Module #19

Solid Solution Hardening

READING LIST

► DIETER: Ch. 6, Pages 203-207


HOMEWORK
Do solute atoms have more of an influence on the Peierls stress or on dislocation locking? Explain your answer.
What is a Solid Solution?

- **Solid Solution**
  
  *When two or more elements are combined such that single phase microstructures are maintained.*

- Solute atoms of roughly similar sizes (i.e., within ±15% of the radii of the parent atoms) can occupy points in the crystal lattice of solvent atoms. We call this a *substitutional solid solution*.

- When solute atoms are considerably smaller than the solvent atoms (i.e., up to 57% of the radii of the solvent atoms), they occupy interstitial sites in the solvent lattice. We call this type of solid solution an *interstitial solid solution*. 
Substitutional solute

Interstitial solute

[From Ashby, Shercliff, and Cebon, 2007, p.120]
Solid Solution Hardening

• A series of elastic, electrical, and chemical interactions occur between the stress fields of the solute atoms and the dislocations that occupy the lattice.

• These interactions ultimately produce an alloy that is (usually) stronger than the pure metal.
Principle

- Inhomogeneities in a crystal lattice will produce a stress field within a lattice.

- Dislocations will interact with those stress fields.
  - The type of interaction will determine the degree of hardening or softening.

- In general, solute atoms increase the strengths of crystals. However, under certain conditions they can decrease the strength.

- The increase arises due to:
  - Short range $\perp$ - solute interactions
  - Long range $\perp$ - solute interactions

- Dislocations interact with solutes that lie on, above, and below slip planes. The most intense interactions will occur in close proximity to the slip plane (i.e., near the dislocation core).
Solute interactions with dislocations

1. Elastic interaction (aka, “size effect”)*
2. Modulus interaction*
3. Stacking fault interaction
4. Electrical (valence) interaction
5. Short-range order interaction
6. Long-range order interaction

- Solid solution strengthening is dominated by type 1 and 2 interactions.
- Type 1, 2, and 6 interactions are “long range,” which means that they are relatively insensitive to temperature and are strong up to $\sim 0.6 - 0.7T_{mp}$.
- Type 3, 4, and 5 interactions are “short range,” which means that they will contribute strongly to flow stress at low temperatures (i.e., approx. $< 0.3T_{mp}$). However they are easily overcome at higher temperatures.
The size effect

- Solute atoms “stretch” (i.e., dilate) the lattice producing different types of stress fields surrounding the solutes.
Influence of stress field shape

• The shape of the stress fields caused by defects and those around dislocations have a significant impact on the strength of a solid.

• **Substitutional solutes** generally stretch the lattice uniformly producing **hydrostatic** ("spherical") stress fields around the solutes.

• These **hydrostatic stress fields** are relatively "weak" obstacles to further dislocation motion in comparison to shear stress fields.
RECALL

Different types of dislocations have different stress fields too. What would the stress field look like surrounding a mixed dislocation?
There is an interaction between the stress fields around solute atoms and the stress fields around dislocations. This interaction is based on reducing the strain energy associated with dislocations and solute atoms.

Using an edge dislocation in this example, the region above an edge dislocation is in compression. The region below the core is in tension. Solute atoms with dilatational stress fields will interact with these regions to cancel out strain and thus reduce the elastic strain energy of the system.

Both attractive and repulsive forces between solutes and dislocations will inhibit the motion of dislocations, thus increasing strength.
In Summary

• Solutes are attracted to dislocations to reduce strain energy of the crystal.

• This results in a binding energy between the solutes and the dislocations.

• The dislocations must drag the solutes along unless/until they have enough energy to “break free” from the solutes.

[Ashby, Shercliff, & Cebon, p. 129]
Stress field interactions

- Hydrostatic (i.e., dilatational) stress fields will interact with other hydrostatic stress fields (i.e., compressive and tensile regions interact with other compressive and tensile regions).

- Shear stress fields will interact with other shear stress fields.

- What does this mean with regard to interactions with dislocations?
Stress fields around dislocations

Edge Dislocation
- Shear strain parallel to $\vec{b}$
- Hydrostatic strain parallel to $\vec{b} \times \xi$

Screw Dislocation
- Shear strain parallel to $\vec{b}$
- No hydrostatic strain
Stress tensors for straight dislocations

Edge \perp moves this way

Edge \perp moves this way

Screw \perp moves this way

\[
\begin{pmatrix}
\sigma_{xx} & \tau_{xy} & 0 \\
\tau_{yx} & \sigma_{yy} & 0 \\
0 & 0 & \sigma_{zz}
\end{pmatrix}
\]

\[
\begin{pmatrix}
\sigma_{zz} & 0 & 0 \\
0 & \sigma_{zz} & 0 \\
\tau_{xy} & \tau_{xy} & 0
\end{pmatrix}
\]

edge  
solute  
screw

Interaction  
No Interaction
Stress fields around solutes (1)

• FCC lattice
  – Substitutional solute: dilatational (hydrostatic) strain.
  – Interstitial solute: dilatational (hydrostatic) strain.

• BCC lattice
  – Substitutional solute: dilatational (hydrostatic) strain
  – Interstitial solute: distortional (shear) strain. This component is asymmetric!

• What interactions might be expected between solutes and dislocations in different lattices?
What interactions might be expected between solutes and dislocations in different lattices?

- **FCC Lattice:**
  - Screw dislocations – little or no interactions with solutes
  - Edge dislocations – strong interactions with both types of solutes

- **BCC Lattice:**
  - Edge dislocations – strong interactions with both types of solutes
  - Screw dislocations – strong interactions possible with interstitial solutes; no interactions with substitutional solutes

- **HCP lattice:**
  - Which solutes will cause the most potent hardening?
Strengthening due to different defects

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>Defect</th>
<th>$\Delta\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Symmetrical Defects</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>fcc</td>
<td>Substitutional</td>
<td>G/10</td>
</tr>
<tr>
<td>Cu</td>
<td>fcc</td>
<td>Substitutional</td>
<td>G/20</td>
</tr>
<tr>
<td>Fe</td>
<td>bcc</td>
<td>Substitutional</td>
<td>G/16</td>
</tr>
<tr>
<td>Ni</td>
<td>fcc</td>
<td>Interstitial atom</td>
<td>G/10</td>
</tr>
<tr>
<td>Nb</td>
<td>bcc</td>
<td>Substitutional</td>
<td>G/10</td>
</tr>
<tr>
<td>NaCl</td>
<td>primitive</td>
<td>Monovalent substitutional</td>
<td>G/100</td>
</tr>
<tr>
<td><strong>Nonsymmetrical Defects</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>fcc</td>
<td>Vacancy disk (quenched in)</td>
<td>2G</td>
</tr>
<tr>
<td>Cu</td>
<td>fcc</td>
<td>Interstitial Cu (irradiation)</td>
<td>9G</td>
</tr>
<tr>
<td>Fe</td>
<td>bcc</td>
<td>Interstitial C</td>
<td>5G</td>
</tr>
<tr>
<td>LiF</td>
<td>primitive</td>
<td>Interstitial F (irradiation)</td>
<td>5G</td>
</tr>
<tr>
<td>NaCl</td>
<td>primitive</td>
<td>Divalent substitutional</td>
<td>2G</td>
</tr>
</tbody>
</table>
Modulus interaction (1)

- Since foreign atoms generally have *different shear moduli* than the parent atoms, they impose additional stress fields on the lattice of the surrounding matrix.

- Modulus interactions occur if the presence of a solute atom changes the local modulus of the crystal.

- When solutes with smaller shear moduli than the solvent (i.e., $G_{\text{solute}} < G_{\text{solvent}}$), the energy of the stress fields around dislocations will be reduced (i.e., elastic strain energy is reduced) which causes an attraction between the solutes and the dislocations.

- Both edge and screw dislocations are subject to this interaction.
References and the ultimate impact

• Size and modulus effects are detailed in some of Fleischer’s classic papers:
  
  
  

► Ultimately, the effectiveness of solid solution strengthening depends upon the size mismatch and the modulus mismatch between foreign atoms and parent atoms.
Strains induced by lattice and modulus mismatch (1)

- **Lattice misfit strains** are proportional to the local change in lattice parameter per unit concentration of solute. This can be expressed as:

  \[ \varepsilon_{\text{lattice}} = \frac{1}{a} \frac{da}{dc} \]

  where \( a \) is the lattice parameter of the solute and \( c \) is the concentration of solute.

- The equation describing the **modulus interaction** is similar:

  \[ \varepsilon_{\text{modulus}} = \frac{1}{G} \frac{dG}{dc} \]

- The modulus interaction energy can be either positive or negative depending upon the sign of \( \varepsilon_{\text{modulus}} \).
Strains induced by lattice and modulus mismatch (2)

- The total strain caused by both lattice and modulus mismatch ($\varepsilon_s$) has been shown by Fleischer to be:

$$\varepsilon_s = |\varepsilon_{\text{modulus}}' - \beta \varepsilon_{\text{lattice}}|$$

where

$$\varepsilon_{\text{modulus}}' = \frac{\varepsilon_{\text{modulus}}}{1 + \frac{1}{2} |\varepsilon_{\text{modulus}}|}$$

- In this equation, $\varepsilon_{\text{lattice}}$ and $\beta$ are always positive. $\varepsilon_{\text{modulus}}'$ is negative for “soft” atoms (size and modulus effects reinforce) and positive for “hard” atoms. $\beta$ is an empirical parameter that is related to the importance of screw and edge dislocations during plastic flow.

- We can relate solid solution strengthening to our general equation for strengthening. If we let $L'$ equal the effective obstacle spacing, then the increase in flow strength for solute atoms is:

$$\tau = \frac{F_{\text{max}}}{bL'}$$
Strains induced by lattice and modulus mismatch (3)

\[ \tau = \frac{F_{\text{max}}}{bL'} \]

- In this equation, \( F_{\text{max}} \) is proportional to \( Gb^2 \).
  - For “strong” obstacles (i.e., things that cause tetragonal lattice distortions):
    \[ F_{\text{max}} \approx \frac{Gb^2}{5} \text{ to } \frac{Gb^2}{10} \]
  - For “weak” obstacles (i.e., things that cause spherical lattice distortions):
    \[ F_{\text{max}} \approx \frac{Gb^2}{130} \]

- For tetragonal defects, solid solution strengthening is given as:
  \[ \tau_{\text{TET}} \approx \gamma Gb \left( \frac{\sqrt{c}}{b} \right) = \gamma G\sqrt{c} \]

- Common examples of tetragonal defects include interstitial solutes in BCC metals and interstitial-vacancy pairs in FCC metals.
Strains induced by lattice and modulus mismatch (4)

• The *general* strengthening *equation* for “conventional” *substitutional solid solution strengthening* has been estimated by Fleischer. It is:

\[ \tau_y = \frac{G\varepsilon_s^{3/2} \sqrt{c}}{700} \]

• Examples of materials showing \( c^{1/2} \) dependence were provided previously.

► In most solid solution materials, *size and modulus effects dominate strengthening.*
Strains induced by lattice and modulus mismatch (5)

- In some materials chemical and electrical factors are also significant.
  - In ionic solids the addition of solute atoms with different valence than the solvent alters the electronic charge distribution and energy leading to interactions with dislocations.
  - The addition of a divalent ion to a monovalent crystal produces a tetragonal distortion and can lead to significant electrical interactions between the impurity and the ions that comprise the dislocation.

- Tetragonal distortions generally produce the largest component of strengthening.
Examples of tetragonal distortions

Figure 5.9
Examples of tetragonal distortions caused by (a) an interstitial atom in a BCC lattice and (b) a divalent ion plus positive ion vacancy in a monovalent ionic solid.

• In (a) the interstitial atom does not fit into the lattice without distortion of the structure. This results in displacement of the solvent atoms along the z axis resulting in a tetragonal distortion.
• In (b) the divalent ion and the associated vacancy “relax” by approaching each other. This also produces a tetragonal distortion.

[Figure adapted from T.H. Courtney, Mechanical Behavior of Materials, 2nd Edition, Waveland Press (2000)]

Tetragonal defects are “strong” obstacles to dislocation glide.

Substitutional atoms produce spherical/uniform lattice strains and are “weak” obstacles.
Consider an octahedral interstitial site in a BCC lattice.

The size of this site is insufficient in the \( \langle 100 \rangle \) direction (i.e., in Fe \( \langle 100 \rangle = 0.38 \, \text{Å} \) while \( \langle 110 \rangle = 1.56 \, \text{Å} \)).

The carbon atom is 1.54 Å in diameter, thus strains induced by C will not be symmetric.

\[ \text{Fig. 6.3 An interstitial atom in the octahedral site of a BCC lattice produces a tetragonal distortion.} \]

The result of this distortion is that carbon atoms in BCC iron are attracted even to pure screw dislocations. This has profound effects, which will be described after considering how the solutes get to the dislocations.
Consider an octahedral interstitial site in a BCC lattice. The size of this site is insufficient in the <100> direction (i.e., in Fe <100> = 0.38 Å while <110> = 1.56 Å). The carbon atom is 1.54 Å in diameter, thus strains induced by C will not be symmetric.

**FIGURE 4.5** Nonsymmetrical stress fields in crystals. (a) Octahedral interstitial site in BCC crystal ⟨⟨100⟩⟩ anisotropy); (b) divalent ion-vacancy pair ⟨⟨110⟩⟩ anisotropy); (c) interstitial pair in FCC crystal ⟨⟨100⟩⟩ anisotropy); (d) vacancy disk ⟨⟨111⟩⟩ anisotropy). [Hertzberg]
The \( c^{1/2} \) dependence of solid-solution hardening is verified for (a) the increase in CRSS for a Cu alloy single crystal hardened by substitutional atoms (spherical distortions), (b) the tensile YS increase due to interstitials in Fe and Nb (tetragonal distortions), and (c) the increase in CRSS due to the presence of divalent Ca ions in NaCl (tetragonal distortions). Tetragonal distortions harden materials to a much larger degree than spherical ones. [Figure adapted from T.H. Courtney, *Mechanical Behavior of Materials, 2nd Edition*, Waveland Press (2000)]
Other types of solid solution strengthening/hardening (4)

- Suzuki atmospheres
  - In materials containing stacking faults, solute atoms can preferentially segregate to the stacking fault producing Suzuki atmospheres, or may be repelled by them.
  - This lowers the SFE for the solid which can lead to hardening.

- Order hardening
  - Atomic ordering can also produce significant strengthening.
  - We’ll discuss this in more detail when we deal with intermetallic compounds.
## Summary of hardening/strengthening mechanisms for crystalline solids

<table>
<thead>
<tr>
<th>Hardening Mechanism</th>
<th>Nature of Obstacle</th>
<th>Strong or Weak</th>
<th>Hardening Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>Work hardening</td>
<td>Other dislocations</td>
<td>Strong</td>
<td>$\Delta \tau = \alpha Gb \sqrt{\rho}$ (see [1])</td>
</tr>
<tr>
<td>Grain size / Hall-Petch</td>
<td>Grain boundaries</td>
<td>Strong</td>
<td>$\Delta \tau = k'_y / \sqrt{d}$ (see [2])</td>
</tr>
<tr>
<td>Solid solution</td>
<td>Solute atoms</td>
<td>Weak (see [3])</td>
<td>$\Delta \tau = G\varepsilon^{3/2} c^{1/2} / 700$ (see [4])</td>
</tr>
<tr>
<td>Deforming particles</td>
<td>Small, coherent particles</td>
<td>Weak (see [5])</td>
<td>$\Delta \tau = C G \varepsilon^{3/2} \sqrt{\frac{fr}{b}}$ (see [6])</td>
</tr>
<tr>
<td>Non-deforming particles</td>
<td>Large, incoherent particles</td>
<td>Strong (see [7])</td>
<td>$\Delta \tau = \frac{Gb}{(L - 2r)}$</td>
</tr>
</tbody>
</table>

1. $\alpha$ equals about 0.2 for FCC metals and about 0.4 for BCC metals.
2. $k'_y$ scales with inherent flow stress and/or shear modulus; therefore $k'_y$ is generally greater for BCC metals than for FCC metals.
3. Exception to weak hardening occurs for interstitials in BCC metals; the shear distortion interacts with screw dislocations leading to strong hardening.
4. Equation apropos to substitutional atoms; parameter $\varepsilon_s$ is empirical, reflecting a combination of size and modulus hardening.
5. Coherent particles can be "strong" in optimally aged materials.
6. Constant $C$ depends on specific mechanism of hardening; parameter $\varepsilon$ relates to hardening mechanism(s).
7. Highly overaged alloys can represent "weak" hardening.

**SYMBOLS:** $G =$ shear modulus; $b =$ Burgers vector; $\rho =$ dislocation density; $d =$ grain size; $c =$ solute atom concentration (at.%); $f =$ precipitate volume fraction; $r =$ precipitate radius; $L =$ spacing between precipitates on slip plane.