Module #26

Ordered Alloys

READING LIST

1. Chapter 12, Meyers & Chawla.
3. Various handouts
What is an intermetallic?

• An intermetallic is a compound phase consisting of two or more metallic elements. Intermetallic compounds can be ordered or disordered.

• There are some 300 intermetallic compounds with melting temperatures above 1,500°C. For this reason there is great interest in developing intermetallic-based alloys and composites for elevated temperature applications.

• Intermetallics also exhibit a number of other attractive properties:
  – Many are very resistant to oxidation and corrosion.
  – Most have very low densities relative to conventional structural materials.
  – Many form strongly adherent surface oxide films.
  – Some exhibit unique optical and magnetic properties (e.g., ordered NiPd and NiPt alloys).
  – Etc.
Ordered intermetallics

• In ordered intermetallics, atoms assume specific atomic sites within the lattice.

![Ordered and Disordered Structures](image)

• The strong bonding that is observed in ordered structures imparts them with:
  - Complex dislocations in comparison to disordered alloys
  - Unusual mechanical behavior (because dislocations are different)
  - Differences in other properties as well.
### Properties of some common intermetallics

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Melting Point, °C</th>
<th>Density, g/cc</th>
<th>Elastic Modulus, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeAl</td>
<td>B2 “Ordered bcc”</td>
<td>1250-1400</td>
<td>5.6</td>
<td>263</td>
</tr>
<tr>
<td>Fe$_3$Al</td>
<td>DO$_3$</td>
<td>1540</td>
<td>6.7</td>
<td>---</td>
</tr>
<tr>
<td>Ni$_3$Al</td>
<td>L1$_2$ “Ordered fcc”</td>
<td>1390</td>
<td>7.5</td>
<td>337</td>
</tr>
<tr>
<td>TiAl</td>
<td>L1$_0$ “Ordered tetragonal”</td>
<td>1460</td>
<td>3.9</td>
<td>94</td>
</tr>
<tr>
<td>Ti$_3$Al</td>
<td>DO$_{19}$ “Ordered hcp”</td>
<td>1600</td>
<td>4.2</td>
<td>210</td>
</tr>
<tr>
<td>MoSi$_2$</td>
<td>Tetragonal</td>
<td>2020</td>
<td>6.31</td>
<td>430</td>
</tr>
<tr>
<td>NiAl</td>
<td>B2 “Ordered bcc”</td>
<td>1640</td>
<td>5.9</td>
<td>206</td>
</tr>
<tr>
<td>Fe</td>
<td>bcc</td>
<td>1538</td>
<td>7.9</td>
<td>211</td>
</tr>
<tr>
<td>Ni</td>
<td>fcc</td>
<td>1455</td>
<td>8.9</td>
<td>200</td>
</tr>
<tr>
<td>Ti</td>
<td>hcp</td>
<td>1669</td>
<td>4.5</td>
<td>116</td>
</tr>
</tbody>
</table>
Ni-base superalloys

- Intermetallic precipitates are the primary reason that they are so strong.

- Phases:
  - Ni solid solution (γ – gamma)
  - Ni₃Al (γ’ – gamma prime) precipitates get stronger as temperature increases. This is an intermetallic.

ASM Specialty Handbook on Heat Resistant Materials, p. 266

Cube-on-cube OR
\[
\{100\}γ // \{100\}γ'
\]
\[
<100>γ // <100>γ'
\]
Why does this occur in $\gamma'$ when $\gamma$ gets weaker as $T$ increases?

Figure 5.6. Temperature dependence of the proportional limit of alloys of the type Ni$_3$Al, after Davies and Stoloff (1965a): circles – Davies and Stoloff (1965), Ni$_{86}$Al$_{14}$; triangles – Flinn (1960), Ni$_{70}$Al$_{20}$Fe$_{10}$; reprinted with permission from Transactions of The Metallurgical Society of AIME, 218, p. 714, Flinn 1960 and 233, p. 145, 1965, a publication of The Minerals, Metals and Materials Society, Warrendale, Pennsylvania 15086.

Dislocation structures in ordered intermetallics

- Dislocation structures in ordered alloys consist of two superpartial dislocations separated by an antiphase boundary (APB).

- **DO YOU RECALL WHY?**

- The whole thing is illustrated for Ni₃Al on the right.

**Figure**
(a) The characteristic dislocation structure in an ordered.  (b) Superpartial dislocations separated by ~5 nm in Ni₃Al deformed at 800°C.  \( \mathbf{b} = [110] \) and superpartials \( \mathbf{b}_1 = \mathbf{b}_2 = \frac{1}{2} [110] \).  [Figure Adapted from Meyers & Chawla, 2nd edition, p. 625.]
Super-dislocations

L$_{12}$ dislocations

$<110> \rightarrow \frac{1}{2} <110> + \text{APB} + \frac{1}{2} <110>$

Super-partial dislocations

APB = anti-phase boundary

a chemical fault in which a preferred atom is not in the right chemical position.

2 shears are required to put the atoms back in their correct chemical positions.
Figure 9.38 Ordered structures and antiphase boundaries (APB): (a) the ordered, FCC-related \( L_1^2 \) unit cell; (b) the ordered FCC-related \( L_1^0 \) unit cell; (c) an A)B in an idealized ordered cubic lattice (embodied by the red horizontal line). Along the APB plane, like atoms are located in nearest-neighbor positions. The APB is bordered by two partials that would be perfect dislocations if the lattice were disordered. [Image adapted from, P. Veyssière, “Dislocations and the Plasticity of Crystals”, in Mechanics and Materials: Fundamentals and Linkages, M.A. Meyers et al. editors, (Wiley, New York, 1999) Ch. 9, p. 343]

- The passage of two partial dislocations and an APB is termed a superdislocation (or superlattice dislocation). WHY? It has a Burgers vector that is twice as large as that of the parent disordered structure.

\[
b \rightarrow \frac{b}{2} + \text{APB} + \frac{b}{2} = \text{partial} \perp + \text{APB} + \text{partial} \perp
\]

\text{Superdislocation}
Strengthening in ordered phases

- Common FCC dislocations

\[ \frac{1}{2} <110> \rightarrow \frac{1}{6} <211> + \text{ISF} + \frac{1}{6} <121> \]

Refresher: Why \{111\} planes? Why are they \( \frac{1}{2} <110> \) dislocations? Why are they \( \frac{1}{6} <211> \) types?

- Since L1\(_2\) is an ordered phase, the full dislocation is [110] and its partials are \( \frac{1}{2}[110] \).
  - Passing a single dislocation through \( \gamma' \) would generate an APB and increase energy.

\[ \text{ISF} = \text{intrinsic stacking fault} \]
Super-partial dislocations

- Superpartial dislocations can dissociate into a pair of Shockley-like partials.

- An intrinsic (unoccupied stacking site) and chemical stacking fault forms (change in chemical environment about sheared atom) → complex stacking fault (CSF)

\[
\frac{1}{6} <110> + \frac{1}{6} <211> + \text{CSF} + \frac{1}{6} <121> + \text{APB} + \frac{1}{6} <211> + \text{CSF} + \frac{1}{6} <121> \]

1.5 nm 15 nm 1.5 nm

**Stacking Fault** = occupying an unoccupied site in the normal stacking sequence

**APB** = *not a stacking fault*, occupying a normal stacking site but not the correct chemical stacking site.

**CSF** = a combination of stacking fault and APB
Kear-Wilsdorf locks

Why do dislocations separate into partials? What keeps the partials together?

Dislocations on \{111\} planes cross slip on cube plane. Why?

Dislocations on cube plane become locked (high Peierls stress on \{001\}) and do not propagate.

More and more dislocations cross slip and become locked. This increases the hardness at elevated temperatures until the thermal energy becomes sufficient to overcome the Peierls stress and glide.
Cross-slip continued

• If dislocations are locked on cube plane, why don’t they cross slip back onto {111}?

• Explained by Paider, Pope & Vitek (PPV) model.
  – Dislocation core is spread and not contained in all of the plane.
  
    – When cross slipped, core not in the plane, dislocation locks (core off the cube plane).
  
    – Temperature increases → core constricted, constricts the partials → cross slip back on {111}.
Dislocation structures in ordered intermetallics

- In ordered alloys such as Ni\textsubscript{3}Al, FeAl, TiAl, etc., movement of dislocations and vacancies results in destruction of the local order, which yields a higher energy state.

- A second dislocation must pass through the lattice to restore order and reduce the energy state to a minimum.

- This requirement places restrictions on dislocation motion and upon the motion of vacancies.

- It is quite complicated.
Restricted dislocation motion

- Such defect structures are restricted because motion of the APB is dictated by cross-slip of the partial dislocations bounding the APB.

- This becomes even more complicated in ordered fcc structures like the ones illustrated on the previous page because the partial dislocations can break down into even smaller segments resulting in superpartials on either side of the APB.

- The table on the following viewgraph illustrates some possible dislocation morphologies for some interesting ordered alloys.
# Dislocation morphologies for some ordered alloys

<table>
<thead>
<tr>
<th>Superlattice</th>
<th>Chemical designation</th>
<th>Unit Cell Dimensions</th>
<th>Alloy Types</th>
<th>Superlattice Dislocation Type</th>
<th>Burgers Vector of each Dislocation</th>
<th>Antiphase Boundary Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>B2</td>
<td>CsCl</td>
<td>(a_o)</td>
<td>NiAl, AgMgAu Zn, CuZn, FeCo, FeAl, FeRh, NiAl, AgMgAu Zn</td>
<td>(\perp)</td>
<td>(a_o\langle\overline{1}\overline{1}\overline{0}\rangle)</td>
<td>none</td>
</tr>
<tr>
<td>DO(_3)</td>
<td>Fe(_3)Al</td>
<td>(a_o)</td>
<td>Fe(_3)Al, Fe(_3)Si, Fe(_3)B</td>
<td>(\perp)</td>
<td>(\frac{a_o}{4}\langle\overline{1}\overline{1}\overline{1}\rangle)</td>
<td>(\overline{1}) NN</td>
</tr>
<tr>
<td>L(_1)(_2)</td>
<td>Cu(_3)Au</td>
<td>(a_o)</td>
<td>Cu(<em>3)Au, Ni(</em>{\overline{1}})Mn, Ni(<em>{\overline{1}})Al, Ni(</em>{\overline{1}})Fe, Cu(<em>{\overline{1}})Pd, Ni(</em>{\overline{3}})Ti, Ag(<em>{\overline{3}})Mg, Ni(</em>{\overline{3}})Ta, Ni(_{\overline{3}})Ga</td>
<td>(\perp)</td>
<td>(\frac{a_o}{6}\langle\overline{1}\overline{1}\overline{2}\rangle)</td>
<td>(\overline{1}) NN + SF</td>
</tr>
<tr>
<td>DO(_{19})</td>
<td>Mg(_3)Cd</td>
<td>(a_o), (c_o)</td>
<td>Mg(_3)Cd, Ti(_3)Al</td>
<td>(\perp)</td>
<td>(\frac{a_o}{6}\langle10\overline{1}0\rangle)</td>
<td>(\overline{1}) NN</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\perp)</td>
<td>(\frac{a_o}{2}\langle2\overline{1}0\rangle)</td>
<td>(\overline{1}) SF</td>
</tr>
<tr>
<td>L(_1)(_0)</td>
<td>CuAu</td>
<td>(a_o), (c_o)</td>
<td>CuAu, CoPtFePt, TiAl</td>
<td>(\perp)</td>
<td>(\frac{a_o}{6}\langle11\overline{2}\rangle)</td>
<td>(\overline{1}) NN + SF</td>
</tr>
</tbody>
</table>

NN = nearest neighbor; NNN = next nearest neighbor; SF = stacking fault

\[
b \rightarrow \frac{b}{2} + APB + \frac{b}{2} = \text{partial } \perp + APB + \text{partial } \perp
\]

Implications of order

- ordered alloys exhibit significantly higher yield and flow stresses.

Implications of order

• Fully ordered alloys deform by means of the movement of superlattice dislocations at low stresses.

• Superdislocations must move as a group to maintain the ordered crystal structure.

• This restricts cross-slip which leads to higher strain hardening rates and higher strengths than are observed in disordered materials.
How does ordering influence:

- Fatigue resistance?
- Precipitation hardened alloys?
- Creep strength?
Effect of Ordering on Ductility

Effect of atomic order on uniform strain (ductility) of Fe–Co–2% V at 25 °C.

Meyers & Chawla, 2nd Ed., p. 630.

(Adapted with permission from N. S. Stoloff and R. G. Davies, Acta Met., 12 (1964) 473.)
Hall–Petch relationship for ordered and disordered alloys.

Meyers & Chawla, 2\textsuperscript{nd} Ed., p. 630.

(Adapted with permission from T. L. Johnston, R. G. Davies, and N. S. Stoloff, \textit{Phil Mag.}, 12 (1965) 305.)
Effect of atomic order on fatigue behavior of Ni$_3$Mn.


(Adapted with permission from R. C. Boettner, N. S. Stoloff, and R. G. Davies, *Trans. AIME*, 236 (1968) 131.)
Strengthening in Ni$_3$Al, $\gamma$, and Mar M-200

(a) Effect of temperature on CRSS for Ni$_3$Al, $\gamma$, and Mar M-200 superalloy ($\gamma + \gamma'$).


(Adapted with permission from S. M. Copley and B. H. Kear, *Trans. TMS-AIME*, 239 (1967) 987.)
Calculated and observed increase in the critical resolved shear stress (CRSS) in a Ni–Cr–Al alloy as a function of the diameter of the precipitate; full lines represent calculations; $\delta$ is atomic percent aluminum. [From Meyers & Chawla, 2nd Ed., p. 632 (Adapted with permission from H. Gleiter and H. Hornbogen, *Phys. Status Solidi*, 12 (1965) 235.)]
Effect of deformation temperature on the dislocation arrangement in the \( \{111\} \) primary slip plane of ordered Ni\(_3\)Ge.

(a) \( T = -196 \, ^\circ C, \, \varepsilon_p = 2.4\% \).
(b) \( T = 27 \, ^\circ C, \, \varepsilon_p = 1.8\% \).

Meyers & Chawla, 2\textsuperscript{nd} Ed., p. 633.
Yield stress as a function of test temperature for Ni$_3$Al based aluminides, Hastelloy-X, and type 316 stainless steel.