

# "Phase Transformation in Materials"

12.02.2015 Eun Soo Park **Contents for previous class** 

## Precipitation in Age-Hardening Alloys



### 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

## **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)

# 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  $\left[ \propto \exp(-t/\tau) \right]$ (next page)  $\tau = -\lambda^2/4\pi^2 D$   $\tau$ : characteristic time constant  $\lambda$ : wavelength of the composition modulations (assumed one-dimensional)

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.

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

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## 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 $\Delta G_{S} \propto E\delta^{2} \iff \delta = (da/dX) \Delta X/a$ 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



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



<u>undercooling ( $\Delta T \sim \Delta X$ ) below the coherent spinodal.</u>

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.

→ 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 5.42A coarsened spinodal microstructure in Al-22.5Zn-0.1Mg (at%) solution treated 2h at 400 °Cand aged 20h at 100 °C.Thin foil electron micrograph.  $\lambda = 25$  nm\_coarsening12

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) low** γ

heat-resistant Nimonic alloys based on Ni-rich Ni-Cr  $\rightarrow$  ordered fcc Ni<sub>3</sub>(Ti,AI) 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
- **b.** strong carbide-forming elements
- $\rightarrow$  more stable carbides  $\rightarrow$  lower  $X_e$  14

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: α ferrite/ Gray: M formed from untransformed γ/ fine constituent: a mixture of ferrite and carbide

Primary ferrite allotriomorphs with a few plates  $\longrightarrow$  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)



Undercooling  $\Delta T$ 

\* 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
 19 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. 21

## 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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Homogeneous NucleationHeterogeneous Nucleation $\Delta G = -V \Delta G_V + A \gamma + V \Delta G_S$  $\Delta G_{het} = -V(\Delta G_V - \Delta G_S) + A \gamma - \Delta G_d$  $N_{hom} = \omega C_0 \exp\left(-\frac{\Delta G_m}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right)$  $\Rightarrow$  suitable nucleation sites ~ nonequilibrium defects<br/>(creation of nucleus~destruction of a defect(- $\Delta G_d$ ))

(b) Eutectoid Transformation

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

→ long-range diffusion

## 5.8. Eutectoid Transformation

**5.8.1 Pearlite Reaction in Fe-C Alloys** 

$$\gamma \rightarrow \alpha + Fe_3C$$



Pearlite nodule nucleate on GBs and grow with a roughly constant radial velocity into the surrounding austenite grains.



#### \* At large undercooling,

- : the nucleation rate is much higher and site saturation occurs, that is all GBs become quickly covered with nodules which grow together forming layers of perlite, Figure 5.61.
- \* At small undercooling below A<sub>1</sub>,
- : the number of pearlite nodules that nucleate is relatively small, and the nodules can grow as <u>hemispheres or spheres</u> without interfering with each other.

## Pearlite Reaction in Fe-C Alloys: nucleation and growth

**Nucleation:** depend on GB structures and composition



- (a) On a "clean" GB.
  - (i) Cementite nucleates on GB with coherent interface and orientation relationship with  $y_1$  and incoherent interface with  $y_2$ .
  - α nucleates adjacent to cementite also **(ii)** with a coherent interface and orientation relationship with  $y_1$ . (This also produces an orientation relationship between the cementite and the ferrite).
  - (iii) The nucleation process repeats side ways, while incoherent interfaces grow into  $\gamma_2$ .
- New plates can also form by a branching (iv) mechanism.
- (b) When a proeutectoid phase (cementite or ferrite) already exists on that boundary, pearlite will nucleate and grow on the incoherent side. A different orientation relationship between the cementite and the ferrite results in this case.
- (c) Pearlite colony at a latest stage of growth. Pearlite grows into the austenite grain with which it does not have an orientation relationship.

## **Growth of Pearlite:** analogous to the growth of a lamellar eutectic

Min. possible:  $(S^*) \propto 1/\Delta T$  / Growth rate: mainly lattice diffusion  $v = kD_c^{\gamma}(\Delta T)^2$ Interlamellar spacingof pearlite coloniesmainly boundary diffusion  $v = kD_b(\Delta T)^3$ 

Relative Positions of the Transformation curves for Pearlite and Bainite in Plain Carbon Eutectoid Steels.



Figure 5.64 Schematic diagram showing relative positions of the transformation curves for pearlite and bainite in plain carbon eutectoid steel.

## 5.8.2 Bainite Transformation

The microstructure of bainite depends mainly on the temperature at which it forms.

#### Upper Banite in medium-carbon steel Lower Bainite in 0.69wt% C low-alloy steel

At high temp. 350 ~ 550°C, ferrite laths, K-S relationship, similar to Widmanstäten plates



(b) Schematic of growth mechanism. Widmanstatten ferrite laths growth into  $\gamma_2$ . Cementite plates nucleate in carbon-enriched austenite.

At sufficiently low temp. laths  $\rightarrow$  plates Carbide dispersion becomes much finer, rather like in tempered M.



Surface tilts by bainite trans. like M trans. Due to Shear mechanism/ordered military manner

(b) A possible growth mechanism.  $\alpha/\gamma$  interface advances as fast as carbides precipitate at interface thereby removing the excess carbon in front of the  $\alpha$ . At the highest temp. where pearlite and bainite grow competitively.



 Fig. 5.67 Hypoeutectoid steel (0.6% C) partially transformed for 30 min at 710 ℃. Inefficiently quenched. Bainitic growth into lower grain of austenite and pearlitic growth into upper grain during quench (x1800).

 Pearlite : no specific orientation relationship

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## 5.8.3 The effect of alloying elements on hardenability

- : adding alloying elements to steels  $\rightarrow$  delay to time required for the decomposition into ferrite and pearlite  $\rightarrow$  M trans under slower cooling rate  $\rightarrow$  increase hardenability
- \* Main factor limiting hardenability is the rate of formation of pearlite at the nose of the C curve in the TTT diagram.
- Austenite stabilizer (Mn, Cu, Ni) depress A3 temperature
- Ferrite stabilizer (Cr, Mo, Si) increase A3 temperature



Figure 5.73 TTT diagrams for two commercial low-alloy steels all of which (a) contain roughly 0.4% C and 1% Mn and (b) contains 0.8% Cr, 0.3% Mo, and 1.8% Ni

## 5.8.4 - 5.8.6 skip

# 5. Diffusion Transformations in solid

#### (c) Order-Disorder Transformation







#### (d) 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.





#### (e) Polymorphic Transformation

γ

α

In single component systems, different crystal structures are stable over different temperature ranges.

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# **5.9 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.



## **5.9 Massive Transformation**

Free energy-composition curves for  $\alpha$  and  $\beta$ 



Fig. 5.86 A schematic representation of the free energy-composition curves for  $\alpha$  and  $\beta$  in the Cu-Zn system at various temperatures.

At the thermodynamic point of view, it may possible for a massive trans. to occur within the twophase region of the phase dia. anywhere below the  $T_0$  temp.. But, in practice, there is evidence that massive trans. usually occur only within the single-phase region of the phase diagram 33

## **5.9 Massive Transformation**

#### Massive $\alpha$ formed at the GBs of $\beta$ and grow rapidly into the surrounding $\beta$

: a diffusionless civilian transformation (change of crystal structure without a change of composition) Migration of the  $\alpha/\beta$  interfaces~ very similar to the migration of GBs during recrystallization of single-phase material but, driving force ~ orders of magnitude greater than for recrystallization  $\rightarrow$  rapid growth: a characteristic irregular appearance.



Figure 5.85 Massive a formed at the GBs of  $\beta$  in Cu-38.7wt% Zn guenched from 850  $^{\circ}$  in brine at 0  $^{\circ}$ . Some high temperature precipitation has also occurred on the boundaries. 34

## \* Massive, Martensite Transformation



Martensite



Massive Transformation

thermally activated jumping across the α/β interface \_\_\_\_\_\_ diffusionless civilian transformation

Fig. 5.75 A possible CCT diagram for systems showing a massive transformation. Slow cooling (1) produces equiaxed  $\alpha$ . Widmanstatten morphologies result from faster cooling (2). Moderately rapid quenching (3) produces the massive transformation, while the highest quench rate (4) leads to a martensitic transformation.

β is sheared into α by the cooperative movement of atoms across a glissile interface diffusionless military transformation
 Martensite Transformation

## 5.9 Massive Transformation : $\gamma \rightarrow \alpha$ transformation in iron and its alloy

# Effect of Cooling Rate on the Transformation Temperature at which transformation starts in pure iron





Massive a in an Fe-0.002wt%C Quenched into iced brine from 1000 °C : characteristically irregular a/a GBs.

## **5.9 Massive Transformation**



Metastable phases can also form massively.

It is not even necessary for the transformation product to be a single phase: two phases, at least one of which must be metastable, can form simultaneously provided they have the same composition as the parent phase.

# 5.10 & 5.11 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.  $\rightarrow$  long-range diffusion

Which transformation proceeds by short-range diffusion?

# 5. Diffusion Transformations in solid

#### (c) Order-Disorder Transformation







#### (d) 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.





(e) Polymorphic Transformation

γ

α

In single component systems, different crystal structures are stable over different temperature ranges.

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\* Homework 5 : Exercises 5 (pages 379-381) until 14th December (before exam)

Good Luck!!