CH10.相變態

相變化分成以下三類

simple diffusion-dependent	相成份、相數量不變，與擴散有關的簡單相變 EX.純金屬凝固、同素異形體、再結晶、晶粒成長
diffusion-dependent	相成份、數量變，與擴散有關，最後微結構常有 2 個相 EX.共晶
diffusionless	Metastable phase　EX.Martensite

相變動力學

相變化(金屬或合金的凝固)兩個階段→nucleation、growth

Nucleation 分成→homogeneous、hetrogeneous
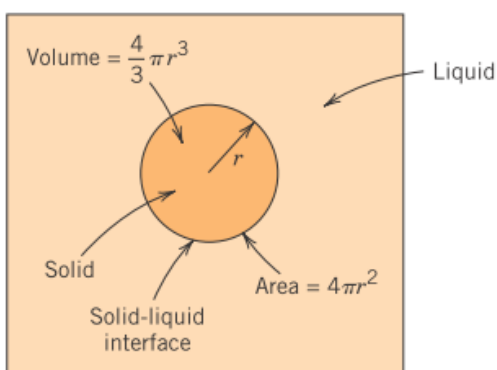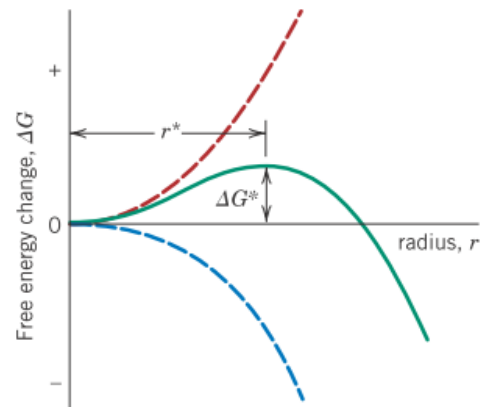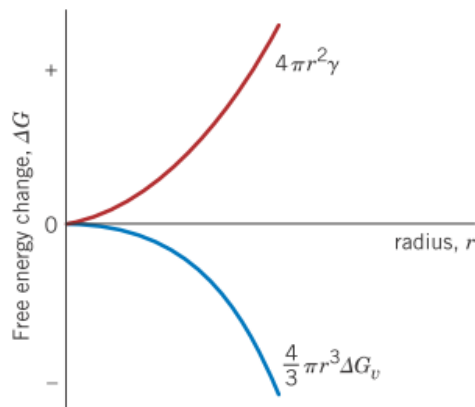
先討論 **homogemeous**

→液態金屬本身能提供原子來形成核，通常需要一定的過冷度(有些甚至到幾百多度 C)

原子鍵結的 cluster 若小於臨界尺寸→embryo→unstable & redissolve

若大於→nucleus

能量考慮

1. 液相轉為固相釋放的體積自由能$\triangle G_v$→驅動能(核的臨界尺寸由他定義)

2. 凝固顆粒形成新固體表面所需的表面能→retarding energy(不會隨溫度有什麼改變)

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

體積　　　　表面

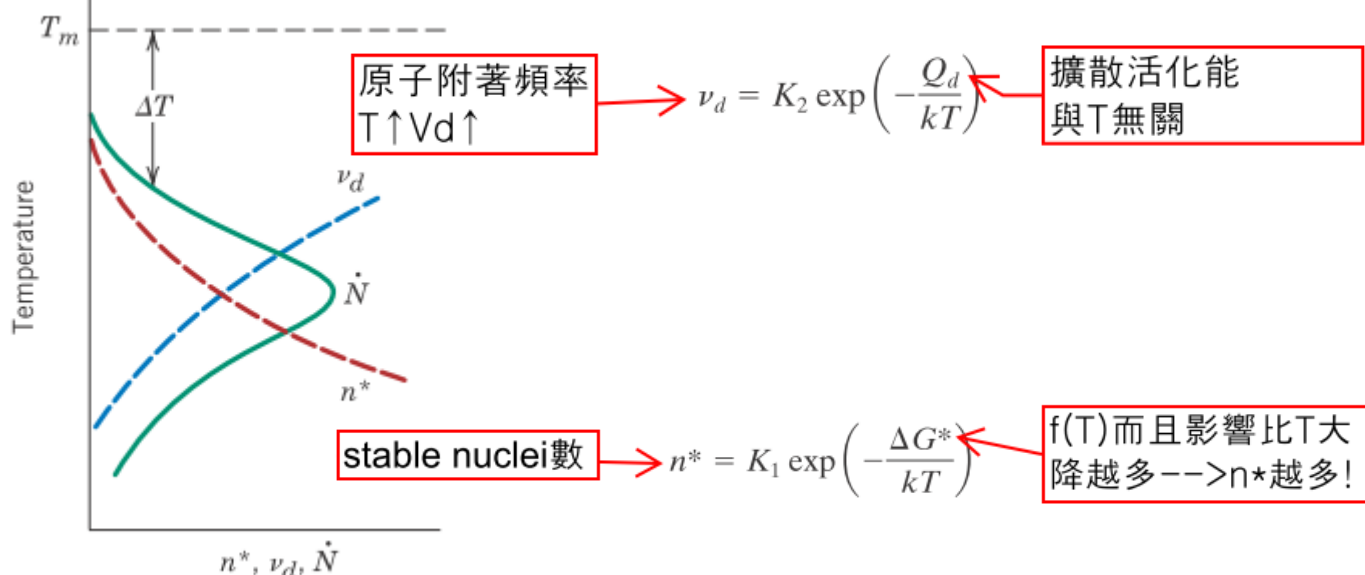對r微分=0 → $r^* = -\frac{2\gamma}{\Delta G_v}$　$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}$

$\triangle G_v$與T關係　$\Delta G_v = \frac{\Delta H_f(T_m - T)}{T_m}$

液相和固相之間的體積自由能差值△G_v 是凝固變化的 driving force!為溫度的函數，溫度↘(過冷度越高)，△G_v 差值越大(越負)，即 nucleation 越快發生→stable nuclei 的數目越多!

過冷度低→接近熔點→臨界尺寸無限大!

然而，擴散與原子的附著頻率有關!溫度越高→附著頻率越大

→成核率 nucleation rate 受 stable nuclei 數和 原子附著頻率 兩因素影響!

原子附著頻率
T↑Vd↑

$$\nu_d = K_2 \exp\left(-\frac{Q_d}{kT}\right)$$

擴散活化能
與T無關

stable nuclei 數

$$n^* = K_1 \exp\left(-\frac{\Delta G^*}{kT}\right)$$

f(T)而且影響比T大
降越多-->n*越多!

高溫→△G_v 越不負→驅動力小，但附著頻率高

低溫→△G_v 越負→驅動力高，但附著頻率低

由圖可看出最棒的成核率在低於熔點處，這種現象叫作→supercooling

有時候最理想的成核率的溫度低於熔點很多，但實際上觀察並沒這麼多，why?

因為核粒成核於已存在之表面→以經是異質成核!!

*工業鑄造作業，過冷度通常 0.1~10°C 左右而已，這一定是異質成核!!
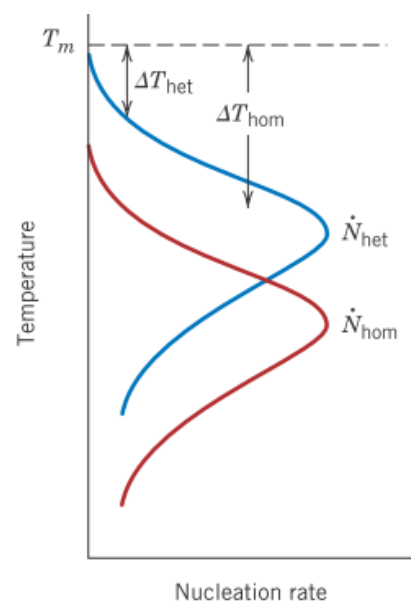
異質成核

表面自由能較低(阻礙能較低)，所需之驅動力(△G_v)也比較小，臨界尺寸也變小，所需過冷度較低。

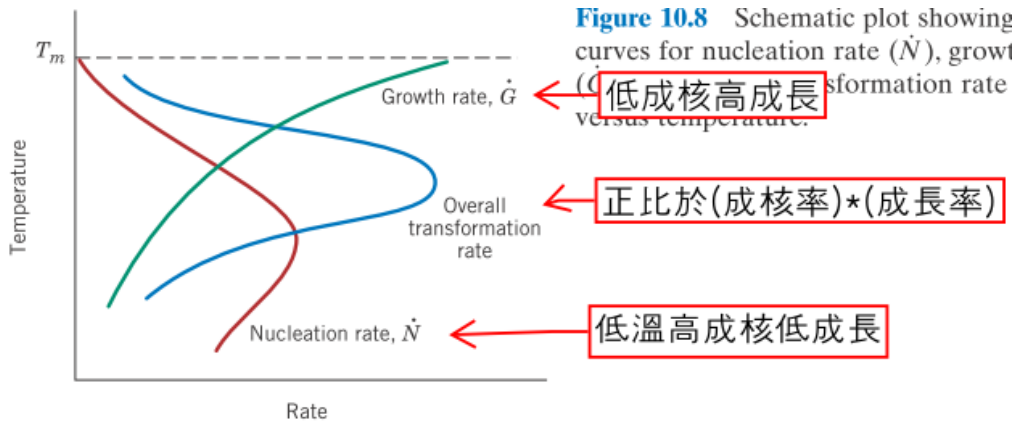$$r^* = -\frac{2\gamma_{SL}}{\Delta G_v} \quad \text{與均質同} \tag{10.13}$$

0~1

$$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3}{3\Delta G_v^2}\right)S(\theta) \quad \text{比均質小} \quad \Delta G^*_{het} = \Delta G^*_{hom}S(\theta)$$
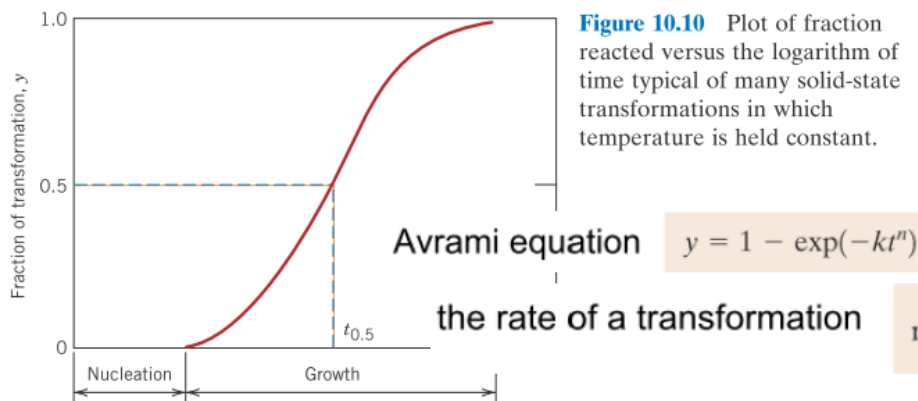
異質成核比較快速!!過冷度也比較小!!所以成核率曲線上升

當 r>r*，開始 growth(長程擴散)

$$\dot{G} = C \exp\left(-\frac{Q}{kT}\right)$$ T↑ $\dot{G}$↑

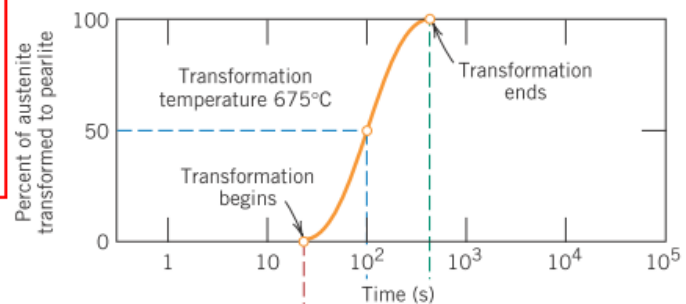Figure 10.8 Schematic plot showing curves for nucleation rate ($\dot{N}$), growth (G) ~~~~ formation rate versus temperature.

Growth rate, $\dot{G}$ ← 低成核高成長

Overall transformation rate ← 正比於(成核率)*(成長率)

Nucleation rate, $\dot{N}$ ← 低溫高成核低成長

現在討論時間相依，固定溫度下，這曲線又叫 S 曲線，用來描述許多固態相變化的分率，搭配的是 avrami equation

Figure 10.10 Plot of fraction reacted versus the logarithm of time typical of many solid-state transformations in which temperature is held constant.

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

the rate of a transformation $\text{rate} = \dfrac{1}{t_{0.5}}$

這圖的幾個限制
1.只適用在共析成分(固定成份)
2.恆溫
恆溫相變化圖
(T–T–T)

Transformation temperature 675°C

Transformation begins

Transformation ends

比較

過共析成份

Eutectoid temp

會有初析Ceminite(C)

Austenite (stable)   Eutectoid temperature

Austenite (unstable)

Pearlite

50% Completion curve

Completion curve (~100% pearlite)

Begin curve (~0% pearlite)

coarse pearlite

fine pearlite
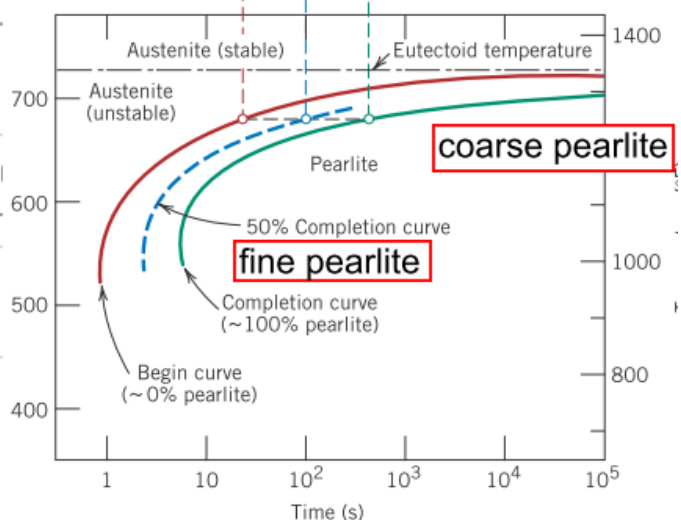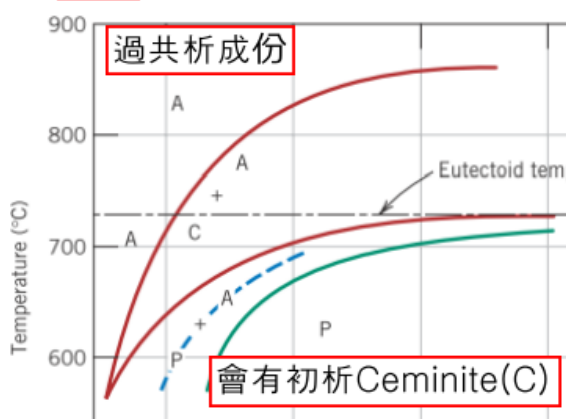
Bainite
forms as needles or plates
it is composed of a ferrite matrix and elongated particles of cememtite
是一種 non-lamellar 共析組織
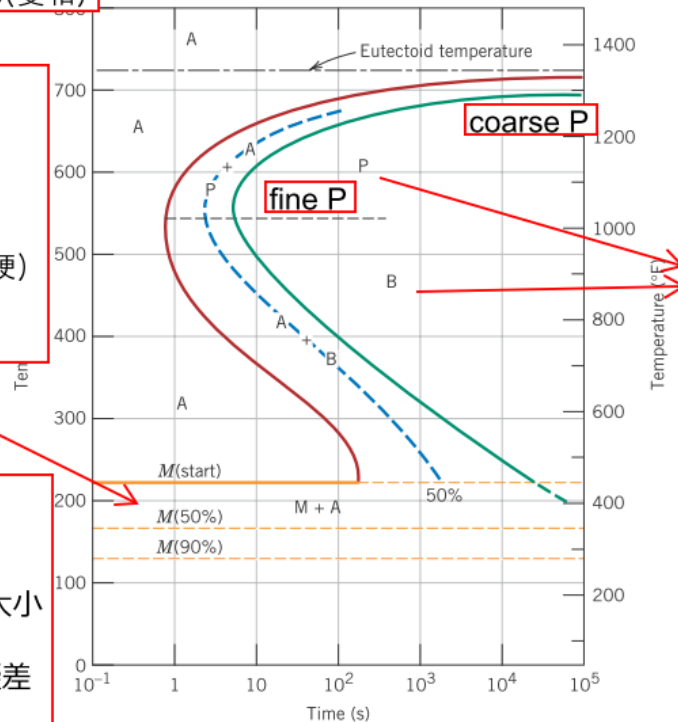分為 upper bainite(桿狀)和 lower bainite(較細)

硬度M>B>fine P>coarse P>S

只有M單相 其他都α-Fe + Fe3C(雙相)

M
1.非擴散性.非平衡
2.與時間無關->athermal 相變
3.γ(FCC)->α(BCT)(扭曲)->slip system少
4.C interstitial->高飽和固溶體(硬)
5.音速成核成長
6.plate-like/needle-like

Temper M
提高延性.韌性.消除內應力
BCT(單相)->α+Fe3C(雙相)
回火溫度時間決定Ceminite的大小
越大，界面面積減小->延
*小Ceminite界面面積大，阻礙差排，限制塑變

Figure 10.22 The complete isothermal transformation diagram for an iron–carbon alloy of eutectoid composition: A, austenite; B, bainite; M, martensite; P, pearlite.

coarse P

fine P

加熱 C原子擴散
形成Spheroidite
drive:降低相界面積
最延!

the Fe 3 C phase appears as sphere-like particles embedded in a continuous phase matrix

*M 可以和其他微組成共存!!(其它會互相競爭 EX.P&B)
Plain carbon steel→主要 C
Alloy steel→含其它合金

Smith 之 Martensite 補充
普通碳鋼的 martensite 結構取決於含碳量多寡
<0.6% →lath 狀，強化機構為高密度差排 tangles，和碳原子格隙固溶體
(>0.2%時，BCC 受格隙碳原子扭曲產生 BCT，所以碳原子格隙影響更為重要)
0.6%~1% →開始產生 plate 狀
>1% →全 plate 狀，通常 plate 會被大量未相變的 austenite 包圍，有 parallel twins
強化機構為 twinned interfaces

plate
1%
mix
0.6%
lath

C-C-T

plain C steel
無法形成B
(都先變成P了)

小於critical->M

冷卻快->fine P

冷卻慢->coarse P
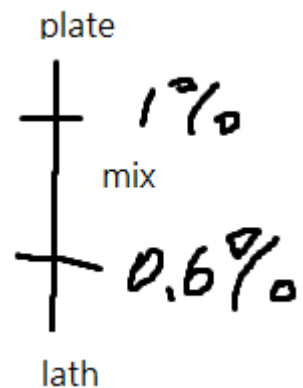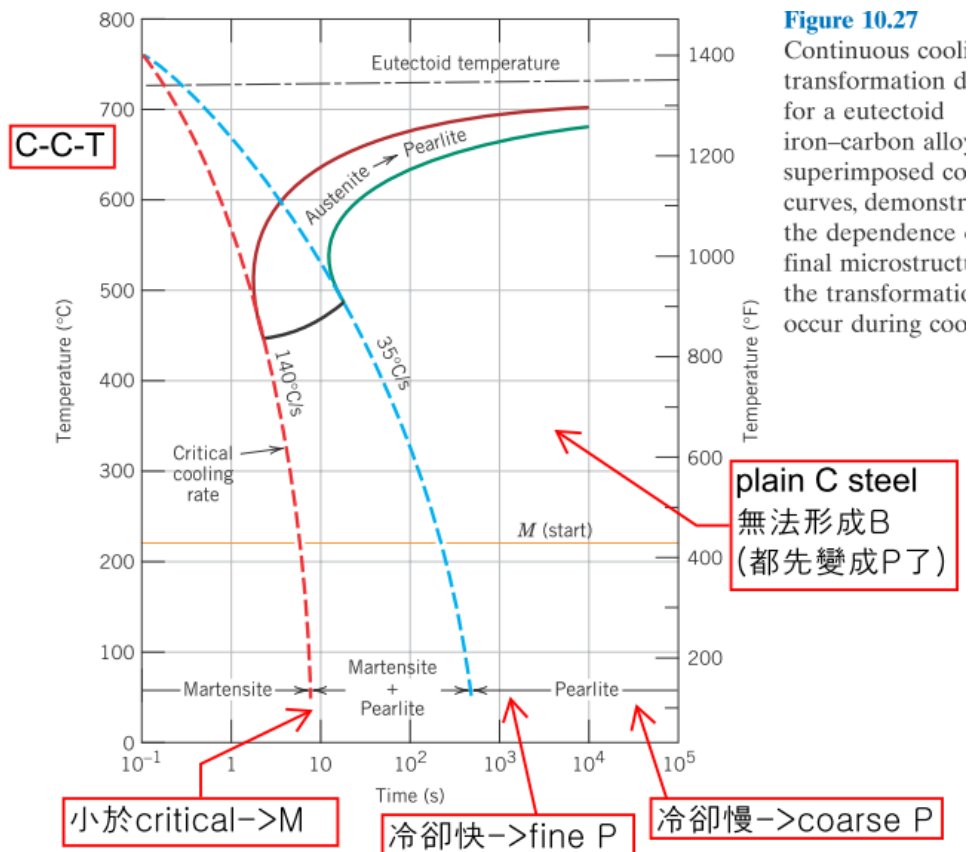
添加合金的合金鋼才可能產生 bainite，但其實添加合金鋼主要的目的是使 M 更容易生成，因為降低了臨界冷卻速率(即增加了可產生 M 的冷卻時間)
添加 C 含量也有同樣的效果
含 C 量太低，通常不能熱處理以產生 M，因為冷卻速度需求太高了

→增加含碳或合金元素(Cr.Ni.Mo.Mn.Si.W)，改變了 C-C-T 圖→使可以熱處理產生 Martensite
注意，在 quenching 時，這些元素必須固溶在 austenite 中!!
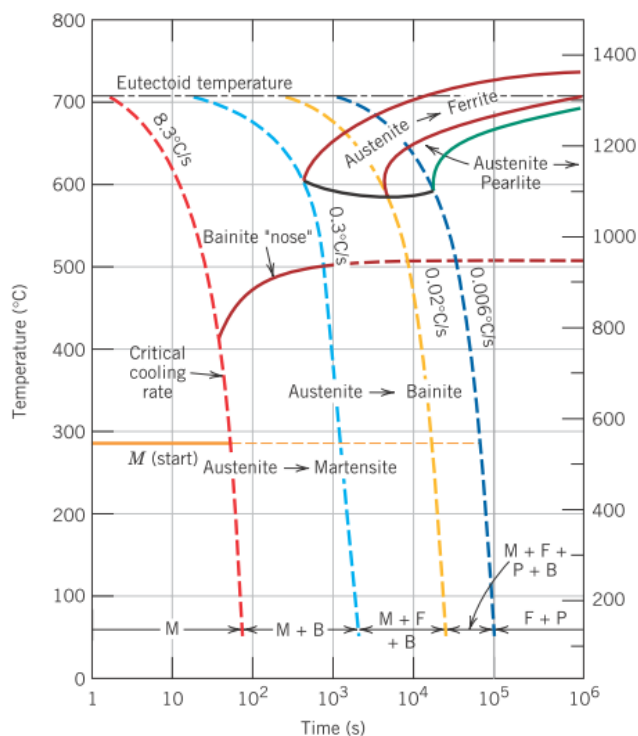
回火脆性 temper Embrittlement

高於 575 度回火後<u>緩慢冷卻</u>，或回火於 375~575 度間，回火後 toughness 反而降低，是由於合金元素(Mn.Ni.Cr...)或不純物導致脆轉溫度上升，使得室溫也在脆性範圍

預防方法

1.控制成份

2.回火溫度高於 575 度或低於 375 度，再<u>急冷</u>至室溫

若已回火脆性，加熱至 600 度，在極冷至 300 度以下可回復韌性。

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                        ┌─────────────┐
                        │  Austenite  │
                        └─────────────┘
         Slow            Moderate          Rapid
        cooling          cooling           quench

  ┌──────────────────┐  ┌─────────┐   ┌─────────────┐
  │    Pearlite      │  │ Bainite │   │ Martensite  │
  │ + a proeutectoid │  └─────────┘   └─────────────┘
  │     phase        │
  └──────────────────┘
                                          Reheat

                                   ┌────────────────────┐
                                   │ Tempered martensite│
                                   └────────────────────┘
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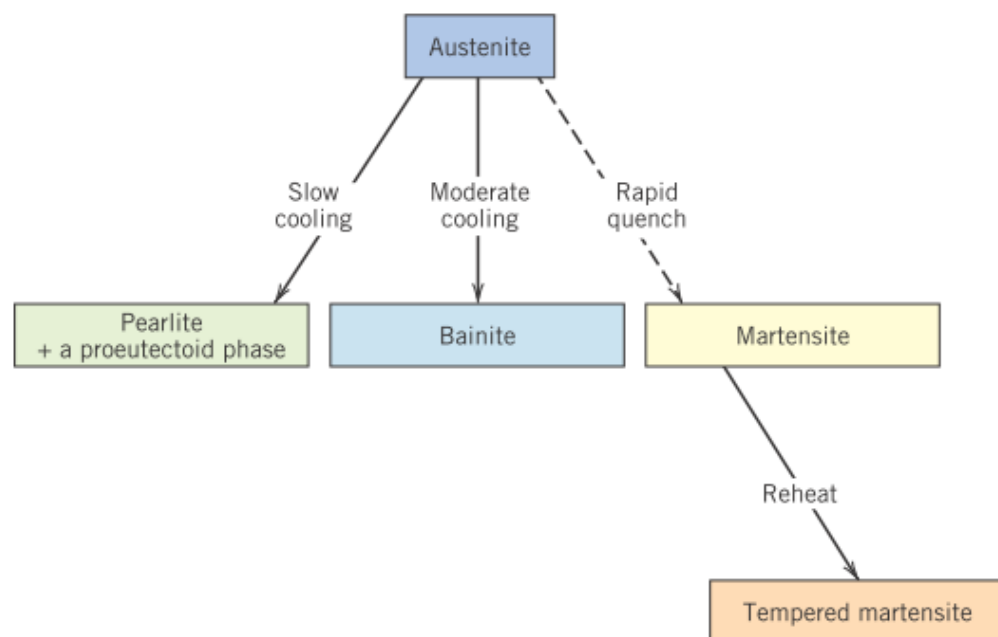
Microconstituent	Phases Present	Arrangement of Phases	Mechanical Properties (Relative)
Spheroidite	α Ferrite + Fe_3C	Relatively small Fe_3C sphere-like particles in an α-ferrite matrix	Soft and ductile
Coarse pearlite	α Ferrite + Fe_3C	Alternating layers of α ferrite and Fe_3C that are relatively thick	Harder and stronger than spheroidite, but not as ductile as spheroidite
Fine pearlite	α Ferrite + Fe_3C	Alternating layers of α ferrite and Fe_3C that are relatively thin	Harder and stronger than coarse pearlite, but not as ductile as coarse pearlite
Bainite	α Ferrite + Fe_3C	Very fine and elongated particles of Fe_3C in an α-ferrite matrix	Hardness and strength greater than fine pearlite; hardness less than martensite; ductility greater than martensite
Tempered martensite	α Ferrite + Fe_3C	Very small Fe_3C sphere-like particles in an α-ferrite matrix	Strong; not as hard as martensite, but much more ductile than martensite
Martensite	Body-centered tetragonal, single phase	Needle-shaped grains	Very hard and very brittle

記憶型合金 shape-memory alloys (or SMAs)
1.nickel–titanium alloys
2.copper-base alloys (viz.Cu–Zn–Al and Cu–Al–Ni alloys).
原理:記憶型合金是 polymorphic，種晶體結構的改變
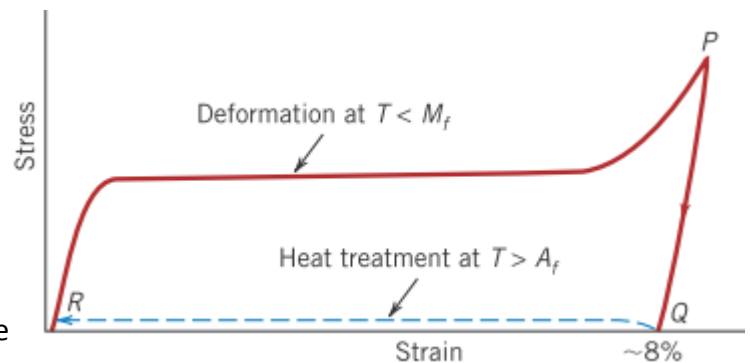較高溫的 austenite 相(BCC)，冷卻時變成 martensite 相(twinned)
受變形後，在加熱，恢復原狀。

Thermoelastic

碳鐵相圖有什麼限制?
1.非平衡相 M 無法表現出來
2.無法提供生成 P.B.S...等等的 time-te

過冷和過熱→超過相變化頓時卻還沒相變
是因為 driving force 還不夠產生相變，所已透過過冷或過熱增加趨動力

10.12 The microstructures of pearlite, bainite, and spheroidite all consist of α-ferrite and cementite phases. For pearlite, the two phases exist as layers that alternate with one another. Bainite consists of very fine and parallel needles of ferrite that are separated by elongated particles of cementite. For spheroidite, the matrix is ferrite, and the cementite phase is in the shape of spheroidal-shaped particles.

10.13 The driving force for the formation of spheroidite is the net reduction in ferrite-cementite phase boundary area.

10.21 Two major differences between martensitic and pearlitic transformations are 1) atomic diffusion is necessary for the pearlitic transformation, whereas the martensitic transformation is diffusionless; and 2) relative to transformation rate, the martensitic transformation is virtually instantaneous, while the pearlitic transformation is time-dependent.

10.22 Two important differences between continuous cooling transformation diagrams for plain carbon and alloy steels are: 1) for an alloy steel, a bainite nose will be present, which nose will be absent for plain carbon alloys; and 2) the pearlite-proeutectoid noses for plain carbon steel alloys are positioned at shorter times than for the alloy steels.

10.27 (a) Spheroiditic microstructures are more stable than pearlitic ones.
(b) Since pearlite transforms to spheroidite, the latter is more stable.

10.28 The hardness and strength of iron-carbon alloys that have microstructures consisting of α-ferrite and cementite phases depend on the boundary area between the two phases. The greater this area, the harder and stronger the alloy inasmuch as these boundaries impede the motion of dislocations. Fine pearlite is harder and stronger than coarse pearlite because the alternating ferrite-cementite layers are thinner for fine, and therefore, there is more phase boundary area. The phase boundary area between the sphere-like cementite particles and the ferrite matrix is less in spheroidite than for the alternating layered microstructure found in coarse pearlite.

10.29 Two reasons why martensite is so hard and brittle are: 1) there are relatively few operable slip systems for the body-centered tetragonal crystal structure, and 2) virtually all of the carbon is in solid solution, which produces a solid-solution hardening effect.

Smith 補充

液態金屬中晶體的成長及晶粒構造的形成

Solidification process 3 stage

1.形成 stable nuclei

2.growth into crystal

3.crystal 結合而形成 grainc 和 grain boundary

Liquid　Nuclei　Liquid　Crystals　Grain Boundaries　Grains
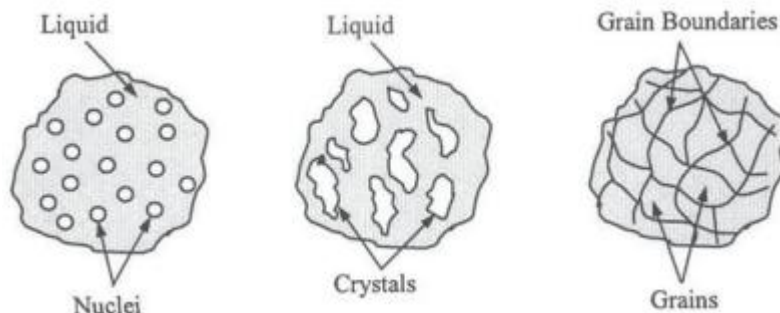
Solidification metal structure

1.在模壁附近，過冷度較大，且快速冷卻→equiaxed grain(各方向均衡成長)

2.高熱梯度，緩慢凝固，所需成核數目較小，長且薄的粗晶粒

→columnar grains(elongated in particular direction)

工業鑄造的晶粒構造

Cast ingot (EX.Al ingots)can be refined by　(產生 equiaxed grain)

1.提高冷卻速率(EX.chilling casting)

2.添加 grain refining agents(heterogeneous nucleation agents)(EX. B、Ti)

單晶凝固

渦輪葉片、矽晶圓需單晶

單晶比較抗潛變→因為在高於金屬熔點一半的溫度，晶界比晶粒脆弱

1.pigtail 選擇器增加晶粒的競爭性產生單晶

2.Czochralski process 製造 silicon seed crystal

→seed 持續旋轉，並從熔融液拉起