.5 μm/sec depending on the type of matrix and particle, no definitive composition and crystallographic effects have been identified.

3) (surprising feature) Critical velocity is independent of particle size change.

→ This CV (up to 2.5 μm / sec or 1 cm / hr) is very slow compared to most practical solidification or crystal growing processes and it is very unlikely that dispersed particles can change the solidification process if they have a similar CV in metal and semiconductor.

* Solidification of a liquid in a porous solid

: Little attention has been paid to the solidification of a liquid metal that is contained in interconnected channels in a porous solid that is chemically inert to the solidifiying liquid.

(ex) Nonmetallic system: Freezing of water in Soil → Induce "frost heaving load"

- These forces arise not because water expands on freezing, but because a water layer persists between ice and solid particles. As ice is formed, more water is drawn into the region of contact to replace what has frozen. This water in turn stars to freeze, causing more water to be "sucked" in, and forcing the existing ice away from the soil particle.

→ Preference, energetically, for the existence of a liquid layer btw the two solids

→ A liquid metal contained in a porous matrix may have a similar surface E relationship, in which case very large forces could be exerted, tending to disrupt the matrix.

7. Macroscopic Heat Flow and Fluid Flow

7.1. General considerations

*** Products made by solidification process should fulfill two major requirements.**

(1) Geometrical consideration

: external shape _satisfactory
& internal voids_within permissible
limits of size, shape, and location

(2) Structural consideration

: whether the desired property is achieved
_determined by its structure

Before considering in detail the interaction of the various factors that control the structure and the geometry, however, it is necessary to review the problems associated with the flow of metal into a mold and the extraction of heat from the metal.

→ These two problems are by no means independent of each other, because loss of heat by the metal while it is flowing into a mold is often a limiting process.

7. Macroscopic Heat Flow and Fluid Flow

7.2. Fluid Flow

* The ability of a molten metal to flow =

(1) poured from a container in which it was melted into a mold in which it is to solidify.

: effect of the macroscopic geometry of the casting (Chapter 7)

(2) Relative motion of different parts of the liquid can occur while it is solidifying.

: its implications in relation to the structure of the solidified metal (Chapter 8)

1) Viscosity of liquid metal

liquid metal : Flow rate depends on the force = shear rate is proportional to the shear stress

ex) Flow rate of a liquid through a tube depends on the pressure difference btw the ends of the tube (**ΔP**), on its length (l), and on the radius of the tube (r).

The quantity flowing per unit time, Q

$$\boxed{Q = \frac{\pi r^4}{8\mu} \cdot \frac{P_1 - P_2}{l}}$$

μ = viscosity

→ **The formula given above applies only in cases in which the flow is of the "stream-line" or laminar type, which occurs at relatively slow rates of flow.**

Mold Filling

Bernouli's Equation:

$$p/w + Z + q^2/2g = \text{constant}$$

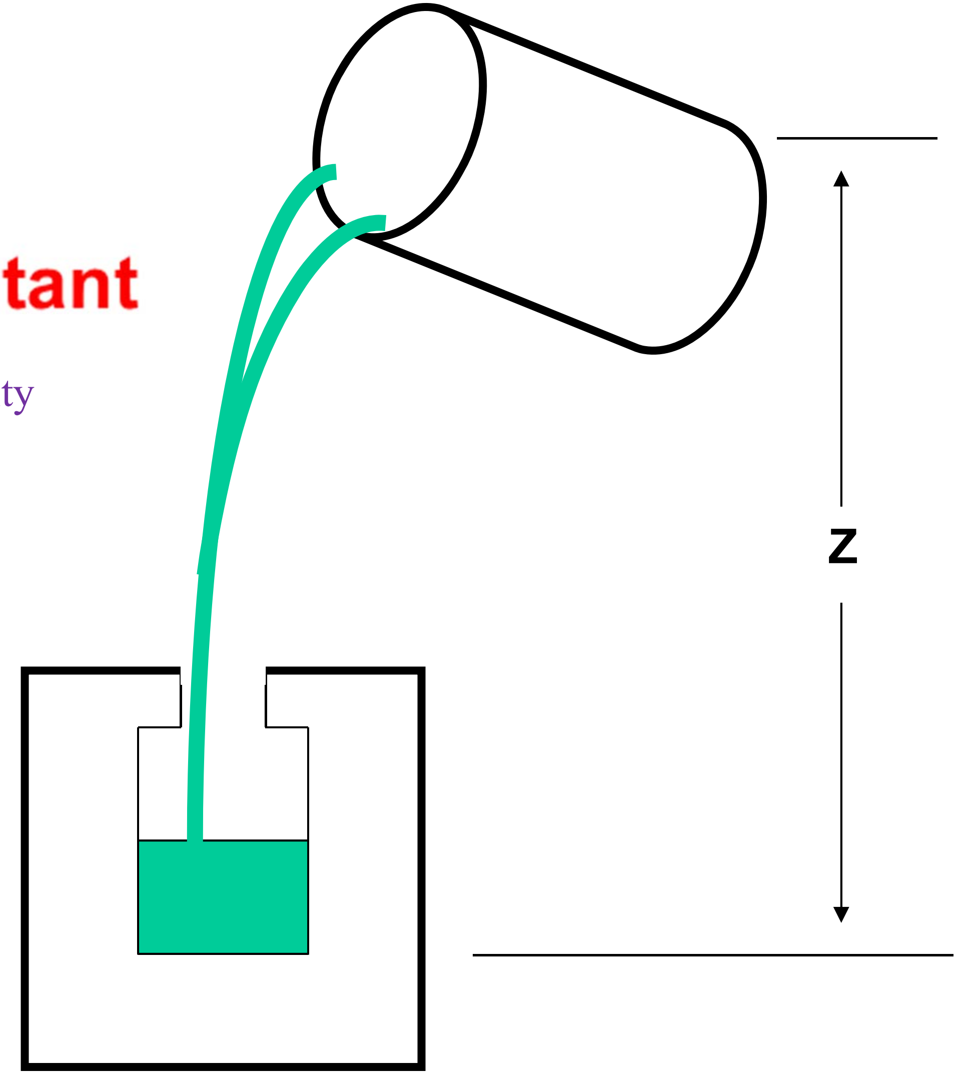
(p= pressure w = specific weight q = velocity
g = gravity z = elevation)

Reynold's Number:

$$\text{Re} = \gamma v l / \mu$$

γ = density , v = velocity,
μ = viscosity, l = linear dimension

- **Short filling times**
- **Potential Turbulence**



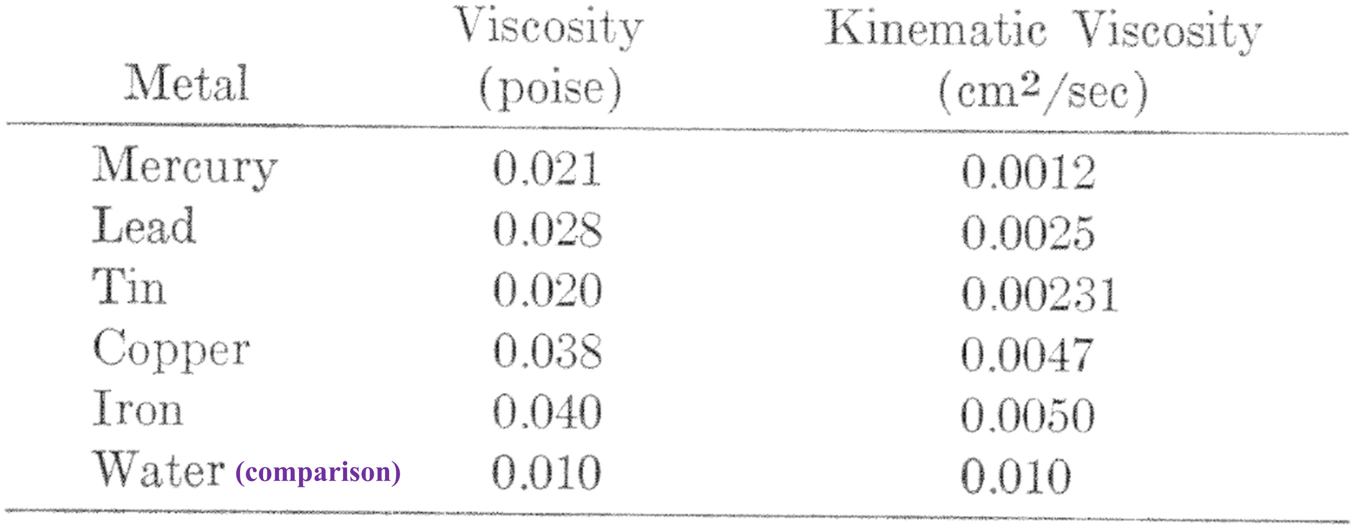
→ To compare "rates of flow" in this case,

Reynolds' number = $\gamma v l / \mu$

γ = density , v = velocity,
μ = viscosity, l = linear dimension

* If the value of Reynolds' number is high (>1400) for a tube leading out of a containing vessel, the flow becomes turbulent and Q drops below the value that would be calculated from the above formula. → Derive the Kinematic viscosity, μ / γ from the above equation : Used for calculation of flow rate when pressure difference is caused by flowing liquid → **For solidification it is considered more important.**

Table 7.1 Values of viscosity and kinematic viscosity of some liquid metals at T_m



Metal	Viscosity (poise)	Kinematic Viscosity (cm^2/sec)
Mercury	0.021	0.0012
Lead	0.028	0.0025
Tin	0.020	0.00231
Copper	0.038	0.0047
Iron	0.040	0.0050
Water **(comparison)**	0.010	0.010

→ Liquid metals, when they are completely liquid, flow rather more easily than water, and that their viscosity is seldom, if ever, a limiting factor in the process of filling a mold, even through a rather narrow channel.

Fragility

- **Fragility** ~ ability of the liquid to withstand changes in medium range order with temp.
  ~ extensively use to figure out liquid dynamics and glass properties
  corresponding to "frozen" liquid state

< Classification of glass >

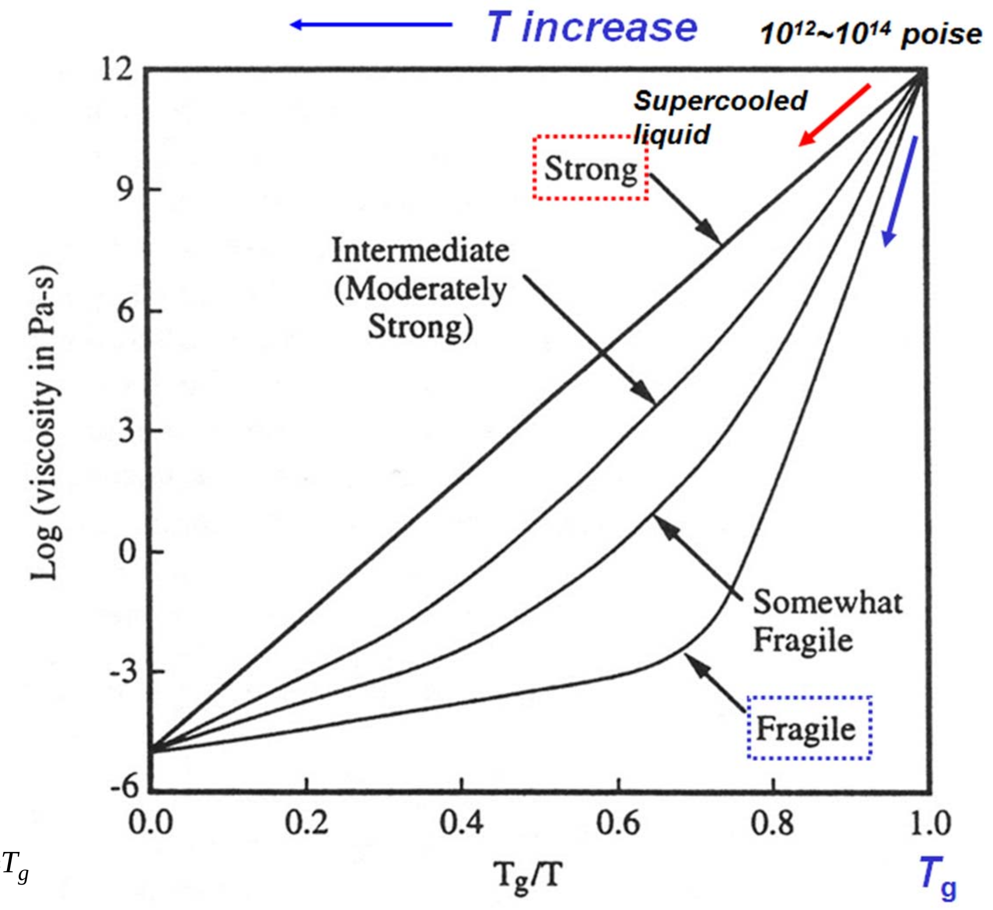
Strong network glass : Arrhenius behavior

$$\eta = \eta_0 \exp[\frac{E_a}{RT}]$$

↕

Fragile network glass : Vogel-Fulcher relation

$$\eta = \eta_0 \exp[\frac{B}{T - T_0}]$$



< Quantification of Fragility >

$$m = \left.\frac{d \log \eta(T)}{d(T_{g,n}/T)}\right|_{T=T_{g,n}} = \left.\frac{d \log \tau(T)}{d(T_g/T)}\right|_{T=T_g}$$

Slope of the logarithm of viscosity, η (or structural relaxation time, τ) at T_g