2018 Fall

# "Phase Transformation in Materials"

10.25.2018

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### Summary for today's class

• Thermally Activated Migration of Grain Boundaries:

Metastable equilibrium of grain boundary (Balances of 1) boundary E + 2) surface tension)

(Pulling force per unit area of boundary)

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- $\rightarrow$  real curvature ( $\Delta P \rightarrow \Delta G$ : Gibbs Thomson Eq.)  $\rightarrow$  F =  $2\gamma/r = \Delta G/V_m$  (by curvature)
- → Grain coarsening at high T annealing
- Kinetics of Grain Growth
  - Grain boundary migration (v) by thermally activated atomic jump



#### Summary for today's class

- Grain Growth
  - Normal grain growth

#### Abnormal grain growth

(high mobility of special GBs
 → development of recrystallization textures)









**Contents for today's class** 

- Interphase Interfaces in Solid (α/β)
  - Types of interphase interfaces in solid ( $\alpha/\beta$ )
  - Second-Phase Shape (Interface Energy Effects)  $\sum A_i \gamma_i + \Delta G_{\rm S} = minimum$
  - Coherency Loss
  - Glissil Interfaces 👄 Solid/Liquid Interfaces
- **Interface migration** 
  - Interface controlled growth 💭 Diffusion controlled growth

Coherent / Semi-coherent / incoherent

**Misfit Strain Effects** 

# Q: What kind of interphase interfaces in solid ( $\alpha/\beta$ ) exist?

= coherent/ semi-coherent / incoherent/ complex semi-coherent

 $\rightarrow$  different interfacial free energy,  $\gamma$ 

## **3.4 Interphase Interfaces in Solids**

Interphase boundary - different two phases : different crystal structure different composition

## 3.4.1 Coherent interfaces

coherent, semicoherent incoherent

Disregarding chemical species, if the interfacial plane has the same atomic configuration in both phases,



Fig. 3.32 Strain-free coherent interfaces. (a) Each crystal has a different chemical composition 6 but the same crystal structure. (b) The two phases have different lattices

#### 3.4.1 Coherent interfaces

Which plane and direction will be coherent between FCC and HCP?

: Interphase interface will make lowest energy and thereby the lowest nucleation barrier

ex) hcp silicon-rich  $\kappa$  phase in fcc copper-rich  $\alpha$  matrix of Cu-Si alloy



When the atomic spacing in the interface is not identical between the adjacent phase, what would happen?



Fig. 3.34 A coherent interface with slight mismatch leads to coherency strains in the adjoining lattices.

8

The strains associated with a coherent interface raise the total energy of the system.

How can this coherent strain can be reduced?

If coherency strain energy is sufficiently large, → "misfit dislocations" → semi-coherent interface



Fig. 3.35 A semi-coherent interface. The misfit parallel to the interface is accommodated by a series of edge dislocations.

#### (2) Semicoherent interfaces



$$\begin{split} &\delta = (d_{\beta} - d_{\alpha})/d_{\alpha} : \text{misfit} \\ &\rightarrow D \text{ vs. } \delta \text{ vs. } n \\ &(n+1) d_{\alpha} = n d_{\beta} = D \\ &\delta = (d_{\beta}/d_{\alpha}) - 1, (d_{\beta}/d_{\alpha}) = 1 + 1/n = 1 + \delta \\ &\rightarrow \delta = 1/n \\ &D = d_{\beta}/\delta \approx b/\delta \quad [b=(d_{\alpha} + d_{\beta})/2] \\ &\delta \sim \text{ small,} \end{split}$$

## $\gamma$ (semicoherent) = $\gamma_{ch} + \gamma_{st}$

 $\gamma_{st} \rightarrow$  due to structural distortions caused by the misfit dislocations

$${\gamma}_{\sf st} \propto \delta$$
 for small  $\delta$ 

In general,  $\gamma$  (semicoherent) ~ 200~500 mJm<sup>-2</sup>



- 3) Incoherent Interfaces ~ high angle grain boudnary
  - 1)  $\delta > 0.25$  No possibility of good matching across the interface

2) different crystal structure (in general)







11

 $\gamma$  (incoherent) ~ 500~1000 mJm<sup>-2</sup>

#### 4) Complex Semicoherent Interfaces



a<sub>α</sub>=2.87



[001] <sub>α</sub>= 2.87



If bcc  $\alpha$  is precipitated from fcc  $\gamma$ , which interface is expected?

Which orientation would make the lowest interface energy?

a<sub>γ</sub>=3.57 For fcc and bcc crystals ~ closest-pack planes in each phase almost parallel to each other Nishiyama-Wasserman (N-W) Relationship

$$(110)_{bcc}$$
 //(111)<sub>fcc</sub>,  $[001]_{bcc}$  // $[\overline{1}01]_{fcc}$ 

Kurdjumov-Sachs (K-S) Relationships

$$(110)_{bcc}$$
 //(111)<sub>fcc</sub>,  $[1\overline{1}1]_{bcc}$  // $[0\overline{1}1]_{fcc}$ 

(The only difference between these two is a rotation in the closest-packed planes of 5.26°.)

## **Complex Semicoherent Interfaces**

Semicoherent interface observed at boundaries formed by low-index planes. (atom pattern and spacing are almost equal.)

**N-W relationship** 

Good fit is restricted to small diamondshaped areas that only contain ~8% of the orientation relationship.

A similar situation can be shown to exist for the K-S orientation relationship.

⇒ But,

impossible to form alarge interfaces→ Incoherent interface



Fig. 3.38 Atomic matching across a (111)fcc/(110)bcc interface bearing the NW orientation relationship for lattice parameters closely corresponding to the case of fcc and bcc iron.

#### **Complex Semicoherent Interfaces**



The degree of coherency can, however, be greatly increased if a macroscopically irrational interface is formed. The detailed structure of such interfaces is, however, uncertain due to their complex nature.

## 3.4 Interphase Interfaces in Solids



**Complex Semicoherent Interfaces** 

Nishiyama-Wasserman (N-W) Relationship Kurdjumov-Sachs (K-S) Relationships

15

(The only difference between these two is a rotation in the closest-packed planes of 5.26°.)

The degree of coherency can, however, be greatly increased if a macroscopically irrational interface is formed.

# **Q: How is the second-phase shape determined?**



(a) Precipitate shapes :  $\sum A_i \gamma_i \downarrow$ 

(b) Calculation of misfit strain energy

## **3.4.2 Second-Phase Shape: Interfacial Energy Effects**

How is the second-phase shape determined?  $\sum A_i \gamma_i = minimum$ Lowest total interfacial free energy by optimizing the shape of the precipitate and its orientation relationship

#### A. Fully Coherent Precipitates (G.P. Zone)

- If  $\alpha,\beta$  have the same structure & a similar lattice parameter
- Happens during early stage of many precipitation hardening
- Good match  $\Box$  can have any shape  $\Box$  spherical



to the total free energy



17

(b) Ag-rich GP zones (Dia. ~10 nm) in Al-4at% Ag alloy

### **B. Partially Coherent Precipitates**

- $\alpha$ ,  $\beta$  have different structure and one plane which provide close match
- <u>Coherent or Semi-coherent in one Plane;</u>
   Disc Shape (also plate, lath, needle-like shapes are possible)



Fig. 3.40 A section through a **γ-plot** for a precipitate showing one coherent or semi-coherent interface, together with the equilibrium shape (a disc).

Precipitate shapes observed in practice

~ not equilibrium shape why? 1) misfit strain E effects ~ ignored.
 through a γ-plot
 2) different growth rates depending on directions

## $hcp \gamma'$ Precipitates in AI – 4% Ag Alloys $\rightarrow$ plate

Semicoherent broad face parallel to the  $\{111\}_{\alpha}$  matrix planes (usual hcp/fcc orientation relationship)



Fig. 3. 42 Electron micrograph showing the Widmanstatten morphology of  $\gamma$ ' precipitates in an Al-4 atomic % Ag alloy. GP zones can be seen between the  $\gamma$ ' e.g. at H (x 7000).

## **C. Incoherent precipitates**

- when  $\alpha$ ,  $\beta$  have completely different structure  $\Box$  Incoherent interfaces or When the two lattices are in a random orientation
- Interface energy is high for all plane with smoothly curved interface
- Polyhedral shapes: certain crystallographic planes of the inclusion lie at cusps in the γ-plot



 $\theta$  phase in Al-Cu alloys (Al<sub>2</sub>Cu) 20

## Q: Example of Second-Phase Shape precipitates from solid solution in Al-Cu alloys



## **Precipitation Hardening**

- Ex: Al-Cu system
- Procedure:
- *Pt A*: solution heat treat (get a solid solution)
- *Pt B*: quench to room temp.
- *Pt C*: reheat to nucleate small  $\theta$  crystals within  $\alpha$  crystals.



 $\alpha + \theta \rightarrow \text{Heat} (\sim 550^{\circ}\text{C}) \rightarrow \text{Quench} (0^{\circ}\text{C}) \rightarrow \alpha \text{ (ssss)} \rightarrow \text{Heat/age} (\sim 150^{\circ}\text{C}) \alpha + \theta_{\text{ppt}}$ 





## **Al-Cu ppt structures**

**GP** zone structure





(a) Bright-field TEM image showing G.P. zones, and (b) HRTEM image of a G.P. zone  $^{24}_{24}$  formed on a single (0 0 0 1)<sub>a</sub> plane. Electron beam is parallel to in both (a) and (b).

 $\theta'$  Phase Al-Cu Alloys

Semicoherent broad face parallel to the  $\{100\}_{\alpha}$  matrix planes (habit plane)



## $\theta$ phase in Al - Cu alloys (Al<sub>2</sub>Cu)



- Polyhedral shapes: certain crystallographic planes of the inclusion lie at cusps  $_{26}$  in the  $\gamma\text{-plot}$ 

#### 5.5.4. Age Hardening

Transition phase precipitation  $\rightarrow$  great improvement in the mechanical properties Coherent precipitates  $\rightarrow$  highly strained matrix  $\rightarrow$  dislocations~forced during deformation



Fig. 5. 37 Hardness vs. time for various Al-Cu alloys at (a) 130  $^\circ$ C (b) 190  $^\circ$ C

## **Precipitates on Grain Boundaries**

Formation of a second-phase particle at the interfaces with two differently oriented grains

- 1) incoherent interfaces with both grains
- 2) a coherent or semi-coherent interface with one grain and an incoherent interface with the other,
- 3) coherent or semi-coherent interface with both grains



Fig. 3. 45 Possible morphologies for grain boundary precipitates. Incoherent interfaces smoothly curved. Coherent or semicoherent interface plannar.

#### **Precipitates on Grain Boundaries**



Fig. 3. 46 An  $\alpha$  precipitate at a grain boundary triple point in an  $\alpha - \beta$  Cu-In alloy. Interfaces A and B are incoherent while C is semicoherent (x 310).

A, B; Incoherent, C; Semi-coherent or coherent 29



2) Second-Phase Shape: precipitate from solid solution in Al-Cu alloys



# Q: How is the second-phase shape determined?

 $\sum A_i \gamma_i + \Delta G_S = minimum$ 

γ - plot + misfit strain E
 Lowest total interfacial free energy
 by optimizing the shape of the precipitate and its orientation relationship



## (a) Precipitate shapes

(b) Calculation of misfit strain energy

## 3.4.3. Second-Phase Shape: Misfit Strain Effects





In situ misfit is no longer equal in all directions



Fig. 3. 48 For a coherent thin disc there is **little misfit parallel to the plane of the disc.** Maximum misfit is perpendicular to the disc. → reduction in coherency strain E

\* Total elastic energy ( $\Delta G_s$ ) depends on the "shape" and "elastic properties" of both matrix and inclusion.



Influence of strain E ( $\delta$  =lattice misfit) on the equilibrium shape of coherent precipitation

#### **B. Incoherent Inclusions**

Lattice sites are not conserved.  $\rightarrow$  no coherency strain,  $\Delta G_s$ But, misfit strain still arise if the inclusion is the wrong size.

δ (lattice misfit)  $\rightarrow Δ$  (volume misfit)



For a homogeneous incompressible inclusion in an isotropic matrix

등방성 기지내 균질 비압축성 개재물



 $\boldsymbol{\mu} \textbf{:}$  the shear modulus of the matrix

1) The elastic strain energy is proportional to the square of the volume misfit  $\Delta^2$ . 34



2) Shape effect for misfit strain  $E \sim function f$  (c/a)

Fig. 3. 50 The variation of misfit strain energy with ellipsoid shape, f(c/a).

$$\Delta G_{s} = \frac{2}{3} \mu \Delta^{2} \cdot V \cdot f(c/a) \qquad \Delta = \frac{V_{\beta} - V_{\alpha}}{V_{\alpha}} \approx 3\delta \text{ for sphere}$$
Elastic strain E Precipitate shape effect  $\neq 3\delta$  for disc or needle

 \* Equil. Shape of an incoherent inclusion: an oblate spheroid with c/a value that balances the opposing effects of interfacial E and strain E
 (here, Δ~ small → Interfacial E dominant → roughly spherical inclusion)

35

## **C. Plate-like precipitates**

<u>Misfit across the broad faces  $\rightarrow$  large coherency strains parallel to the plate</u>



In situ misfit across the broad faces increases with increasing plate thickness

- → the precipitate behaves as an incoherent inclusion with comparatively little misfit strain E, ex)  $\theta$ ' phase in Al-Cu alloy  $\theta$  (001)

(001) Coherent or semicoherent

(100)

 $\times_{(010)}$ 



# Q: Which state produces the lowest total E for a spherical precipitate?

## "Coherency loss"

If a coherent precipitate grows, during aging for example, It should lose coherency when it exceeds  $r_{crit}$ .



#### **Coherency Loss** Precipitates with coherent interfaces=low interfacial E + coherency strain E Precipitates with non-coherent interfaces=higher interfacial E

If a coherent precipitate grows, it should lose coherency to maintain minimum interfacial free E.



Fig. 3. 52 The total energy of matrix + precipitate vs. precipitate radius for spherical coherent and <u>non-coherent (semicoherent of incoherent)</u> precipitates.

If a coherent precipitate grows, during aging for example, It should lose coherency when it exceeds  $r_{crit}$ .



#### Fig. 3.53. <u>Coherency loss</u> for a spherical precipitate

In practice, this phenomena can be rather difficult to achieve. — Coherent precipitates are often found with sizes much larger than r<sub>crit</sub>.

#### Dislocation \* Punching stress ( $P_s$ ) ~ independent of size, 1) spherical precipitate but $P_{\rm s} \propto \text{constrained misfit}$ , $\varepsilon (\geq \epsilon_{\rm crit} \sim 0.05)$ , "precipitates with a smaller $\varepsilon$ cannot lose coherency by (a), no matter how large." Matrix dislocation wraps around the precipitate with a Precipitate suitable Burgers vector Punched-out **Dislocation** loop punching from requires the stresses at the interface interface to exceed the theoretical strength of the matrix assisted by mechanical deformation Interfacial (a) dislocation (b) Capture of matrix dislocation 2) Plate precipitate **Prismatic dislocation loop** High stress at the edges Misfit New dislocation Nucleation of D loops within the precipitate dislocation as plate **Constant inter D spacing** (d) Vacancies can be attracted to coherent (c) lengthens interfaces and 'condense' to form a

"Mechanisms for coherency loss": all require the precipitate to reach a larger size than r<sub>crit</sub>

Nucleation of dislocation at the edge  $\rightarrow$  maintain a roughly prismatic dislocation loop which can constant inter-dislocation spacing during plate lengthening

expand across the precipitate

## Contents for previous class

## 3.4 Interphase Interfaces in Solids

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Interphase boundary - different two phases : different crystal structure different composition
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Perfect atomic matching at interface
coherent.
                      \gamma (coherent) = \gamma_{ch} \gamma (coherent) ~ 200 mJM<sup>-2</sup>
                                                                          semi D \downarrow \rightarrow Strain field overlap
semicoherent \gamma(semicoherent) = \gamma_{ch} + \gamma_{st}
                                                                                      \rightarrow cancel out
                                                                 γ
                        \gamma_{st} \rightarrow due to <u>structural distortions</u>
                        caused by the misfit dislocations
                      \gamma(semicoherent) ~ 200~500 mJM<sup>-2</sup>
                                                                                           δ
                                                                           0.25
                                                                     \delta=4: 1 dislocation per 4 lattices
incoherent
                     1) \delta > 0.25 No possibility of good matching across the interface
                     2) different crystal structure (in general)
                     \gamma (incoherent) ~ 500~1000 mJM<sup>-2</sup>
 Complex Semicoherent Interfaces
  Nishiyama-Wasserman (N-W) Relationship
                                                      Kurdjumov-Sachs (K-S) Relationships
                                                                                                          41
  (The only difference between these two is a rotation in the closest-packed planes of 5.26°.)
  The degree of coherency can, however, be greatly increased if a macroscopically irrational interface is formed.
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## 3.4 Interphase Interfaces in Solids

