EMA5001 Lecture 16
Diffusional Transformation in Solids - Introduction
Introduction

- **Phase transformation**
  - Solid-gas reaction: e.g., sublimation, oxidation of metals
  - Solid-liquid conversion: e.g., solidification
  - Solid-solid phase transformation: precipitation; polymorph transformation;

- **At least one (can be both) of the following changes for solid-state phase transformation**
  - (Crystal) structure
    - $\alpha$-Fe $\leftrightarrow \gamma$-Fe
    - Extent of ordering
  - (Chemical) composition
    - Spinodal decomposition

- **Thermodynamics vs. Kinetics**
  - Lowering (not necessarily minimization) of system free energy
  - Overcome kinetic barriers
Characteristics of Solid-State Phase Transformation (1)

- **Large barrier**
  - Volume strain energy (difference in molar volume)
  - Interfacial energy (chemical term + geometric term)

- **Slow migration (mobility) of atoms**
  - (Self) diffusion coefficient in solid is $\sim 10^{-6}$ of that in liquid

- **Mostly heterogeneous nucleation**
  - All types of defects as potential heterogeneous nucleation sites
    - Vacancy
    - Dislocation
    - Grain boundary
    - Stacking fault
    - Second phase
    - Surface

Meta-stable phase may appear

- Although I → II is energetically favorable
- Too large barrier (especially at lower T) makes existence of meta-stable phase possible

New phase often has specific shapes

- Interface energy controlled – Matching of low energy interfaces
- Strain energy controlled – Plate like

Various interface structures (coherent, semi-coherent, incoherent)

Match of certain orientation and crystal planes between new phase and matrix

\[ \Delta G \]

\[ \Delta G_a \]

Classification of Solid-State Phase Transformation by Thermodynamics

1\textsuperscript{st} order phase transformation

\begin{align*}
G_1 &= G_2 \\
\mu_i^1 &= \mu_i^2 \\
\left( \frac{\partial G_1}{\partial T} \right)_P &\neq \left( \frac{\partial G_2}{\partial T} \right)_P \\
\Delta V &\neq 0
\end{align*}

\begin{align*}
\left( \frac{\partial G_1}{\partial P} \right)_T &\neq \left( \frac{\partial G_2}{\partial P} \right)_T \\
dG &= VdP - SdT \\
\Delta S &\neq 0
\end{align*}

Examples: most solid phase transformation including solidification, precipitation

2\textsuperscript{nd} order phase transformation

\begin{align*}
G_1 &= G_2 \\
\mu_i^1 &= \mu_i^2 \\
\left( \frac{\partial G_1}{\partial T} \right)_P &= \left( \frac{\partial G_2}{\partial T} \right)_P \\
\left( \frac{\partial^2 G_1}{\partial T^2} \right)_P &\neq \left( \frac{\partial^2 G_2}{\partial T^2} \right)_P \\
\left( \frac{\partial^2 G_1}{\partial P^2} \right)_T &\neq \left( \frac{\partial^2 G_2}{\partial P^2} \right)_T \\
\frac{\partial^2 G_1}{\partial P \partial T} &\neq \frac{\partial^2 G_2}{\partial P \partial T} \\
\Delta C_p &\neq 0 \\
\Delta \beta &\neq 0 \\
\Delta \alpha &\neq 0
\end{align*}

Examples: some order-disorder transformation
1st Order Phase Transformation vs. 2nd Order Phase Transformation

- Change of $G$, $S$, $V$, $H$, and $C_p$ with $T$

![Graphs showing the change of various properties with temperature for 1st and 2nd order phase transformations.](image)

Classification of Solid-State Phase Transformation by Kinetics

- **By diffusion**
  - Diffusionless
  - Diffusion
    - a) Precipitation: \( \alpha' \rightarrow \alpha + \beta \)
      Change in solubility with temperature
      - \( \gamma - \text{Fe} \rightarrow \alpha - \text{Fe} + \gamma - \text{Fe} \)
    - b) Eutectoid transformation: \( \gamma \rightarrow \alpha + \beta \)
      - \( \gamma - \text{Fe} \rightarrow \alpha - \text{Fe} + \text{Fe}_3\text{C} \)
    - c) Ordering: \( \alpha \) (disordered) \( \rightarrow \alpha \) (ordered)
      - \( \text{Cu-Zn; Cu-Au} \)
    - d) Massive transformation
      - \( \beta \text{ brass} \rightarrow \alpha \text{ brass} \) at 38 atom% Zn
    - e) Polymorphic changes
      - \( \text{Diamond} \rightarrow \text{graphite} \)
      - \( \gamma - \text{Fe} \rightarrow \alpha - \text{Fe} \)

*Phase Transformations in Metals & Alloys, Porter, 3rd Ed, 2008, p. 262*