Deformation of alloys:
Precipitation hardening
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, $\downarrow T \rightarrow \downarrow$ 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 \( r \):

\[
\Delta G = \frac{4}{3} \pi r^3 \Delta G_V(\alpha \rightarrow \beta) + 4\pi r^2 \sigma_{\alpha\beta} + \frac{4}{3} \pi r^3 \varepsilon
\]

- energy change to create a unit area of \( \alpha/\beta \) interface
- free energy change per unit volume
- strain energy per unit volume

- nucleation – easiest on surfaces already present in the material (minimizing the surface energy term) \( \rightarrow \) 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

Al-rich end of the Al-Cu phase diagram schematically showing the three steps in age-hardening heat treatment and the resulting microstructures [2]
Types of precipitate interfaces

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

- **semitcoherent**
  - 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 \( \approx \) 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
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 precipitation hardening behaviour

- Typical behaviour of precipitation-hardening systems: formation of coherent precipitates ($\uparrow \sigma_y$) → increasing size → loss of coherency when a critical size is reached ($\uparrow \sigma_y$)
### 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 ${1 0 0}_{{\text{Al}}}$; (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 ${1 1 1}_{{\text{Al}}}$</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 ${1 0 0}_{{\text{Al}}}$ planes; (ii) ordered zones of $\beta'$.</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 ${1 0 0}<em>{{\text{Al}}}$ planes; (ii) $S'$ platelets on ${0 2 1}</em>{{\text{Al}}}$ 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 ${1 1 1}_{{\text{Al}}}$</td>
<td>$\eta$-MgZn$_2$ (plates)</td>
</tr>
<tr>
<td>Cu</td>
<td>Be</td>
<td>(i) Be-rich regions on ${1 0 0}_{{\text{Cu}}}$ planes; (ii) $\gamma'$.</td>
<td>$\gamma$-CuBe</td>
</tr>
<tr>
<td>Cu</td>
<td>Co</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>Fe</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.

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
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:**

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

**Fleischer:**

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

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

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

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

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

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

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
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, $\phi_c \in (0, 60^\circ)$, ↓ $\phi_c$ with ↑ $(L - D)$

- **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
Alternative Orowan mechanism (Hirsch)

Movement of dislocation around a particle a) without cross slip (Orowan mechanism), b) – d) with cross slip of screw segments (Hirsch mechanism) [3]

