Deformation of alloys: Precipitation hardening

NFPL135: Physics of Materials I

Faculty of Mathematics and Physics, Charles University
Prague, Czech Republic

Jana Šmilauerová
Precipitation hardening

- precipitation hardening (age hardening) – important and versatile method for strengthening certain alloys
- for concentrations of solute above the solubility limit
- many commercial alloys – heterogeneous microstructure consisting of two or more phases
- generally, two classes of microstructures:
  - aggregated
    - size of second-phase particles \(\approx\) grain size of the matrix
    - e.g. \(\beta\)-brass particles in \(\alpha\)-brass, pearlite colonies in ferrite matrix in annealed steel
  - dispersed
    - each second-phase particle completely surrounded by matrix of a single orientation (grain)
    - particle size much smaller than the matrix grain size

Types of two-phase microstructures: 
(a) aggregated and (b) dispersed [1]
Aggregated structures

- strengthening by second-phase particles – additive to solid solution strengthening
- many factors influencing precipitation hardening:
  - size, shape, distribution and number of precipitates
  - strength, ductility and strain hardening behaviour of the matrix and the second phase
  - crystallographic relationship between matrix and precipitates
  - interfacial energy
  - interfacial bonding
  - almost impossible to separate the contributions of individual factors
- independent contributions of each phase → properties of the multiphase alloy are a weighted average of the properties of individual phases, e.g. density $\rho = f_1 \rho_1 + f_2 \rho_2$ ($f_i$ are volume fractions of constituent phases)
Aggregated structures

- properties of an aggregated two-phase alloy – two simplifying models:
  - assumption: strain in each phase is equal
  - the average stress for a given strain increases linearly with the volume fraction of the strong phase
    \[ \sigma_{\text{avg}} = f_1 \sigma_1 + f_2 \sigma_2 \quad (f_1 + f_2 = 1) \]
  - example: calculation of \( \sigma_{\text{avg}} \) for \( f_2 = 0.5 \) from known \( \sigma_1 \) and \( \sigma_2 \)
  - assumption: the two phases are subjected to equal stresses
  - the average strain in the alloy is
    \[ \varepsilon_{\text{avg}} = f_1 \varepsilon_1 + f_2 \varepsilon_2 \]
  - example: flow curve calculated for \( f_2 = 0.5 \) on the basis of equal-stress hypothesis

- reality – between these two simple approximations
Strengthening by fine particles

- **dispersion hardening**
  - powder metallurgy – hard particles (e.g. carbides, oxides, borides, etc.) are mixed and consolidated with matrix powder
  - dispersoids have very little solubility even at higher temperatures

- **precipitation hardening**
  - the second phase is soluble in the matrix at high temperatures, \( \downarrow T \rightarrow \downarrow \text{solubility} \)
  - precipitates form during phase transformations induced by *ageing* (*heat treatment*)
  - typically non-ferrous alloys – Al, Mg, Ti, Cu alloys
Requirements for precipitation hardening

1. the alloy must form a single phase when heated above the solvus and enter a two-phase region on cooling
2. matrix – relatively soft and ductile; precipitates – hard and brittle
3. the alloy must be quenchable (e.g. no distortion of the material due to residual stresses)
4. coherent precipitate formation
Nucleation and growth in solid-state reactions

- The total change in free energy required for nucleation of a spherical precipitate of radius $r$:

$$\Delta G = \frac{4}{3} \pi r^3 \Delta G_{V(\alpha \rightarrow \beta)} + 4\pi r^2 \sigma_{\alpha \beta} + \frac{4}{3} \pi r^3 \varepsilon$$

- **Nucleation** – easiest on surfaces already present in the material (minimizing the surface energy term) → *heterogeneous* precipitation on grain boundaries and other defects

- **Growth** – long-range diffusion
Microstructure evolution in precipitation hardening

1. **solution treatment** – alloy heated above the solvus → homogeneous solid solution

2. **quenching** – rapid cooling (no time for atoms to diffuse and form precipitates) → supersaturated solid solution – non-equilibrium structure (for Al-4%Cu – 40× more dissolved Cu than equilibrium)

3. **ageing** – heating to a temperature below the solvus → formation of very fine precipitates; equilibrium structure reached after a sufficient time

▶ note that the microstructure differs from that in a slow-cooled material
Types of precipitate interfaces

- **coherent**
  - precipitate and matrix lattices are continuous
  - elastic strains may exist around the particle (↑ strain with ↑ size)

- **semicoherent**
  - coherent with the matrix on some faces but not all
  - incoherency compensated by misfit dislocations

- **incoherent**
  - no continuity between precipitate and matrix lattices
  - interface structure ≈ grain boundary
  - negligible lattice strains

- different resistance to dislocation motion for each type – different yield strength
Non-equilibrium precipitates in Al-Cu system

- metastable precursor phases may appear during ageing
- Al-Cu system – large supersaturation of Cu $\rightarrow$ large driving force for nucleation which starts quickly, homogeneously and at many places

**Guinier-Preston (GP) zones**

1. GP-I – Cu atoms concentrate on $\{100\}$ planes and create very thin clusters, coherent
2. GP-II ($\theta''$) – thin discs on $\{100\}$, much larger than GP-I $\rightarrow$ many GP-I zones must dissolve and release their Cu content; coherent, ↑ strain energy with ↑ thickness
3. $\theta'$ – precipitates with a higher degree of order, semicoherent
4. $\theta$ (CuAl$_2$) – stable precipitates, incoherent; increasing size and decreasing density (Ostwald ripening); overageing – reduction of strength and hardness due to large precipitates formed after long ageing times

Schematic representation of a $\{100\}$ section through a GP zone [3]
Non-equilibrium precipitates in Al-Cu system

Hardness evolution with ageing time for Al-Cu alloys aged at 130°C and 190°C [4]

- low ageing temperatures - two-stage hardening – high maximum hardness
- higher ageing temperatures – single-stage hardening – lower maximum hardness
typical behaviour of precipitation-hardening systems: formation of coherent precipitates (↑ $\sigma_y$) → increasing size → loss of coherency when a critical size is reached (↑ $\sigma_y$)
Examples of precipitation-hardening alloys

<table>
<thead>
<tr>
<th>Base metal</th>
<th>Solute</th>
<th>Transition structure</th>
<th>Equilibrium precipitate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Cu</td>
<td>(i) Plate-like solute-rich GP[1] zones on {1 0 0}_Al; (ii) ordered zones of GP[2]; (iii) (\theta)'-phase (plates).</td>
<td>(\theta)-CuAl(_2)</td>
</tr>
<tr>
<td>Ag</td>
<td></td>
<td>(i) Spherical solute-rich zones; (ii) platelets of hexagonal (\gamma)' on {1 1 1}_Al.</td>
<td>(\gamma)-Ag(_2)Al</td>
</tr>
<tr>
<td>Mg, Si</td>
<td></td>
<td>(i) GP zones rich in Mg and Si atoms on {1 0 0}_Al planes; (ii) ordered zones of (\beta)'-phase.</td>
<td>(\beta)-Mg(_2)Si (plates)</td>
</tr>
<tr>
<td>Mg, Cu</td>
<td></td>
<td>(i) GP zones rich in Mg and Cu atoms on {1 0 0}_Al planes; (ii) (S') platelets on {0 2 1}_Al planes.</td>
<td>S-Al(_2)CuMg (laths)</td>
</tr>
<tr>
<td>Mg, Zn</td>
<td></td>
<td>(i) Spherical zones rich in Mg and Zn; (ii) platelets of (\eta)'-phase on {1 1 1}_Al.</td>
<td>(\eta)-MgZn(_2) (plates)</td>
</tr>
<tr>
<td>Cu</td>
<td>Be</td>
<td>(i) Be-rich regions on {1 0 0}_Cu planes; (ii) (\gamma)'-phase.</td>
<td>(\gamma)-CuBe</td>
</tr>
<tr>
<td>Co</td>
<td></td>
<td>Spherical GP zones.</td>
<td>(\beta)-Co plates</td>
</tr>
<tr>
<td>Fe</td>
<td>C</td>
<td>(i) Martensite ((\alpha')); (ii) martensite ((\alpha'')); (iii) (\varepsilon)-carbide.</td>
<td>Fe(_3)C plates cementite</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>(i) Nitrogen martensite ((\alpha')); (ii) martensite ((\alpha'')) disks.</td>
<td>Fe(_4)N</td>
</tr>
<tr>
<td>Ni</td>
<td>Al, Ti</td>
<td>(\gamma)' cubes</td>
<td>(\gamma)-Ni(_3)(AlTi)</td>
</tr>
</tbody>
</table>

Strengthening of precipitation-hardening alloys

- second-phase particles – obstacles for dislocation motion
- typically, the strongest alloys are produced by combination of strain and precipitation hardening, i.e. deformation precedes ageing treatment → finer particle distribution (nucleation at dislocations)
- two types of interactions between fine particles and dislocations
  - strong impenetrable particles – dislocation must bypass them
  - coherent particles through which dislocations can pass, but at much higher stresses than required for dislocation motion through the matrix
Mechanisms of strengthening by coherent precipitates

A dislocation cuts through a coherent particle, i.e. it passes through the precipitate on the same slip plane as in the matrix.

**Strengthening mechanisms**

1. **Anti-phase boundary (APB) formation**
   - Particle with an ordered structure – after a dislocation moves through → APB
   - Cutting by second dislocation – the order is re-established → energetically favourable → superdislocations

Schematics of APB formation
Mechanisms of strengthening by coherent precipitates

2. Interfaces
   ▶ the surface of the particle/matrix interface increases after shearing

3. coherency strain hardening
   ▶ due to mismatch between particle and matrix lattices

4. stacking fault energy
   ▶ particles having stacking fault energies significantly different from the matrix → dislocations–particles interactions can be dominated by the local variation of stacking fault width

5. modulus effect
   ▶ dislocation energy depends linearly on the local modulus → particles with the modulus significantly different from the matrix raise or lower the energy of passing dislocation
   ▶ most alloys – only small difference → small contribution
Mechanisms of strengthening by coherent precipitates

- The total strengthening is given by the sum of individual contributions

\[ \tau_{\text{tot}} = \tau_{\text{APB}} + \tau_{\text{int}} + \tau_{\text{coh}} + \tau_{\text{SF}} + \tau_{\text{mod}} \]

- For all contributions

\[
\begin{align*}
\tau &\propto f^{2/3} \\
\tau &\propto r_0^{1/3} \\
\tau &\propto F^{4/3}
\end{align*}
\]

Labusch:

\[
\begin{align*}
\tau &\propto f^{1/2} \\
\tau &\propto r_0^{1/2} \\
\tau &\propto F^{3/2}
\end{align*}
\]

Fleischer:

where \( f \) is the volume fraction of (spherical) particles, \( r_0 \) is the radius of spherical particles and \( F \) is the interaction force characteristic for the type of interaction.
Mechanisms of strengthening by coherent precipitates

Ni$_3$Al particles in a Ni-base alloy that were sheared by dislocations (Haasen: *Physical Metallurgy*, 1986)
Mechanisms of strengthening by coherent precipitates

**Critical size of coherent precipitate**

- as the particle size increases, cutting through it becomes more difficult

\[ \tau \propto r \]

and dislocations tend to bow around the particle by *Orowan looping*

\[ \tau \propto \frac{1}{r} \]

- a critical radius of the particle at which the maximum strength occurs, typically 5 – 30 nm

See [Shear strength vs. particle radius](http://en.wikipedia.org/wiki/Precipitation_strengthening)
Strengthening by incoherent precipitates

- dislocation bows out between incoherent precipitates ($L \gg R$)
- dislocation segments on the other side of particles are of opposite signs $\rightarrow$ annihilation
- similar to Frank-Read source – difference: a loop is left around each particle

- Orowan stress – the stress required to push a dislocation between particles

\[ \Delta \tau_{\text{OR}} = \frac{2E_L}{b(L - D)}, \]

where $E_L = \alpha G b^2$ is the dislocation line tension, $L$ is the interparticle distance and $D$ is the particle diameter.
Strengthening by incoherent precipitates

▶ *Orowan-Ashby equation* – modified Orowan equation

\[ \Delta \tau_{OR} = \frac{Gb}{A(L - D)} \ln \left( \frac{D}{2b} \right), \]

where \( A = 2\pi \) for screw dislocation and \( A = 2\pi(1 - \nu) \) for edge dislocation

▶ \( E_L^{(screw)} \neq E_L^{(edge)} \)
▶ interaction of dislocation segments behind the obstacle taken into account
▶ the effective distance of obstacles along the dislocation line treated by statistical methods

Orowan loops around impenetrable particles in Cu [5]
Strengthening by incoherent precipitates

Characterization of obstacles – critical angle $\phi_c$

- dislocation interacts with a row of regularly spaced particles, further dislocation motion $\rightarrow \uparrow \tau$
- critical curvature $\Leftrightarrow$ increasing of $\tau$ is not necessary for further dislocation movement $\rightarrow$ characterized by the critical angle $\phi_c$ between the two dislocation segments
- $\phi_c$ is a general obstacle characteristic, regardless of the mechanism of overcoming it
- Orowan: $\phi_c = 0$
- reality: $\phi_c \neq 0$ – attractive force between the segments behind the obstacle
Strengthening by incoherent precipitates

**Characterization of obstacles – critical angle \( \phi_c \)**

- **strong obstacles** – large curvature of dislocation line, \( \phi_c \in (0, 60^\circ) \), \( \downarrow \phi_c \) with \( \uparrow (L - D) \)

- **intermediately strong obstacles** – \( \phi_c \approx \pi/2 \); dislocation curves less, formation of fewer dislocation loops

- **weak obstacles** – \( \phi_c \approx \pi \), dislocation does not bend around obstacles, no dislocation loops form
Movement of dislocation around a particle a) without cross slip (Orowan mechanism), b) – d) with cross slip of screw segments (Hirsch mechanism) [3]
Questions

1. Which of the following alloy systems cannot be age-hardened?
   a) β-Ti alloys
   b) Al-Cu
   c) Cu-Ni

2. How does the magnitude of strengthening change during growth of precipitates? Why?
   a) it increases
   b) it decreases
   c) it stays about the same
   d) first it increases, then decreases

3. Does the magnitude of strengthening depend on alloy composition (in precipitation hardenable systems)?
References


