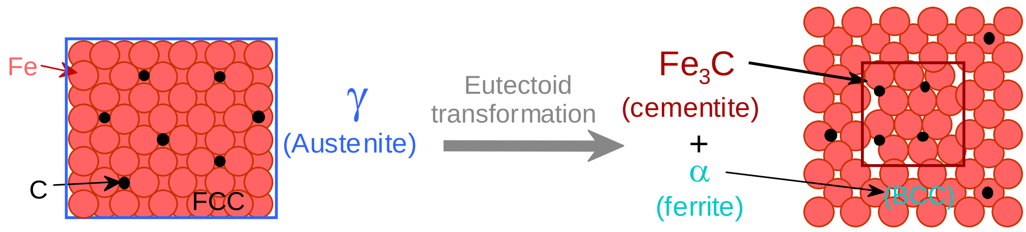
Chapter 7 Phase Transformations

§ 7-1 Phase Transformations in Metals



A. The Kinetics of Phase Transformations

Kinetics - study of reaction rates of phase transformations

– **measure degree of transformation as function of time (while holding temperature constant)**

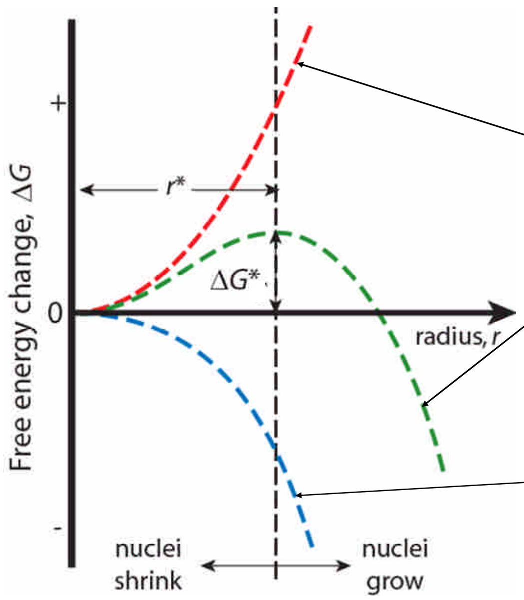
Solidification stages:

① Nucleation

- **nuclei (seeds) act as templates on which crystals grow**
- **once nucleated, growth proceeds until equilibrium is attained**

Nucleation Types

- **Homogeneous nucleation (均質成核)**
  - **nuclei form in the bulk of liquid metal**
  - **requires considerable supercooling (typically 80-300˚C)**



$$\Delta G_S = 4\pi r^2 \gamma$$

γ = surface tension

ΔG_T = Total Free Energy $= \Delta G_S + \Delta G_V$

Volume (Bulk) Free Energy

$$\Delta G_V = \frac{4}{3}\pi r^3 \Delta G_\upsilon$$

$$\Delta G_\upsilon = \frac{\text{volume free energy}}{\text{unit volume}}$$

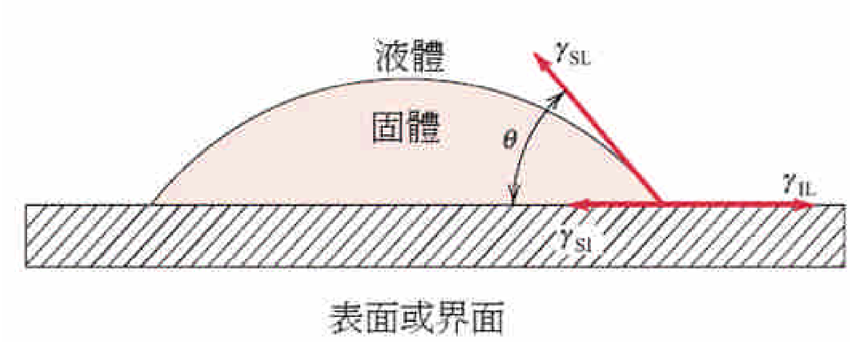
$$r^* = \frac{-2\gamma T_m}{\Delta H_f \Delta T}$$

r^* = critical radius
γ = surface free energy
T_m = melting temperature
ΔH_f = latent heat of solidification
$\Delta T = T_m - T$ = supercooling

Driving force to nucleate increases as we increase ΔT

Small supercooling ⇒ slow nucleation rate - few nuclei - large crystals
Large supercooling ⇒ rapid nucleation rate - many nuclei - small crystals

- **Heterogeneous nucleation (異質成核)**
  - **much easier since stable "nucleating surface" is already present — e.g., mold wall, impurities in liquid phase**
  - **only very slight supercooling (0.1-10 ^{o}C)**

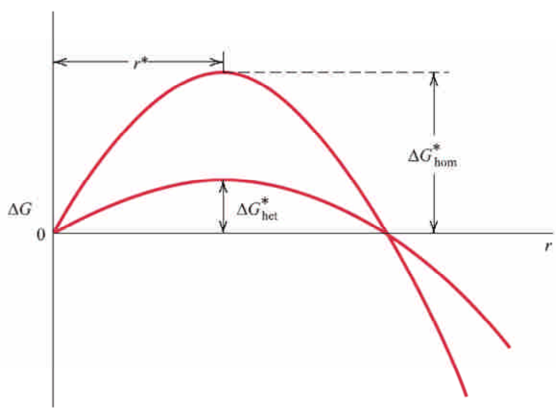


$$\gamma_{IL} = \gamma_{SI} + \gamma_{SL}\cos\theta$$

$$r^* = -\frac{2\gamma_{SL}}{\Delta G_v}$$

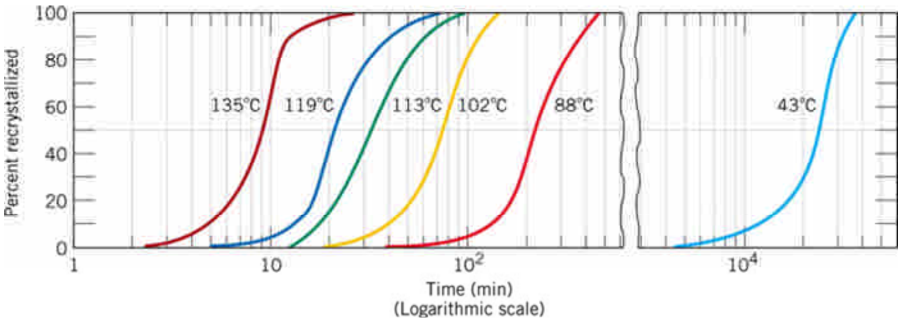
$$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3}{3\Delta G_v^2}\right) S(\theta)$$

$$\Delta G^*_{het} = \Delta G^*_{home} S(\theta)$$



② **Growth**

Avrami equation $\Rightarrow$ $y = 1 - \exp(-kt^n)$



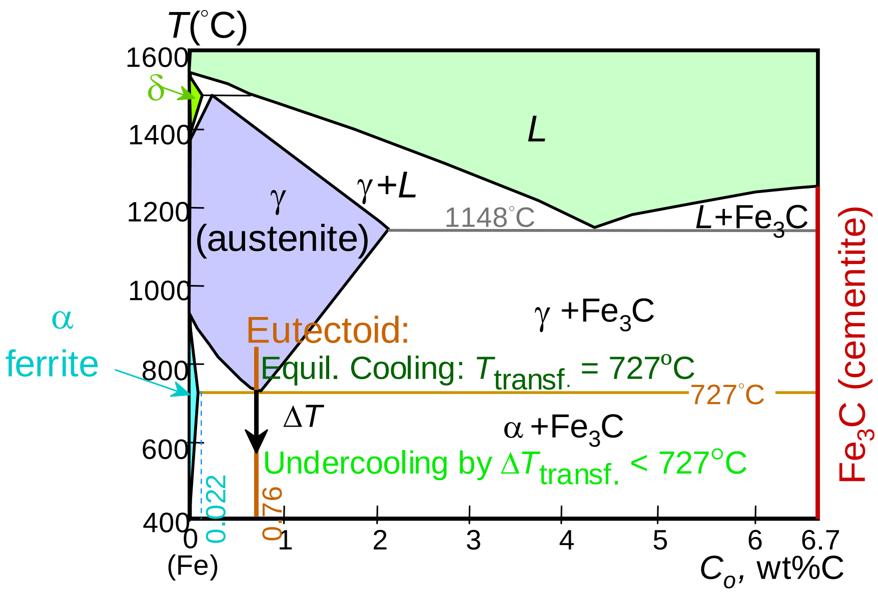
§ 7-2 Microstructural and Property Changes in Iron-Carbon Alloys

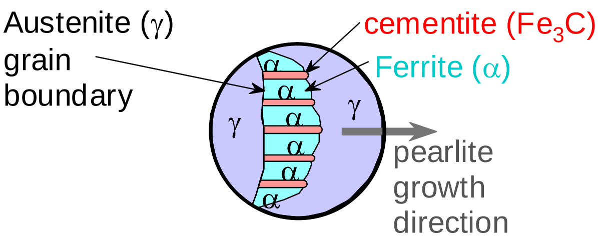
A. Isothermal Transformation Diagrams (TTT, 恆溫相變化圖)

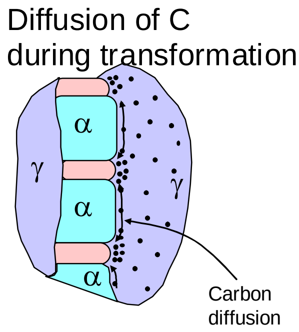
❶. Eutectoid transformation: Transformation of austenite to pearlite

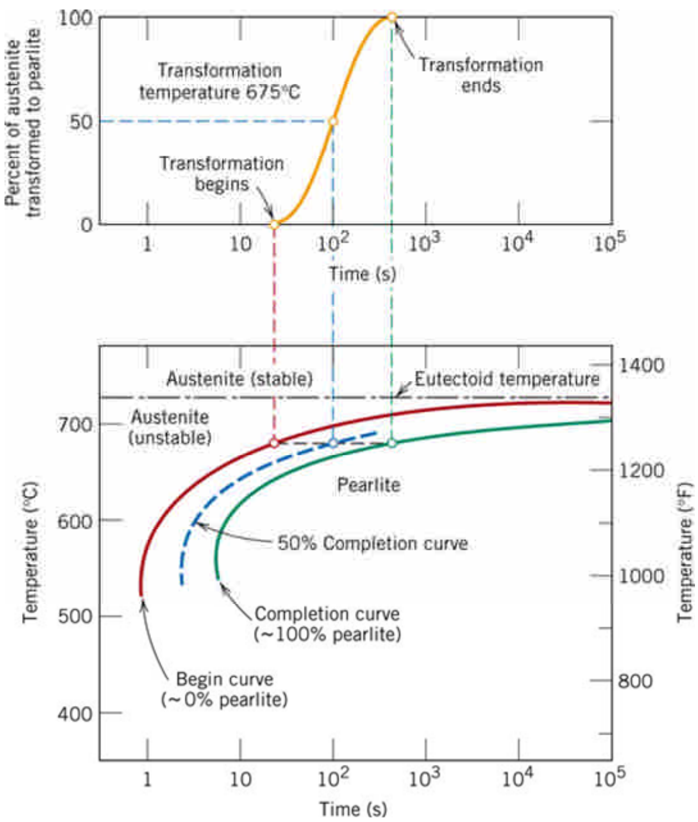
$$\gamma \Rightarrow \alpha + Fe_3C$$

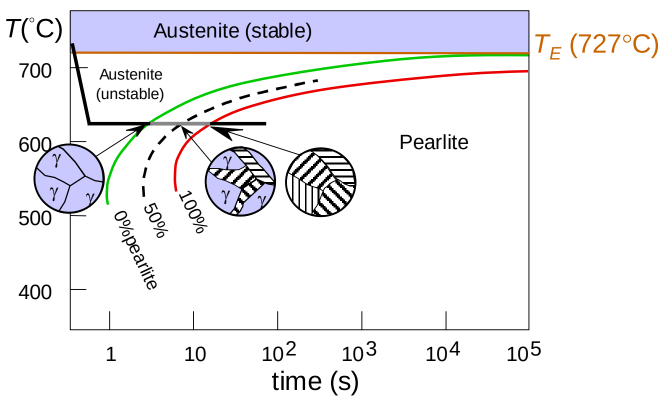
0.76 wt% C (γ)   0.022 wt% C (α)   6.7 wt% C (Fe_3C)

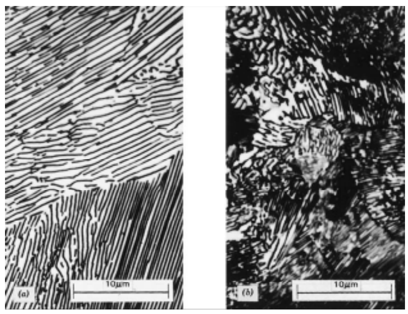








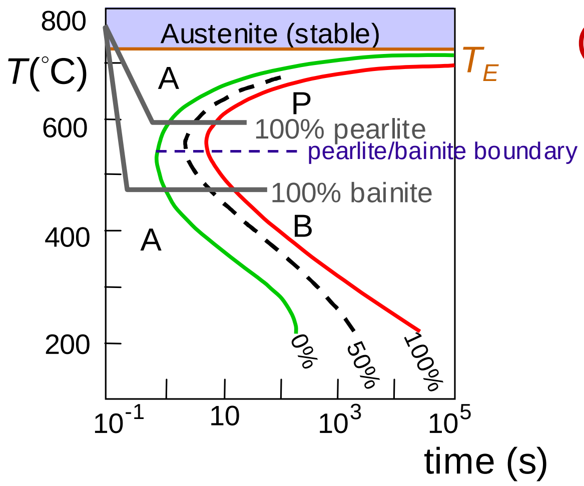


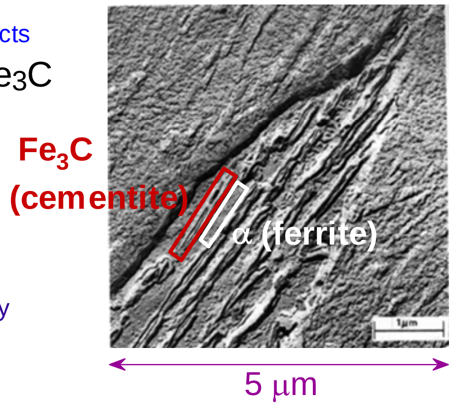


Coarse pearlite (粗波來鐵) ⇒ formed at higher temperatures – relatively soft

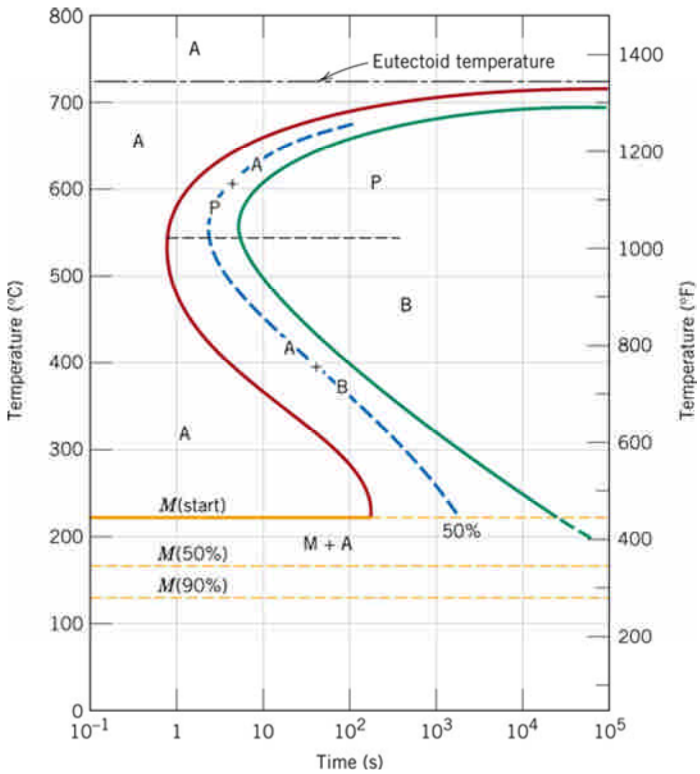
Fine pearlite (細波來鐵) ⇒ formed at lower temperatures – relatively hard

- Bainite: Non-Equilibrium Transformation Products
  --α lathes (strips) with long rods of Fe_3C
  --diffusion controlled.





Isothermal Transformation Diagrams (TTT, 恆溫相變化圖)



• 共析鋼恆溫相變化圖特徵

① 波來鐵不易在溫度接近A_1時出現

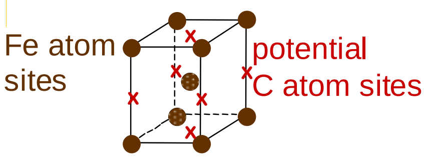
② 增加過冷度（低於A_1），縮短波來鐵變態時間

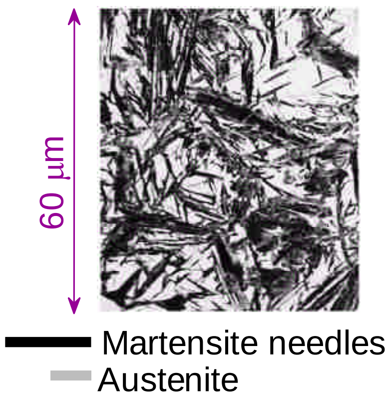
③ 變態鼻部出現在 540℃，且變態時間僅需數秒鐘

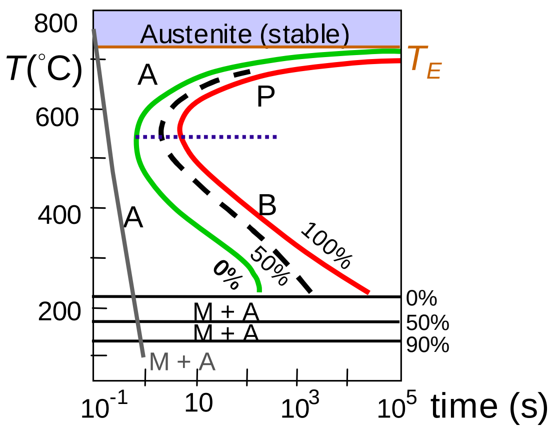
④ 變態溫度低於 540℃ ，
非層狀的肥粒鐵 + 雪明碳鐵（變韌鐵）出現

⑤ 變態溫度急速降低至 200℃ ，形成麻田散鐵

- **Martensite:**
  -- γ (FCC) to Martensite (BCT)
  -- γ to M transformation..
    -- is rapid!
    -- % transf. depends on T only.

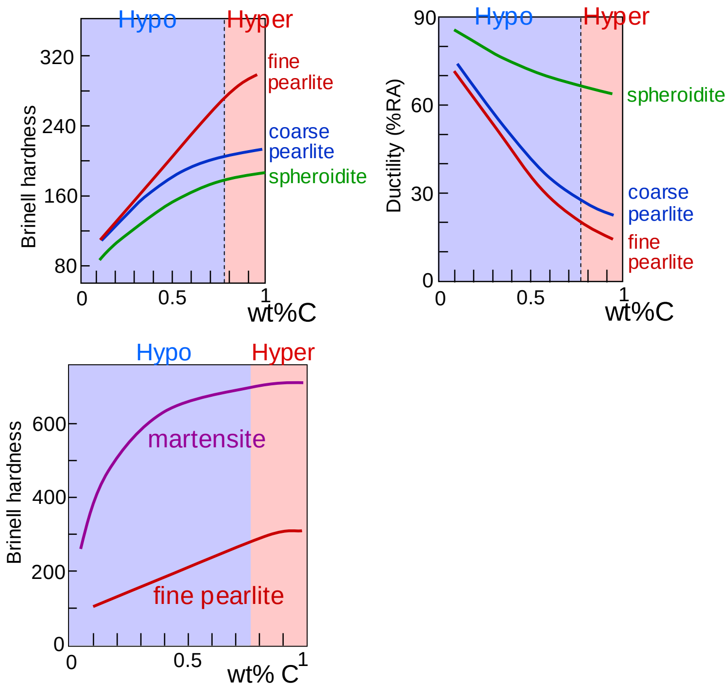




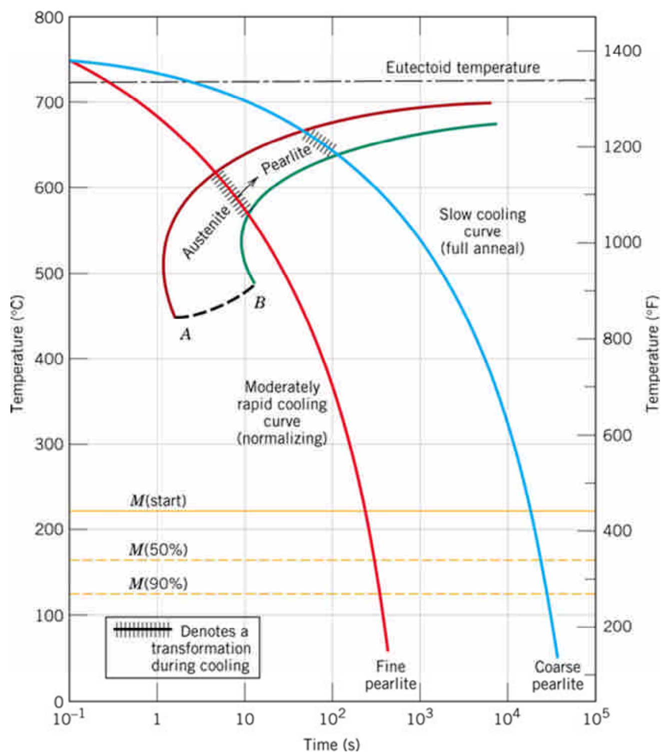


❷. Mechanical Behavior of Iron-Carbon Alloys

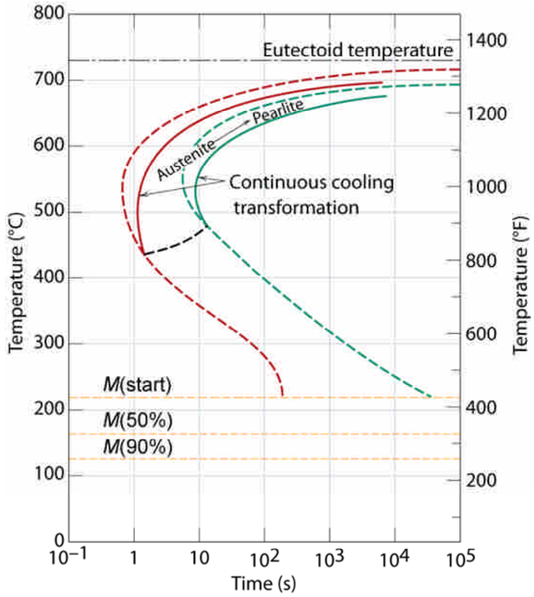
- **Increase C content: *TS* and *YS* increase, %*EL* decreases**
- **Hardness: martensite>> fine > coarse > spheroidite**
- **%RA: martensite <<fine < coarse < spheroidite**



B. Continuous Cooling Transformation Diagrams (CCT, 連續冷卻相變化圖)



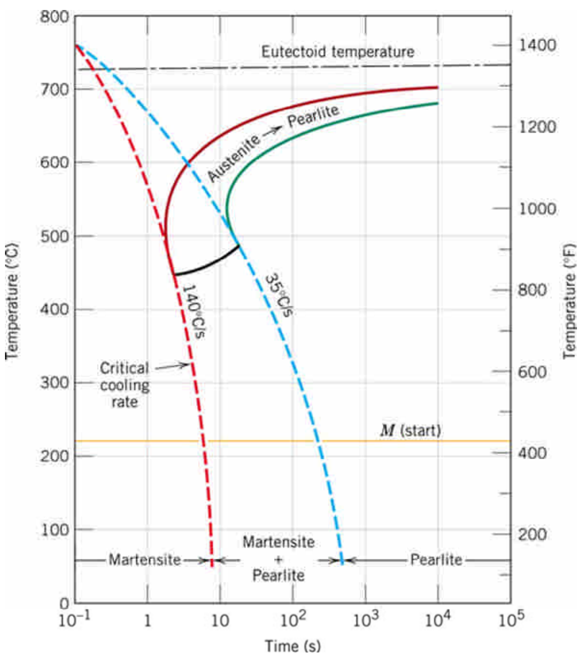
❶. Superimposition of isothermal & continuous cooling transformation diagrams



共析鋼的 CCT 圖特徵

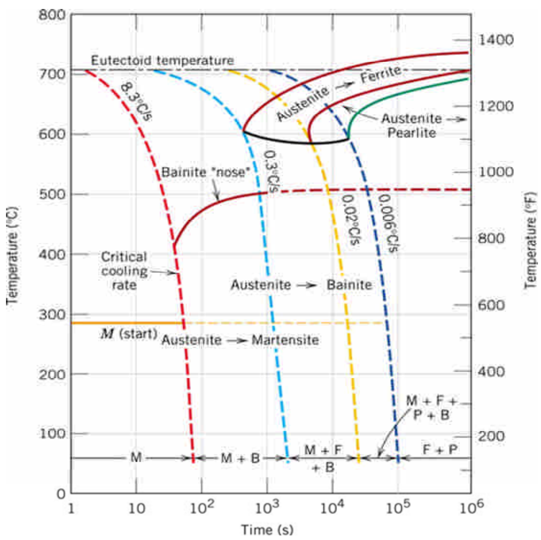
① CCT 圖中，波來鐵的變態起始與變態終止時間延遲
② CCT 圖中沒有變韌鐵出現
③ CCT 圖中出現變態中止線

❷. Critical cooling rate



Upper critical cooling rate (上臨界冷卻速率)
Lower critical cooling rate (下臨界冷卻速率)

❸. CCT curve for the 4340 steel alloy



鋼材中添加合金元素的目的

① 提高硬化能 (hardenability)
② 改善鋼材機械性質
③ 提供肥粒鐵的固溶強化
④ 產生合金碳化物，增加鋼材耐蝕、耐熱、耐磨等特性

§ 7-3 Heat Treatment of Steels

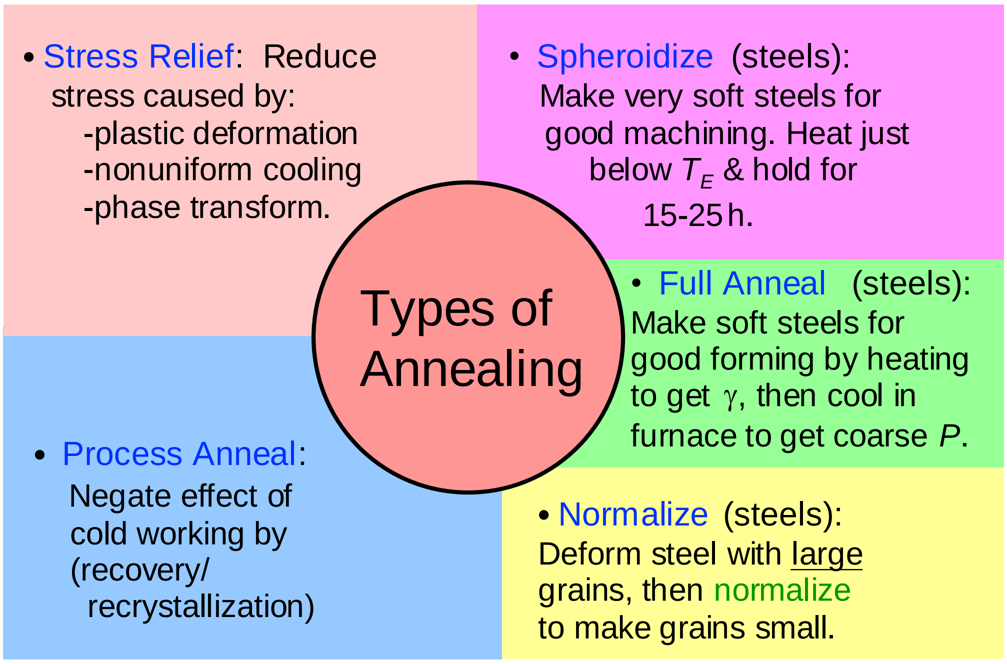
A. Annealing (退火): Heat to T_{anneal}, then cool slowly

退火的目的

① 消除由冷卻或由常溫加工時所產生的應力
② 降低硬度
③ 改良材料的機械加工性
④ 調整結晶組織
⑤ 獲得所需的機械性質或物理性質
⑥ 消除化學成分的不均勻性

退火的種類

① 完全退火 (**full annealing**)
② 弛力退火 (**stress relief annealing**)
③ 製程退火 (**process annealing**)……



B. Normalizing (正常化)

正常化的目的

調整不良鑄造或鍛造組織，使其獲得略近於平衡狀態組織，以利後續工作

C. Homogenizing (均質化)

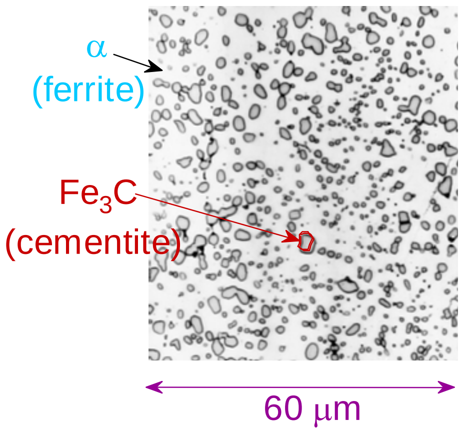
均質化的目的

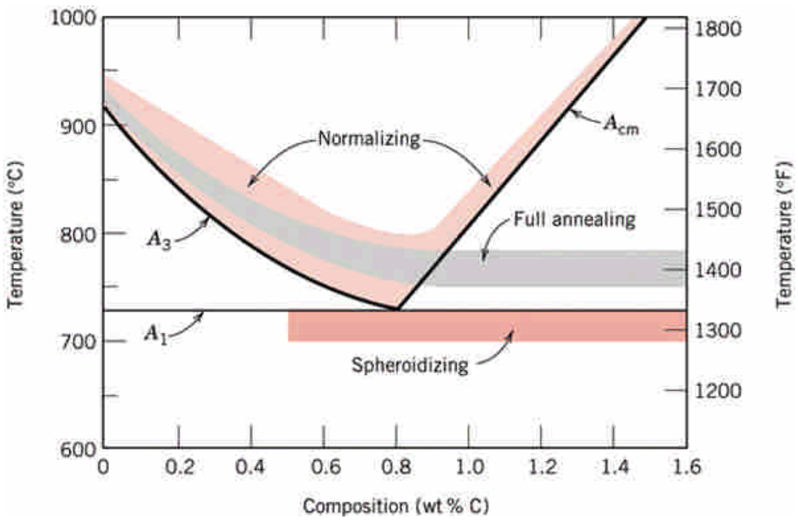
利用擴散作用消除鋼材內部巨觀或微觀的化學成分偏析現象

D. Spheroidizing (球化處理)

球化處理的目的

改善過共析鋼的切削性和塑性加工性、或增加材料淬火後的韌性





E. Quenching & Tempering (淬火與回火)

淬火的目的

使鋼材獲得麻田散鐵組織

回火的目的

消除淬火鋼材的內部應力，調節硬度，改善韌性

£ 回火過程鋼鐵材料的組織變化：(麻田散鐵 → 回火麻田散鐵)

①第一階段：麻田散鐵 → 低碳麻田散鐵 +ε 碳化物

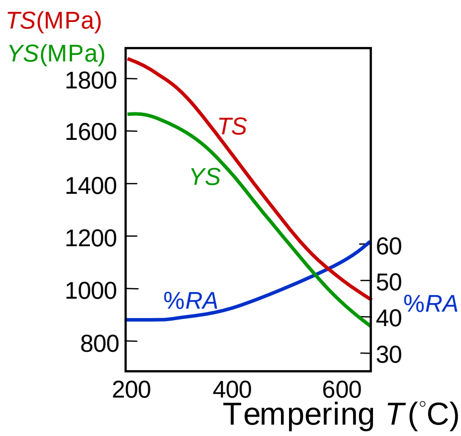
②第二階段：殘留沃斯田鐵 → 變韌鐵

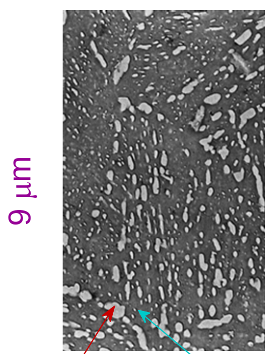
③第三階段：低碳麻田散鐵 +ε 碳化物 → 肥粒鐵 + 雪明碳鐵

④第四階段：雪明碳鐵 → 合金碳化物 (針對合金鋼)

Tempering Martensite

- **reduces brittleness of martensite,**
- **reduces internal stress caused by quenching.**



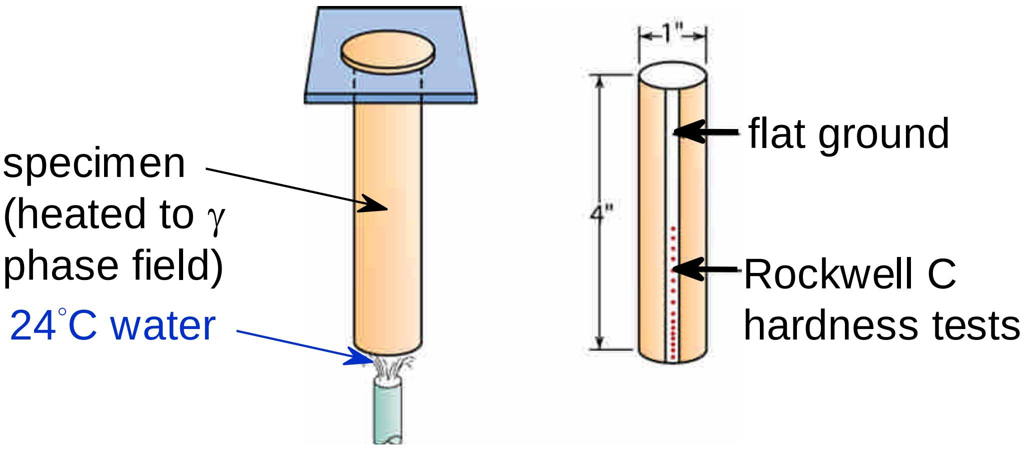


- produces extremely small Fe_3C particles surrounded by α.
- decreases *TS*, *YS* but increases %*RA*

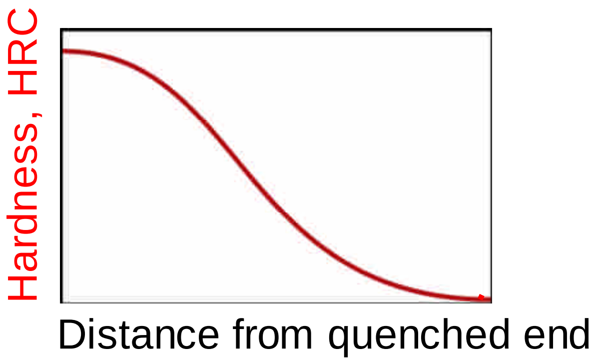
F. Hardenability (硬化能)

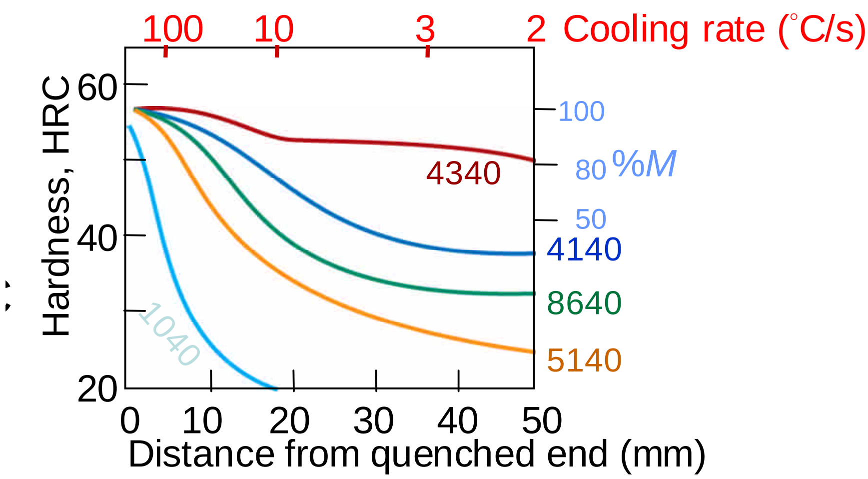
- 定義：鋼材在相同淬火條件下，材料斷面硬化之深度及硬度之分佈性能
  $\Rightarrow$ Ability to form martensite

- 硬化能試驗：
  ❶ **The Jominy End-Quench Test**



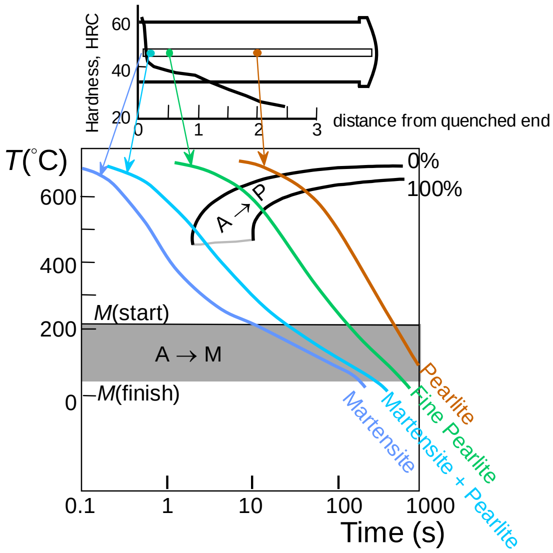
Hardness versus distance from the quenched end

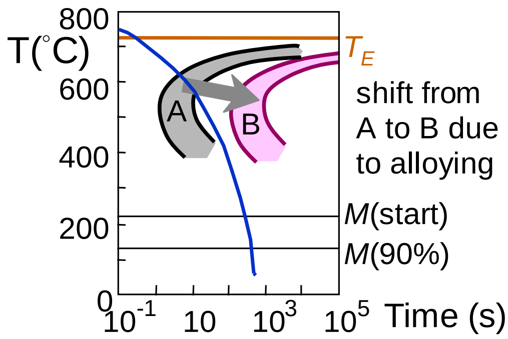




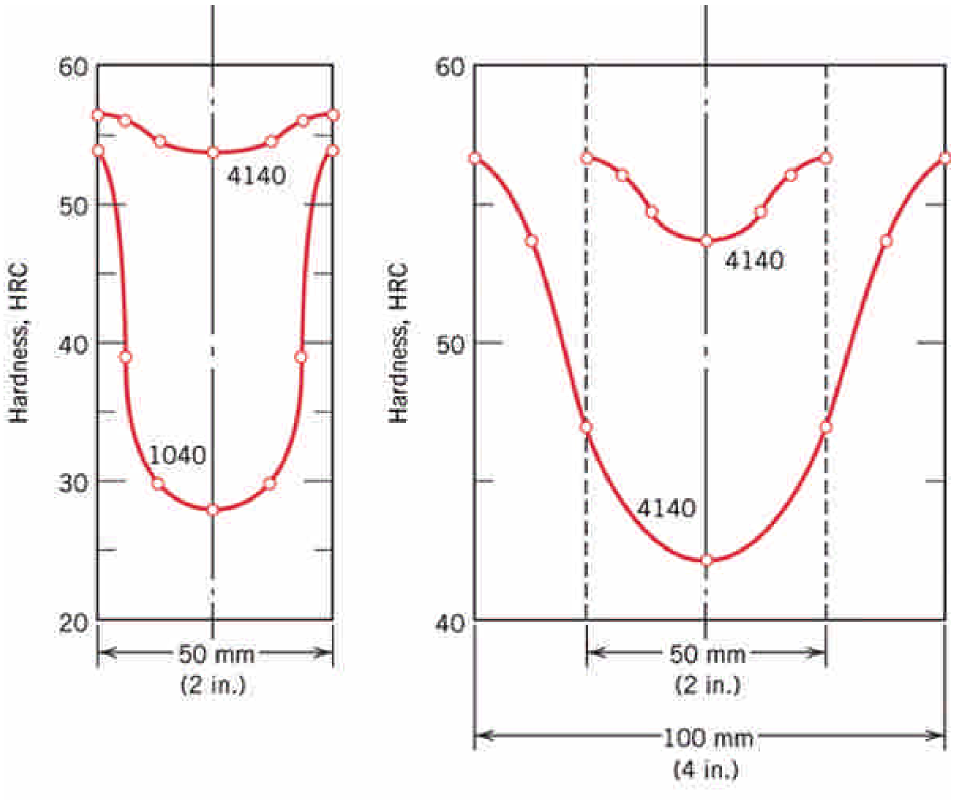
- **Hardenability:** **4340 > 4140 > 8640 > 5140 > 1040**

❷ CCT curves



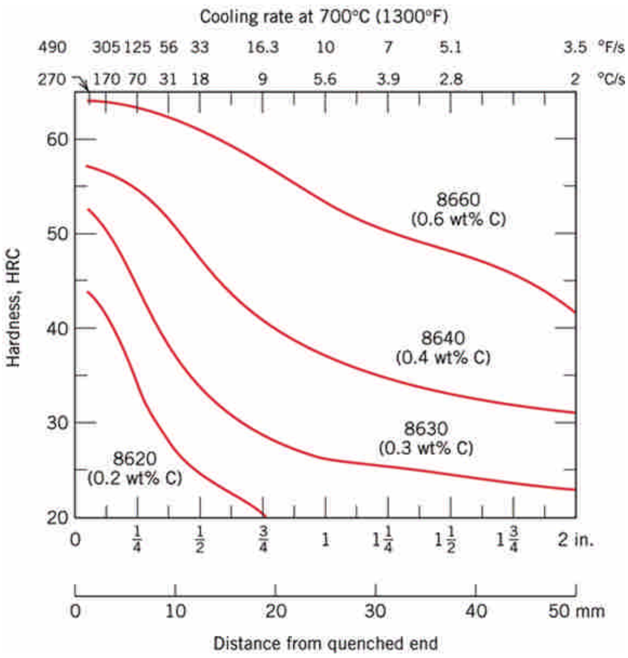


❸ Ideal Critical Diameter (DI，理想臨界直徑)



- 影響鋼材硬化能的因素：
  ① 含碳量　② 淬火液種類　③ 尺寸效應
  ④ 沃斯田鐵晶粒尺寸　⑤ 合金元素種類及含量

- **Effect of carbon content:**



- **Effect of quenching medium:**

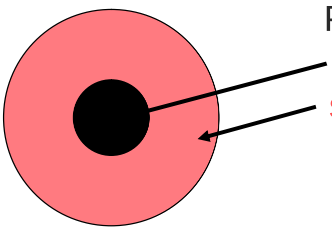
Medium	Severity of Quench	Hardness
air	low	low
oil	moderate	moderate
water	high	high

- **Effect of geometry:**

  When surface-to-volume ratio increases:

  -- cooling rate increases

  -- hardness increases



Position	Cooling rate	Hardness
center	low	low
surface	high	high

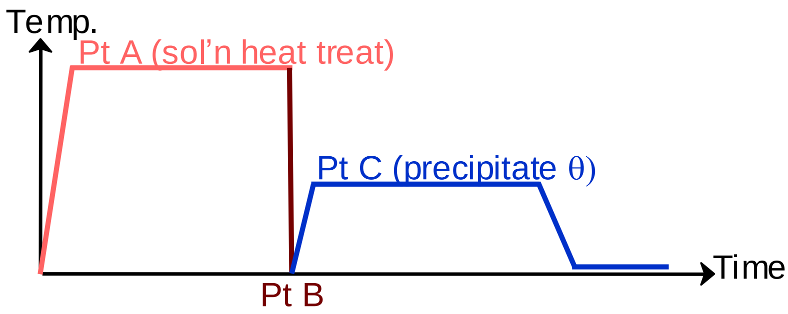
§ 7-4 Precipitation Hardening (Age hardening)

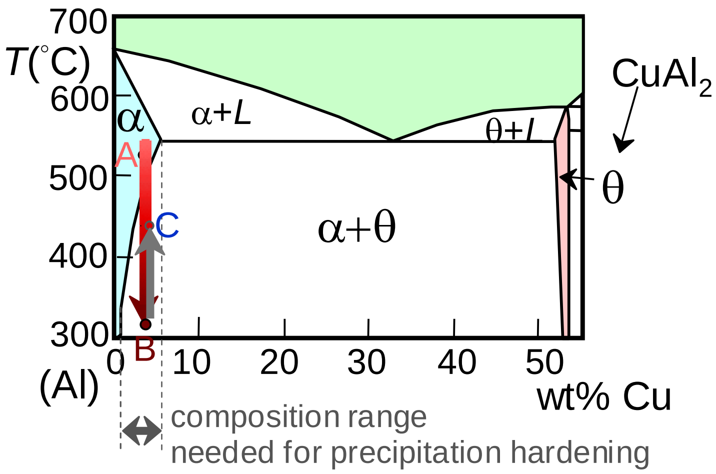
⇒ 藉由析出物阻止差排移動以增強材料強度

Procedure:

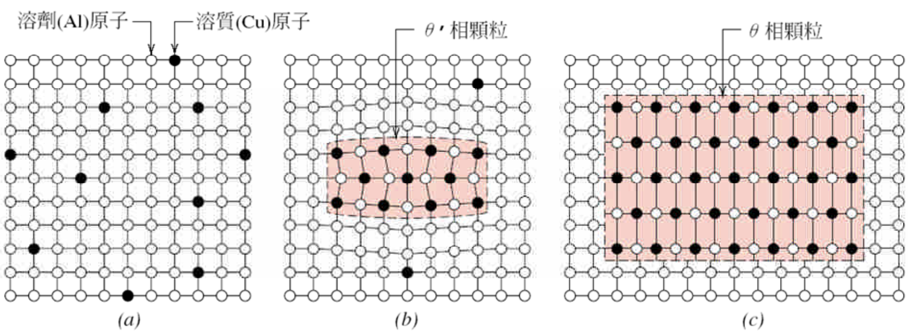
solution heat treatment ⇒ quench to room temperature ⇒ precipitation

固溶處理 ⇒ 淬火 ⇒ 析出硬化

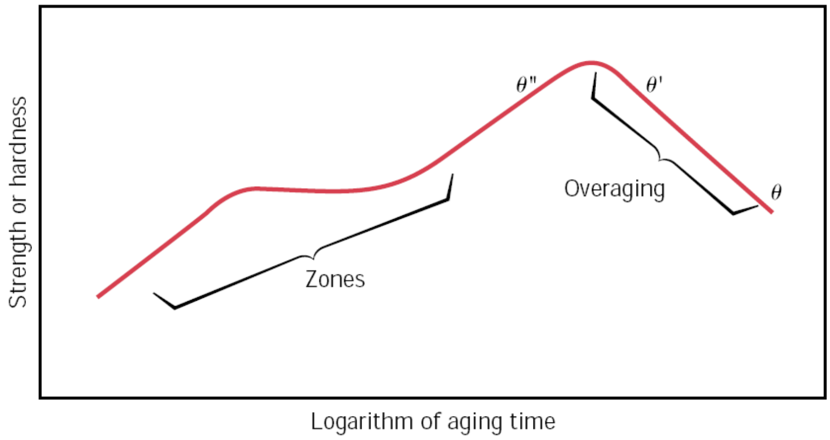




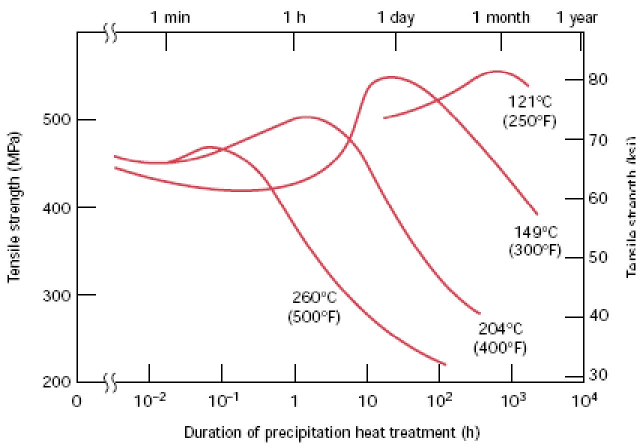
$$\alpha_{(ss)} \rightarrow \theta'' \rightarrow \theta' \rightarrow \theta\left(CuAl_2\right)$$



Strength and hardness as a function of the aging time at constant temperature



The strengthening process is accelerated as the temperature is increased.



§ 7-5 Glass Transition Phenomena in Polymers

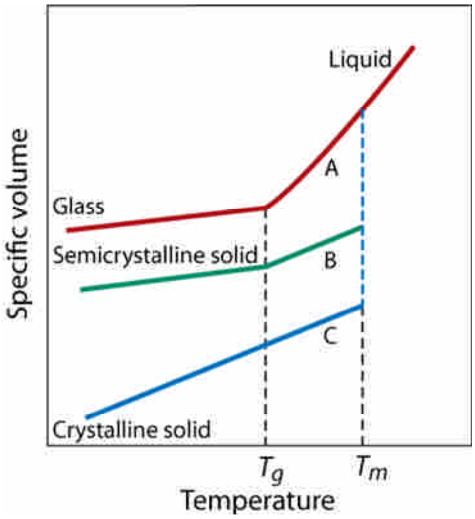
The temperature at which the polymer experiences the transition from rubbery to rigid states is called the glass transition temperature, *Tg*.

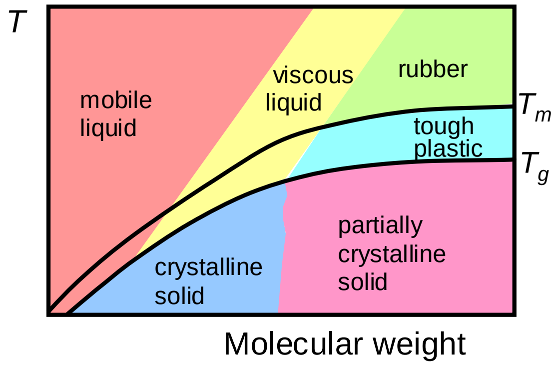
What factors affect *Tm* and *Tg*?

Both *Tm and Tg* increase with increasing chain stiffness

- Chain stiffness increased by presence of
  1. Bulky side groups
  2. Polar groups
  3. Chain double bonds and aromatic chain groups

- Regularity of repeat unit arrangements － affects *Tm* only
- Increasing the molecular weight tends to raise *Tm and Tg* .





§ 7-5 Summary

- Heat treatments of Fe-C alloys produce microstructures including: -- pearlite, bainite, spheroidite, martensite, tempered martensite

- Precipitation hardening
  --hardening, strengthening due to formation of precipitate particles.
  --Al, Mg alloys precipitation hardenable.

- Melting and glass transition temperatures for polymer
  -- Both *Tm and Tg* increase with increasing chain stiffness
  -- Regularity of repeat unit arrangements － affects *Tm* only
  -- Increasing the molecular weight tends to raise *Tm and Tg* .