Phase transformations

Lecture for „Mechanical Engineering“ and „Materials Science and Engineering“
Dr.-Ing. Alexander Kauffmann (Bldg. 10.91, R. 375)
Topics

- Allotropic Transformations
  - Driving Force and Latent Heat
  - Nucleation, Impact of Strain Energy
Extension to Solidification

For allotropic transformations, the same considerations on phase transformations as for solidification need to be considered but with taking into account

- that the newly formed and surrounding phase are elastically stiff and, hence, strain energy of both need to be considered during both, nucleation and growth,

- and that the growing phase cannot rearrange when getting in contact. (The nucleation sites in the liquid are free and can move, in the solid they are fixed and cannot move. This needs to be considered during integration to obtain the transformed volume)
Driving Force and Latent Heat

Note that for solid modifications, the differences in $H_0$ are typically smaller. So slight variations in $S$ might lead to phase transformations, e.g. magnetism, dielectricity, chemistry, etc.

Iron Fe
Driving Force and Latent Heat

Since both $\alpha$ and $\delta$ are bcc, both can be described by a single $G$ curve. $\gamma$ is treated individually.

Iron Fe
Driving Force and Latent Heat

\[ G \]

\[ H_0^L \]

\[ T_{\alpha-\gamma} \]

\[ T_{\gamma-\delta} \]

\[ T_m \]

\[ \alpha \] exhibits ferromagnetic order at \( T < T_C \). Above \( T_C \), the ferrite is paramagnetic.

At low temperatures, the ferromagnetic order causes slightly lower \( S \) of \( \alpha \) over \( \gamma \). By the transition to the paramagnetic state, the \( S \) contribution to \( G \) of \( \alpha \) increases.
Homogeneous Nucleation

\[ \Delta G \]

\[ \Delta G^I \propto +r^2 \]

\[ \Delta G^I \propto +r^2 \]

\[ \Delta G^D \propto -r^3 \]

\[ \Delta G^{hom} = -V^N \Delta g^D + A^I \gamma^I \]

Revision of Ch. 3a
Homogeneous Nucleation

\[ \Delta G = \Delta G^{\text{hom}} + \Delta G^{D} + \Delta G^{S} + A^{I} \gamma^{I} \]

In the case of a transformation within the solid, the newly formed phase is of different shape and volume than the matrix. Hence, an adaption by elastic strain of the newly formed phase and the matrix occurs. The total strain energy \( \Delta G^{S} \) associated with this scales with the volume of the newly formed phase.

Note the subtle impact of \( \Delta G^{S} \) on the \( \propto -r^3 \) dependence but the significant shift of \( \Delta G^{\text{hom}} \) over the strain-free case on the slide before.
Homogeneous Nucleation

\[
\frac{d\Delta G}{dr} = -4\pi r^2 (\Delta g^D - \Delta g^S) + 8\pi r \gamma^I
\]

\[-r^c \Delta g^D + 2r^c \gamma^I = 0\]

\[r^c = \frac{2 \gamma^I}{\Delta g^D - \Delta g^S}\]

The strain energy term essentially acts like a reduced driving force for the transformation to occur.

\[\Delta G^c = \Delta G(r^c) = -\frac{4}{3} \pi \left( \frac{2 \gamma^I}{\Delta g^D} \right)^3 \Delta g^D + 4\pi \left( \frac{2 \gamma^I}{\Delta g^D} \right)^2 \gamma\]

\[= \frac{16\pi}{3} \gamma^I^3 \frac{16\pi}{(\Delta g^D - \Delta g^S)^2}\]
Strain Energy

The strain contribution to the transformation depends on the type of interface of the newly formed phase:

- **Coherent:** atomic positions in the interface between the two phases match and accommodation of the different lattice types is needed.
- **Semi-coherent:** at least some atomic positions in the interface match.
- **Incoherent:** the atomic positions of the two phases do not match within the interface.
Strain Energy

Coherent interface:

\[ \delta = \frac{a^N - a^M}{a^M} \]

\[ \Delta = \frac{V^N - V^M}{V^M} \approx 3\delta \]

\[ \varepsilon = \frac{a'^N - a^M}{a^M} \]

The newly formed phase has a similar crystal structure but with slightly different dimensions and a lattice misfit \( \delta \). There is an according volume misfit \( \Delta \).

When embedded in the matrix, both matrix and nucleus are strained in order to get matching lattice positions (maintaining coherency). See Ch. 2.
Strain Energy

- Coherent interface:

- With typically $0.5\delta < \varepsilon < \delta$, for example $\varepsilon \approx \frac{2}{3}\delta$, for $\nu^M = \nu^N = \nu \approx \frac{1}{3}$ and $G^M = G^N = G$.

- For a spherical nucleus, the distortion of the nucleus is hydrostatic (uniform in all directions) while being concentrated along the thin axis for a thin plate-like nucleus.

- The volume-specific elastic strain energy can be estimated for isotropic elastic behavior of both the matrix and the newly formed phase:

  - $G^M = G^N = G$: $\Delta g^S = \frac{\Delta G^S}{V} = 2\ G\ \delta^2\ \frac{1+v}{1-v}$ (independent of its shape)
  - $G^M < G^N$: $\Delta g^S$ gets minimized for a flat ellipsoid
  - $G^M > G^N$: $\Delta g^S$ gets minimized for a sphere

  In any case, $\Delta g^S$ is a constant. $V$ denotes the unconstraint volume of the hole.
Strain Energy

- Coherent interface:
  - For anisotropic elastic behavior, minimization of the shape also depends on the crystallographic arrangement of the shape within the lattice.
  - For most metallic materials, positive Zener anisotropies are observed, e.g. \(\langle 001\rangle\) are more compliant than the stiff \(\langle 111\rangle\). Under these conditions, discs parallel to \(\{001\}\) are favorable to accommodate most strain in the compliant direction.
## Compliance and stiffness

<table>
<thead>
<tr>
<th>material</th>
<th>prototype</th>
<th>Strukturbericht</th>
<th>$C_{11}$ / GPa</th>
<th>$C_{12}$ / GPa</th>
<th>$C_{44}$ / GPa</th>
<th>$A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Cu</td>
<td>A1</td>
<td>166</td>
<td>120</td>
<td>76</td>
<td>3.3</td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td></td>
<td>106</td>
<td>60</td>
<td>28</td>
<td>1.2</td>
</tr>
<tr>
<td>Au</td>
<td></td>
<td></td>
<td>193</td>
<td>164</td>
<td>42</td>
<td>2.9</td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td></td>
<td>251</td>
<td>150</td>
<td>124</td>
<td>2.5</td>
</tr>
<tr>
<td>α-Fe</td>
<td>W</td>
<td>A2</td>
<td>230</td>
<td>135</td>
<td>117</td>
<td>2.5</td>
</tr>
<tr>
<td>W</td>
<td></td>
<td></td>
<td>501</td>
<td>198</td>
<td>151</td>
<td>1.0</td>
</tr>
<tr>
<td>Si</td>
<td>diamond</td>
<td>A4</td>
<td>166</td>
<td>64</td>
<td>80</td>
<td>1.6</td>
</tr>
<tr>
<td>NaCl</td>
<td>NaCl</td>
<td>B1</td>
<td>49</td>
<td>13</td>
<td>13</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Compliance and stiffness

Visualization of the anisotropic Young’s moduli of single crystals deformed uniaxial along certain axes:

- **Cu**
  - $A = 3.3$
  - $A_{[001]} = 65$ GPa, $A_{[100]} = 192$ GPa

- **W**
  - $A = 1.0$
  - $A_{[010]} = 387.7$ GPa, $A_{[110]} = 388.8$ GPa

- **NaCl**
  - $A = 0.7$
  - $A_{[001]} = 33.2$ GPa, $A_{[111]} = 43.5$ GPa
Strain Energy

- Incoherent interface:

\[ \Delta = \frac{V^N - V^M}{V^M} \neq 3\delta \]

The newly formed phase is of different crystal structure and a different volume.

Due to the incoherency, no coherence strain of the nucleus occurs, but still the phases need to be deformed to accommodate the different volume. Note that a rigid body rotation might occur to accommodate anisotropic interface energy.

Notice the different number of lattice sites, in the nucleus vs. the matrix before making the hole.
Strain Energy

- Incoherent interface:

- The volume-specific elastic strain energy can be estimated for isotropic elastic behavior of both the matrix and an incompressible, spheroidal nucleus (cigar-like of the dimensions $a$ and $c$):
  - $G^M = G^N = G$, $\nu^M = \nu^N = \nu \approx \frac{1}{3}$: $\Delta g^S = \frac{\Delta g^S}{\nu} = \frac{2}{3} G \Delta^2 \frac{c}{a}$
  - Hence, sphere and disc have maximum and minimal strain energy, respectively.
  - Anisotropy has only small impact on the elastic strain energy in this case.

\[
f \left( \frac{c}{a} \rightarrow \infty \right) = \frac{3}{4}
\]
Semi-coherent interface:

For the case of semi-coherent interfaces, the strain energy by the incorporation of misfit dislocations needs to be considered. This strain energy contribution must be smaller than the energy contribution for the coherent interface to allow for the formation of misfit dislocations.
Heterogeneous Nucleation

- Apart from super cooling, $\Delta G$ can be manipulated by modification of the interface contribution.
- For example, wetting of the nucleus at an already existing catalyst (e.g. walls of molds and dies) can be assumed:

\[ V^N = \frac{\pi}{3} r^3 (2 + \cos \theta)(1 - \cos \theta)^2 \]
\[ A^{SL} = 2\pi r^2 (1 - \cos \theta) \]
\[ A^{CS} = \pi r^2 (1 - \cos^2 \theta) \]
Heterogeneous Nucleation

The situation for the solid-solid transformation is similar but with a double cap nucleus nucleating at a boundary present in the matrix:

\[ V^N = \frac{2\pi}{3} r^3 (2 + \cos \theta)(1 - \cos \theta)^2 \]
\[ A^I = 4\pi r^2 (1 - \cos \theta) \]
\[ A^{GB} = \pi r^2 (1 - \cos^2 \theta) \]
Heterogeneous Nucleation

In order to estimate the interface energies, Young’s pseudo equilibrium can be considered:

\[
\Delta G^{\text{het}} = -V^N (\Delta g^D - \Delta g^S) + A^I \gamma^I - A^{\text{GB}} \gamma^{\text{GB}}
\]

\[
= -\frac{2\pi}{3} r^3 (2 + \cos \theta)(1 - \cos \theta)^2(\Delta g^D - \Delta g^S) + 4\pi r^2 (1 - \cos \theta) \gamma^I \\
- \pi r^2 (1 - \cos^2 \theta) \gamma^{\text{GB}}
\]

\[
= -\frac{2\pi}{3} r^3 (2 + \cos \theta)(1 - \cos \theta)^2(\Delta g^D - \Delta g^S) + 4\pi r^2 (1 - \cos \theta) \gamma^I \\
- \pi r^2 (1 - \cos^2 \theta) 2\gamma^I \cos \theta
\]

\[
= -\frac{2\pi}{3} r^3 (\Delta g^D - \Delta g^S)(2 - 3 \cos \theta + \cos^3 \theta) + 2\pi r^2 \gamma^I (2 - 3 \cos \theta + \cos^3 \theta)
\]

\[
= \left( -\frac{4}{3} \pi r^3 (\Delta g^D - \Delta g^S) + 4\pi r^2 \gamma^I \right) \frac{1}{2} (2 - 3 \cos \theta + \cos^3 \theta)
\]

Note that the grain boundary GB exists before nucleation and is removed by nucleation. Instead, the interface I is formed.
Heterogeneous Nucleation

\[ \Delta G^{\text{het}} = f(\Theta) \Delta G^{\text{hom}} \]

The critical radius \( r^{\text{het},c} \) remains the same for both situations while the \( \Delta G^{\text{het},c} \) barrier gets smaller depending on \( \Theta \).

\[ \text{with } f(\Theta) = \frac{1}{2} (2 - 3 \cos \Theta + \cos^3 \Theta) \leq f(\Theta) \leq 0.5 \]
Heterogeneous Nucleation

The heterogeneous nucleation becomes more effective for high energy boundaries $\gamma_{GB}$, e.g. arbitrary high angle grain boundaries. The nucleation at grain edges and corners is even more feasible. The formation of coherent or semi-coherent facets might further reduce the nucleation barrier close to grain boundaries.

$$f(\theta) = \frac{1}{2} \left(2 - 3 \cos \theta + \cos^3 \theta\right)$$

$$= \frac{1}{2} (2 + \cos \theta)(1 - \cos \theta)^2$$

$$\cos \theta = \frac{\gamma_{GB}}{2\gamma_I}$$