

# "Phase Transformation in Materials"

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### **5.4 Overall Transformation Kinetics**

If isothermal transformation,

The fraction of Transformation as a function of Time and Temp.  $\rightarrow f(t,T)$ TTT Diagram  $\iff$  CCT Diagram



or (rapid nucleation and growth rates)

# **Time-Temperature-Transformation Curves (TTT)**

- How much time does it take at any one temperature for a given fraction of the liquid to transform (nucleate and grow) into a crystal?
- $f(t,T) \sim \pi I(T) \mu(T)^{3} t^{4}/3$

where <u>*f* is the fractional volume of crystals</u> formed, typically taken to be 10<sup>-6</sup>, a barely observable crystal volume.





\* Time-Temperature-Transformation diagrams

**FIGURE 10.11** A more complete TTT diagram for eutectoid steel than was given in Figure 10.7. The various stages of the time-independent (or diffusionless) martensitic transformation are shown as horizontal lines.  $M_s$  represents the start,  $M_{50}$  represents 50% transformation, and  $M_{90}$  represents 90% transformation. One hundred percent transformation to martensite is not complete until a final temperature ( $M_f$ ) of  $-46^{\circ}C$ .

### \* Continuous Cooling Transformation diagrams



FIGURE 10.14 A continuous cooling transformation (CCT) diagram is shown superimposed on the isothermal transformation diagram of Figure 10.11. The general effect of continuous cooling is to shift the transformation curves downward and toward the right. (After Atlas of Isothermal Transformation and Cooling Transformation Diagrams, American Society for Metals, Metals Park, OH, 1977.)

Let us now turn to a consideration of some examples of the great variety of civilian transformations in solid.

### **5.5 Precipitation in Age-Hardening Alloys**

### **Precipitation in Aluminum-Copper Alloys**





incoherent nuclei with large  $\chi \sim$  impossible to homogeneous nucleation of  $\beta \rightarrow$  Homogeneous nucleation of metastable phase  $\beta'$  (GP Zones, Section 5.5.1)

### **Transition phases**



Fig. 5.27 A schematic molar free energy diagram for the Al-Cu system.

### $\alpha_{0} \rightarrow \alpha_{1} + \text{GP zone} \rightarrow \alpha_{2} + \theta'' \rightarrow \alpha_{3} + \theta' \rightarrow \alpha_{4} + \theta \text{ (CuAl}_{2}\text{)}$



∵ the crystal structures of the transition phases are intermediate between those of the matrix and the equilibrium phase.

Transition phases (중간상, θ" & θ'): a high degree of coherence, low interfacial E contribution to min ΔG\*.

Equilibrium phase (평형상,  $\theta$ ): complex crystal structure that is incompatible with the matrix  $\rightarrow$ high E interfaces and high  $\Delta G^*$ .



(a) The activation E barrier to the formation of each transition phase is very small in comparison to the barrier against the direct precipitation of the equilibrium phase. (b) Schematic diagram showing the total free E of the alloy versus time.

### \* Effect of Aging Temperature on the Sequence of Precipitates



### 5.5.4. Age Hardening

Transition phase precipitation  $\rightarrow$  great improvement in the mechanical properties Coherent precipitates  $\rightarrow$  highly strained matrix  $\rightarrow$  the main resistance to the D movement: solid solution hardening



Fig. 5. 37 Hardness vs. time for various Al-Cu alloys at (a) 130 °C (b) 190 °C best heat treatment in practice

### 5.5.3. Quenched-in Vacancies

If  $X_v < X_v^c$  critical vacancy supersaturation, Precipitate nucleation  $X \rightarrow$  formation of PFZ

- a) Excess (D→ (D) nucleation and moving ↑: Heterogeneous nucleation sites ↑
- b) Excess (𝔅) → atomic mobility ↑ at ageing temp: speeds up the process of nucleation and growth
- ex) rapid formation of GP zones at the relatively low

In the vicinity of grain boundaries on subsequent aging,

#### aging temperature. (possible to RT aging in Al-Cu alloy)

### a) Precipitate-Free Zone(PFZ) due to Vacancy Diffusion during quenching

Solute concentration within the zone ~ largely unchanged, but no precipitate at GB : a critical vacancy supersaturation must be exceeded for nucleation to occur.



Fig. 5.35 A PFZ due to vacancy diffusion to a grain boundary during quenching.

- (a) Vacancy concentration profile. (b) A PFZ in an Al-Ge alloy (x 20,000)
- (c) Dependence of PFZ width on critical vacancy concentration X<sub>v</sub><sup>c</sup> and rate of quenching.

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b) Another cause of PFZs can be the nucleation and growth of GB precipitates during cooling from the solution treatment temperature.



Fig. 5.36 PFZs around grain boundaries in a high-strength commercial AI-Zn-Mg-Cu alloy. 12 Precipitates on grain boundaries have extracted solute from surrounding matrix. (x 59,200)

# **Q5: Spinodal Decomposition**

# 5.5.5 Spinodal Decomposition

### Spinodal mode of transformation has no barrier to nucleation

: describing the transformation of a system of two or more components in a metastable phase into two stable phases



Fig. 5.38 Alloys between the spinodal points are unstable and can decompose into two coherent phasees  $\alpha_1$  and  $\alpha_2$  without overcoming an activation energy barrier. Alloys between the coherent miscibility gaps and the spinodal are metastable and can decompose only after nucleation of the other phase.

How does it differ between inside and outside the inflection point of Gibbs free energy curve?

1) Within the spinodal  $\frac{d^2G}{dX^2} < 0$ 

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: phase separation by small fluctuations in composition/ "up-hill diffusion"

2) If the alloy lies outside the spinodal, small variation in composition leads to an increase in free energy and the alloy is therefore metastable.

> The free energy can only be decreased if nuclei are formed with a composition very different from the matrix.

 $\rightarrow$  nucleation and growth : "down-hill diffusion"



Fig. 5.39 & 5.40 schematic composition profiles at increasing times in (a) an alloy quenched into the spinodal region ( $X_0$  in Figure 5.38) and (b) an alloy outside the spinodal points ( $X_0$ ' in Figure 5.38) <sup>15</sup>

### **Phase separation**



 $(\mathbf{Y}_{56}\mathbf{Al}_{24}\mathbf{Co}_{20})_{25}(\mathbf{Ti}_{56}\mathbf{Al}_{24}\mathbf{Co}_{20})_{75}$ 

 $(Y_{56}Al_{24}Co_{20})_{50}(Ti_{56}Al_{24}Co_{20})_{50}$ 

 $(\mathbf{Y}_{56}\mathbf{Al}_{24}\mathbf{Co}_{20})_{65}(\mathbf{Ti}_{56}\mathbf{Al}_{24}\mathbf{Co}_{20})_{35}$  16

# 5.5.5 Spinodal Decomposition

\* The Rate of Spinodal decomposition

a) Rate controlled by interdiffusion coefficient D (상호확산계수)

Within the spinodal D < 0, composition fluctuation (next page)  $\propto \exp(-t/\tau)$ 

 $\tau = -\lambda^2 / 4\pi^2 D$ <sup> $\tau$ : characteristic time constant</sup>
<sup> $\lambda$ : wavelength of the composition modulations
(assumed one-dimensional)</sup>

**b)** Kinetics depends on  $\lambda$ : Transformation rate  $\uparrow$  as  $\lambda \downarrow$  (as small as possible).

But, minimum value of  $\lambda$  below which spinodal decomposition cannot occur.

### Solutions to the diffusion equations

Ex1. Homogenization of sinusoidal varying composition in the elimination of segregation in casting



The initial concentration profile will not usually be sinusoidal, but in general any concentration profile can be considered as <u>the sum of an infinite series of sine waves of</u> <u>varying wavelength and amplitude</u>, and each wave decays at a rate determined by its own " $\tau$ ". Thus, the short wavelength terms die away very rapidly and <u>the homogenization</u> <u>will ultimately be determined by  $\tau$  for the longest wavelength component</u>.

- \* <u>Calculation of the wavelength ( $\lambda$ )</u> of the composition fluctuations
  - → Free Energy change for the decomposition

**1)** Decomposition of  $X_0$  into  $X_0 + \Delta X$  and  $X_0 - \Delta X$ 

What would be an additional energy affecting spinodal decomposition?

In practice, it is necessary to consider two important factors

- 2) interfacial energy
- 3) coherency strain energy

**1) Decomposition of X<sub>0</sub> into X<sub>0</sub> + \Delta X and X<sub>0</sub> - \Delta X \Delta G\_{chem} = \frac{1}{2} \frac{d^2 G}{dV^2} (\Delta X)^2** Gibb's free energy reduction by compositional change  $f(a+h) = f(a) + f'(a)h + \frac{f''(a)}{2!}h^2 + \cdots$  $\begin{bmatrix} G(X_0 + \Delta X) \approx G(X_0) + G'(X_0)\Delta X + \frac{G''(X_0)}{2!}\Delta X^2 \\ G(X_0 - \Delta X) \approx G(X_0) - G'(X_0)\Delta X + \frac{G''(X_0)}{2!}\Delta X^2 \end{bmatrix}$  $\Delta G_{chem} = \frac{G(X_0 + \Delta X) + G(X_0 - \Delta X)}{2} - G(X_0)$  $=\frac{G''(X_0)}{2!}\Delta X^2 = \frac{1}{2}\frac{d^2G}{dY^2}\Delta X^2$ 19

# 5.5.5 Spinodal Decomposition

### 2) <u>During the early stages</u>, the interface between A-rich and B-rich region is not sharp but very diffuse. $\rightarrow$ diffuse interface

ΔG by formation of interface btw decomposed phases

Interfacial Energy (gradient energy)

: increased # of unlike nearest neighbors in

 $\Delta \mathbf{G}_{\gamma} = \mathbf{K} \left( \frac{\Delta \mathbf{X}}{\lambda} \right)^2$  $\propto$  composition gradient across the interface a solution containing composition gradients

Max. compositional gradient  $\Delta X/\lambda$ 

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*K*: a proportionality constant dependent on the difference in the bond energies of like and unlike atom pair

If the size of the atoms making up the solid solution are different, the generation of composition differences,  $\Delta X$  will introduce a coherency strain energy term,  $\Delta G_s$ .

#### 3) Coherency $\Delta G_{\rm S} \propto E\delta^2 \iff \delta = (da/dX) \Delta X/a$ **Strain Energy**

**δ: misfit** between the A-rich & B-rich regions, E: Young's modulus, a: lattice parameter (atomic size difference)

$$\Delta G_{S} = \eta^{2} (\Delta X)^{2} E' V_{m}$$
 where  $\eta = \frac{1}{a} \left( \frac{da}{dX} \right), E' = E/(1-\nu)$   $\Delta G_{S} \sim \text{ independent of } \lambda$ 

n: the fractional change in lattice parameter per unit composition change

\* Total free E change by the formation of a composition fluctuation (1) + 2) + 3)

$$\Delta G = \left\{ \frac{d^2 G}{dX^2} + \frac{2K}{\lambda^2} + 2\eta^2 E' V_m \right\} \frac{(\Delta X)^2}{2}$$

# 5.5.5 Spinodal Decomposition



undercooling ( $\Delta T \sim \Delta X$ ) below the coherent spinodal.

This figure include the lines <u>defining the equilibrium compositions</u> of the <u>coherent/incoherent phases</u> that result from spinodal decomposition.

### \* Incoherent(or equilibrium) miscibility gap: $\Delta H > 0$

The miscibility gap the normally appears on an equilibrium phase is the incoherent (or equilibrium) miscibility gap.→ equilibrium compositions of incoherent phases without strain fields.

- a) chemical spinodal: d<sup>2</sup>G/dX<sup>2</sup>=0\_no practical importance X
- b) Area ② ,  $\Delta G_V \Delta G_S < 0 \rightarrow$  only incoherent strain-free nuclei can form.



#### Composition Figure 5.41 Schematic phase diagram for a clustering system.

Region 1: <u>homogeneous  $\alpha$  stable</u>. Region 2: homogeneous  $\alpha$  metastable, <u>only incoherent phases</u> can nucleate. Region 3: homogeneous  $\alpha$  metastable, <u>coherent phase</u> can nucleate. Region 4: homogeneous  $\alpha$  unstable, no nucleation barrier, <u>spinodal decomposition</u> occurs.

Spinodal decomposition is not only limited to systems containing a stable miscibility gap All systems in which <u>GP zones</u> form, for example, containing a <u>metastable coherent</u> <u>miscibility gap</u>, i.e., the GP zone solvus.

 $\rightarrow$  at high supersaturation, GP zone can form by the spinodal mechanism.



#### Figure 5.34

Al-Ag phase diagram showing metastable two-phase field corresponding to GP zones.

- The difference in T between the coherent and incoherent miscibility gaps, or the chemical and coherent spinodals  $\propto$  magnitude of  $|\eta| \eta$ : the fractional change in lattice parameter per unit composition change
- Large atomic size difference  $\rightarrow |\eta|$  large  $\rightarrow$  large undercooling to overcome the strain E effects
- Like Al-Cu, large values of |η| in cubic metals can be mitigated if the misfit strains are accommodated in the elastically soft <100> directions. → composition modulations building up normal to {100}



Figure 5.42 A coarsened spinodal microstructure in Al-22.5 Zn-0.1 Mg (at%) solution treated 2h at 400  $^{\circ}$ C and aged 20h at 100 $^{\circ}$ C. Thin foil electron micrograph.  $\lambda$  = 25 nm\_coarsening

Q6: How can you design an alloy with high strength at high T? Microstructure of a two phase alloy is always unstable if the total interfacial free E is not a minimum.  $\rightarrow$ 

5.5.6. Particle Coarsening (smaller total interfacial area→loss of strength or disappearance of GB pining effect→ particular concern in the design of materials for high temp. applications) Two Adjacent Spherical Precipitates with Different Diameters



: Concentration gradient in matrix → diffusion → small particle\_shrink/ large particle\_grow

### 5.5.6. Particle Coarsening

# The Rate of Coarsening with Increasing Time and Temp.



Time

 Particular concern in the design of materials for high temperature applications

> Undesirable degradation of properties: less strength/ disappearance of GB pinning effects

How can you design an alloy with high strength at high T?

→ fine precipitate dispersion

hint) 
$$\frac{d\bar{r}}{dt} \propto \frac{k}{\bar{r}^2} \qquad k \propto D\gamma X_e$$

### **1) Ιοw** γ

heat-resistant Nimonic alloys based on Ni-rich Ni-Cr  $\rightarrow$  ordered fcc Ni<sub>3</sub>(Ti,Al) in Ni-rich matrix  $\rightarrow$  high strength Ni/ $\gamma'$  interface~ <u>"fully coherent"</u> (10 ~ 30 mJ m<sup>-2</sup>) Maintain a fine structure at high temperature  $\rightarrow$  improve creep-rupture life

2) low X<sub>e</sub> (Oxide~ very insoluble in metals)
: fine oxide dispersion in a metal matrix
Ex) dispersed fine ThO<sub>2</sub> (thoria) in W and Ni

 $\rightarrow$  strengthened for high temperature

### 3) low *D*

**Cementite** dispersions in tempered steel

- $\rightarrow$  high *D* of carbon  $\rightarrow$  very quickly coarsening
- a. substitutional alloying element
- $\rightarrow$  segregates to carbide  $\rightarrow$  slow coarsening

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**b.** strong carbide-forming elements

 $\rightarrow$  more stable carbides  $\rightarrow$  lower X<sub>e</sub>

# Q7: Precipitation of Ferrite from Austenite $(\gamma \rightarrow \alpha)$

3) Precipitation of equilibrium phase by diffusional transformation

### 5.6. The Precipitation of Ferrite from Austenite ( $\gamma \rightarrow \alpha$ )

(Most important nucleation site: Grain boundary and the surface of inclusions)

### The Iron-Carbon Phase Diagram



Microstructure (0.4 wt%C) evolved by slow cooling (air, furnace) ?



## 5.6. The Precipitation of Ferrite from Austenite

### **Diffusional Transformation of Austenite into Ferrite**



Figure 5.45 Holding temperature for steel in Figure. 5.46

### Microstructures of an austenitized Fe-0.15%C alloy (x 100 except (d, x300))

White:  $\alpha$  ferrite/ Gray: M formed from untransformed  $\gamma$ / fine constituent: a mixture of ferrite and carbide

Primary ferrite allotriomorphs with a few plates  $\implies$  Many more plates, mostly growing from GBs/ inside  $\alpha$  grain



Widmanstätten ferrite side-plates (b), (c), (d) \_ Finer & faceted coherent interface with increasing "undercooling"



치환형 확산이 일어나는 경우 매우 중요/ 침입형 고용체에서는 체적 확산 속도가 크기 때문에 입계나 전위를 통한 단거리 확산은 상대적으로 중요하지 않음.

Fig. 5.18 Grain-boundary diffusion can lead to rapid lengthening and thickening of grain boundary precipitates, especially by substitutional diffusion.

The reason for the transition from grain boundary allotriomorphs to Widman -stätten side-plates with increasing undercooling is not fully understood.

- → possible answer: Relative Velocity of Incoherent & Semicoherent Interfaces vary with undercooling
- a) At small undercoolings, both semi-coherent and incoherent interfaces ~similar rates
- b) At large undercoolings, only incoherent interfaces~full use of increased driving force (Continuous growth)



\* Intragranular ferrite in <u>large-grained specimen</u>

: ferrite can also precipitate within the austenite grains (Fig. in page 17)
 suitable heterogeneous nucleation site~inclusions and dislocations
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 generally equiaxed at low undercooling ↔ more platelike at higher undercolings

# 5.6. The Precipitation of Ferrite from Austenite



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For alloys of different carbon content,  $A_3$  and  $T_w$  vary and show parallel manner each other.



(GBA: GB allotriomorphs, W: Widmanstatten sideplates/intermolecular plates, M: Massive ferrite)

Figure 5.48 (b) Temperature-composition regions in which the various morphologies are dominant at late reaction times in specimens with ASTM grain size Nos. 0-1. <sup>35</sup>

### 5.6.1 & 5.7 skip

# 5. Diffusion Transformations in solid

: diffusional nucleation & growth

### (a) Precipitation

$$\alpha' \rightarrow \alpha + \beta$$

Metastable supersaturated Solid solution



 $\gamma \rightarrow \alpha + \beta$ 

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(b) Eutectoid Transformation

Composition of product phases differs from that of a parent phase.

→ long-range diffusion