High Performance Alloys

Engineering 4th year. 4 lectures.
Steve Roberts

• What is “high performance”? Light weight, stiff, high strength, toughness, high-temperature capability.

• The basics revisited.
  – Mechanical properties of materials, Hardening mechanisms,
  – Alloy structures, Phase diagrams, Microstructural development.

• Aluminium alloys. Types of Al-alloys. 5000 series, 2000 series, 7000 series. Al-Li alloys

• Magnesium alloys. Cast and wrought alloys.

• Titanium alloys. Types of Ti-alloys. “Single phase” alloys, $\alpha/\beta$ alloys.


• Nickel based alloys. Ni$_3$Al. Superalloys.
Books

- “Introduction to Dislocations”, D. Hull and D.J. Bacon (3rd edn.).
- “Worked Examples in the Strength of Metals and Alloys” J.W. Martin
- “Metals, Ceramics and Polymers”, Wyatt and D.W. Dew-Hughes
- “Engineering Materials I”, M.F. Ashby and D.R.H. Jones
- “Engineering Materials II”, M.F. Ashby and D.R.H. Jones
- “Light Alloys”, I.J. Polmear
Basic parameters

- **Density** (Mg m\(^{-3}\))
  - “Intrinsic” property of the alloy:
  - Mostly depends on atomic weights of component atoms.

- **Stiffness** (Young’s Modulus, Shear modulus, Bulk modulus) (GPa)
  - Resistance to elastic deformation
  - “Intrinsic” property of the alloy:
  - Depends on atomic bonding strength

- **Strength** (Yield strength, Ultimate tensile strength) (MPa or GPa)
  - Resistance to plastic flow
  - “Extrinsic” property of the alloy
  - Depends very strongly on microstructure of the alloy.
  - How does microstructure impede dislocation motion?

- **Toughness** (Fracture toughness: MPam\(^{1/2}\), strain to fracture: %, energy to fracture: J,Jm\(^{-2}\))
  - Resistance to fracture
  - “Extrinsic” property of the alloy:
  - Depends very strongly on microstructure of the alloy.
  - How easy is plastic flow near cracks?
“Secondary” parameters

• **Temperature capability** (Creep, oxidation)
  – Melting point
  – Oxidation resistance
  – Microstructural stability
  – Content of “anomalous” intermetallic compounds

• **Fatigue resistance** (Crack initiation and growth in cyclic loading)
  – Hardness
  – Crystal structure / hardening mechanism
  – Crack paths through microstructure

• **Corrosion resistance**
  – Electrochemistry of basic material, esp properties of oxide films
  – Microstructure – local regions of different chemistry

• **Formability** (You have to make things from it!)
  – Castability
    – Melting point, fluidity
  – Forgability
    – Flow behaviour in compression and at high temperatures
    – Can you shape it then heat treat it?
  – Weldability
    – What welding process is suitable?
    – Will welding mess up the microstructure?

• **Cost**
  • Rarity
  • Economics of extraction
  • Total cost to final component

• **Strategic sensitivity**
  • Can anything else do the job?
  • Are deposits in only a few “politically sensitive” areas?
The elastic moduli are “intrinsic” properties of the material.
- They depend only on the basic character of the interatomic bonding.
- They depend only on the base material used
- They are not sensitive to microstructure.

The yield stress and tensile strength of an alloy can be “tailored” by tinkering with alloying elements and microstructure:
The Young’s modulus does not change.
Many metals, including most structural engineering alloys, have the same ratio of modulus (E) to density (ρ).

For many structures (e.g. tensile struts, simple beams) the optimum operational stiffness to weight ratio is given by \( \frac{E}{\rho} \)....

“What you pay for (ρ) is what you get (E)”
Stress - strain curve

- **Yield Stress** ($\sigma_y$)
  - Elastic Limit

- **Limit of Proportionality**

- **0.2% Proof Stress**

- **Elastic Modulus**

- **Ultimate Tensile Stress (UTS)**

- **Fracture Stress, Strain**

- **Fracture Energy**

N.B. - this is a typical “engineering stress” vs “engineering strain” curve.

The **true stress** vs **true strain** curve is different and its shape determines the UTS.

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Dislocations and plastic flow

- “Theoretical shear strength” is much higher than observed strength values.

\[ \tau_{\text{max}} = \frac{G}{10} \]

Formation & motion of dislocations was postulated to explain this.

Dislocations can be much easier to move as applied stress just makes a few atoms move a small distance.

Stress to move a dislocation is low if bonds are non-directional (e.g. FCC metals).

If bonds are highly directional, may still be difficult to move dislocations (e.g. diamond).
How does dislocation motion give plasticity?

1) Unsheared crystal. Potential slip plane shaded.

2) Shear stress applied. Dislocation has moved in from left. Material to left of dislocation line has sheared by one atomic spacing.

3) Shear stress continues. Dislocation has moved further in from left. Amount of sheared material (to left of dislocation line) has increased.

4) Dislocation line has emerged at right hand side. Whole crystal has sheared on the slip plane by one atomic spacing.
**Why are dislocations easy to move?**

We have a new model for how slip occurs, but we still have to show why this gives flow stresses of ~G/1000.

When the dislocation moves,
* the position of the extra half plane shifts by one atomic spacing;
* even the atoms at the core (e.g., A, B) each move very little;
* energy fluctuations with position are small; some atoms near the core increase energy, some decrease.

[*force to move dislocation is likely to be sensitive to material type and structure. - resistance to bending and breaking of interatomic bonds*]
Why do materials have any strength?

Calculations show that it should only need a few Nm$^{-2}$ to move dislocations about in metals - and experiments on pure metals show that this is the case.

We must do things to restrict dislocation motion.

- Effects on bonding type on ease of dislocation motion.
  - choice of basic material
- Grain boundaries as blocks to dislocation motion
  - “grain refinement” hardening (and toughening)
- Internal stress fields from dissolved atoms interact with dislocation stress fields
  - “solute hardening”
- Internal stress fields from precipitates interact with dislocation stress fields
  - “precipitation hardening” (“age hardening”)
- Precipitates with “hard” crystal structures act as local blocks to dislocations
  - “precipitation hardening” (“age hardening”)
- Immobile dislocations block mobile dislocations
  - “work hardening”
- Use phase changes in basic material to produce fine, strained microstructures
  - “quenching”
Effects of bonding type on yield strength

**Yield Strength** - resistance to slip by dislocation motion increases as the directionality and rigidity of interatomic bonding increases.

<table>
<thead>
<tr>
<th>Close-packed metals</th>
<th>Other metals</th>
<th>Ionic compounds</th>
<th>Intermetallic compounds</th>
<th>Covalent solids</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>e.g.</strong></td>
<td>copper, aluminium</td>
<td>iron, tungsten</td>
<td>NaCl, MgO</td>
<td>CuAl₂, TiAl, Ni₃Al</td>
</tr>
<tr>
<td>Dislocation motion easy</td>
<td>Dislocation motion fairly easy (varies with temperature)</td>
<td>Dislocation motion difficult.</td>
<td>Can use as fine dispersions to harden metallic alloys</td>
<td>Can use in composites</td>
</tr>
</tbody>
</table>

Increasing directionality of bonding: increasing yield stress and hardness.
Stopping dislocations – Grain boundaries

Slip planes in both grains have common line in g.b. (may happen at twin boundaries)

Burgers vector lies in g.b. plane.

Still may be problems if dislocation is dissociated.

Most general case - most likely case!

Direct transmission of dislocations almost impossible.
Stopping dislocations – Grain boundaries

Pile up in Cu – 4.5% Al.

Every dislocation in the pile up exerts stress back on the source - tending to stop it operating.

Slip must also be transmitted from one grain to the next.

This is assisted by a stress concentration at the head of the pile-up.
**Stopping dislocations – Grain boundaries**

Stress felt by the possible new dislocation source is proportional to the stress at the head of the pile up, $\tau_{g.b.}$:

$$\tau_{g.b.} = N_{\text{dis}} \tau_{\text{dis}}$$

$N_{\text{dis}}$ is the number of dislocations in the pile-up; $\tau_{\text{dis}}$ is the stress each "passes on" to the next one in the array.

$$\tau_{\text{dis}} = \tau_{\text{app}} - \tau_{\text{frict}}$$

$\tau_{\text{frict}}$ is the minimum stress to move dislocations within the grain.

The number of dislocations in the pile up is:

$$N_{\text{dis}} = \left(\frac{\pi}{Gb}\right) d' \tau_{\text{dis}}$$

where $d'$ is equal to $d$, or $d/2$ - exact value not important.

so:

$$\tau_{g.b.} = \alpha d (\tau_{\text{app}} - \tau_{\text{frict}})^2$$

For slip to be passed from one grain to the next, the source must be activated at some critical $\tau^*_{\text{source}}$. Applied stress needed:

$$\tau_{\text{app}}^* = \tau_{\text{frict}} + \left(\frac{\tau^*_{\text{source}}}{\alpha'' d}\right)^{1/2}$$

The Hall-Petch equation.

$$\sigma_y = \sigma_i + k d^{-\frac{1}{2}}$$
Hall-Petch Effect

Effect of grain size on yield strength of mild steel.

Note:
- range of grain sizes – typical for an engineering alloy
  - (martensites may have interfaces spaced by only a few 10’s of nm)
  - (in pearlite, interfaces may be a few µm apart).
- ~3x range in yield strength over this grain size range
- variation of strength with temperature
  - relatively high $\sigma_i$ due to strengthening mechanisms other than grain size.
Hardening by substitutional solutes

Add a few atoms of size different from the basic metal.

compression  tension
If we move the dislocation...

Stress fields overlap and **ADD** – high energy

Stress fields overlap and **CANCEL** – low energy
Solution hardening

Interaction energies between stress fields of the moving dislocation and the static misfitting solute atoms give rise to widely varying dislocation energy with position.

Since

\[ F = \frac{dE}{dx} \]

This implies a high stress to move dislocations through such an array of obstacles.

[Any array of small regions with associated stress fields will give similar effects]
Solution hardening in 3D

Case shown is for solute atoms \textit{smaller} than the “parent” atoms.

- Solutes \textbf{below} the dislocation’s slip plane
- Solutes \textbf{above} the dislocation’s slip plane

(N.B. – only one sort of solute atom – colour is just to indicate position.)

Minimum energy configurations of dislocations are a compromise between “line tension” (energy / length) and attraction to / repulsion from solute atoms.
Strength of solution hardening

- Flow Stress (MPa)

Ag | Au
---|---

- Al %Cu

- Atomic size data: www.webelements.com

- misfit = ~ 0.17 %
- misfit = ~ 8 %

Strength of hardening effect is (to a good approx.) proportional to:
1. amount of solute
2. solute misfit
3. elastic modulus of matrix

Effects of multiple solutes are roughly additive.
Solution hardening – interstitial solutes

A limited number of cases, but of great importance:

C, N in Iron (body centred cubic)
(and other b.c.c. metals)

O in Titanium (close packed hexagonal)

The atoms here are shown smaller than they actually are relative to the b.c.c. unit cell.

The A-A spacing is smaller than the B-B spacing, and determines the size of interstitial atom that will “fit”.

\[
\frac{r_{\text{int.}}}{r_{\text{host}}} < 0.29
\]

Actual radius ratios:

\[
\frac{r_{\text{nitrogen}}}{r_{\text{iron}}} = 0.44 \quad \frac{r_{\text{carbon}}}{r_{\text{iron}}} = 0.46
\]

Result: each interstitial atom has a large and non-spherically symmetric stress field around it.
Two features of interstitial solutes in bcc metals make them powerful hardening agents:

- They have very large stress fields around them  
  - so they can lower energy by “sitting” at dislocation cores
- They can diffuse rapidly, even at room temperature  
  - so they can “find” the dislocations in hours or days.
Yield point and strain ageing

Stress (MPa)

0 5 10 15 20 25 30 35

0 100 200 300

0.03%C steel, 60ºC

Upper Yield Stress

Lower Yield Stress

Ageing

Unload – age - reload

Hardening by precipitates

Hardening by strain fields

Small precipitates may be "coherent" with the matrix.

All lattice planes, including slip planes are continuous as they pass through the precipitates.

But the change in lattice parameters in the precipitate causes each one to be surrounded by a (relatively long range) stress field.

This interacts with the stress field of dislocations.
Dislocations and weak obstacles

Precipitates on dislocation’s slip plane

Dislocation line
Dislocations and weak obstacles
Dislocations and weak obstacles
Dislocations and obstacles
Dislocations and weak obstacles
Dislocations and weak obstacles
Dislocations and weak obstacles
Dislocations and weak obstacles
Dislocations can *cut through* the precipitates (and their stress fields): but the bigger and more “compound-like” they are, the more difficult this is.

Note that the precipitates get “chopped up” with increasing strain. Affects *work-hardening rate*.
Hardening by precipitates

- By heat-treatment, we can produce *precipitates* in the solid material.

- These can have very different composition and crystal structure to the basic metal.

- They are very effective blocks to dislocation motion, especially if:
  - They are “ordered intermetallic” compounds – directional bonding preferences (e.g. CuAl₂ in Al alloys, Ni₃Al in Ni-based superalloys, Fe₇Mo₆ in maraging steels)
  - They are [near] covalent compounds: e.g. Fe₃C, WC, AlN in steels, MoSi₂ in Al alloys
  - They have a distinct interface with the “matrix” metal
  - They have an associated stress field
  - They are large, and thus difficult to cut through.
    - However, *larger* means *fewer* and *more widely spaced*. 
Dislocations and strong obstacles

Precipitates on dislocation’s slip plane

Dislocation line
Dislocations and strong obstacles
Dislocations and strong obstacles
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Dislocations and strong obstacles

The bigger the spacing between the obstacles, the easier it is for dislocations to squeeze through the gaps.

Each “bypass” event leaves a dislocation behind – narrowing the gaps. Affects work-hardenning rate.
Increasing $\tau$ is needed as the dislocation “bows out”, because more dislocation line is present between the two end points (i.e. more energy). Line energy / unit length ($\sim \frac{1}{2}G b^2$) is equivalent to a line tension.

Curved dislocations need stress to keep them curved.

“Upward” force on line segment
\[ = \tau b R \delta \theta \]

“Downward” force from line tensions
\[ = 2 \left( \frac{1}{2} G b^2 \sin(\delta \theta/2) \right) \]
\[ = G b^2 \frac{\delta \theta}{2} \]

These must balance:
\[ \tau b = \frac{G b^2}{2R} \]
Precipitation hardening

When the loop shape is a half-circle, dislocation curvature is a maximum.

\[ \tau b = \frac{Gb^2}{2R} \]

or if we only take component of \( \tau \) in direction of \( b \):

\[ \tau = \frac{Gb}{2R} \]

Typically (Steels),
\[ G = \sim 90 \text{ GPa} \]
\[ b = \sim 0.25 \text{ nm} \]

<table>
<thead>
<tr>
<th>2R (( \mu \text{m} ))</th>
<th>( \tau ) (MPa)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>2250</td>
<td>feasible?</td>
</tr>
<tr>
<td>0.1</td>
<td>225</td>
<td>useful</td>
</tr>
<tr>
<td>1</td>
<td>22.5</td>
<td>Not a useful strength increase</td>
</tr>
<tr>
<td>10</td>
<td>2.25</td>
<td></td>
</tr>
</tbody>
</table>
Work Hardening

Most dislocations are not mobile – they are just obstacles to the few that are.

\[
\text{stress} \propto \frac{1}{\text{disln. spacing}} = \sqrt{\text{(disln. density)}}
\]
True stress vs True strain

Critical point at C is when \[ \frac{d\sigma}{d\varepsilon} = \sigma \]

This is where the workhardening rate is no longer high enough to offset increase in stress in an incipient neck.

*Workhardening rate controls ductility.*
Ideal microstructure for “strength”?

- Can’t use a non-metal as base of alloy
  - could get high yield strength this way but toughness would be far too low.
- Can use work-hardening to improve strength, but:
  - effectiveness very limited for materials with yield stress increased close to UTS by other means
  - reduces toughness (by reducing work-hardening capacity)
  - will “anneal out” at moderate temperatures
- Can use fine grain sizes to improve strength (and toughness!)
  - relatively limited (but useful) strength improvement (a few hundred MPa)
  - fine grain sizes no good at high temperatures
    - grain size will grow
    - grain boundaries are fast diffusion paths – creep strength will be poor
- Can use solution strengthening
  - in bcc, interstitial solutes give a limited but useful increase in strength (+ 50 to 80 MPa)
    - (most steels are well over the solubility limit for C anyway)
    - can quench in excess C, N into solution in martensite. (up to + 1000 MPa)
      - but this form of martensite is very brittle (all dislocations are locked)
      - substitutional solutes can give moderate strength increases (a few hundred MPa)
        - limited by solubility – solutes with big misfits will have low solubilities
- Can use precipitation hardening
  - need to achieve a very fine dispersion of very hard precipitates (up to + 1000 MPa)
  - or a very fine dispersion of weaker precipitates with strong associated strain fields (not quite so effective)
“Ideal” Microstructures

- Use **precipitation hardening**
  - need as fine a dispersion as possible of particles as hard as possible.
- Topped up with **solution strengthening**
  - Solutes may be present anyway for a variety of reasons:
    - to scavenge undesirable impurities (e.g. Mn, Si, Al in steels)
    - to slow down diffusional reactions and thus promote martensite
    - to confer corrosion resistance (e.g. Cr in steels)
    - to react with other elements present and produce precipitates
- Why not have a **fine grain size** anyway?
  - Generally a good idea, as toughness is improved
  - (Can we make spatial variations: e.g. surface different from bulk?)
- Extra constraints if **high temperature** use is likely:
  - base material must have a high melting point (!)
  - any precipitates must be “stable” (there is a T’dynamic driving force to reduce number and increase size)
    - reduce driving force (interface energy)
    - slow down “coarsening” (reduce diffusion rate)
  - fine grain size may not be good
    - grain boundaries are fast diffusion paths 0 can get high creep rates
    - grain size will tend to grow anyway
  - beware (or use!) further reactions between elements present.
Making Microstructures
Basics of ..... Phase diagrams

“Two-phase field”: for any average composition in here, a mixture of $\alpha$ phase and liquid is most stable.

“$\alpha$-phase”: solid with same crystal structure as pure A, but with some atoms of type B dissolved in it

“$\beta$-phase”: solid with same crystal structure as pure B, but with some atoms of type A dissolved in it

Solubility Limit for B in A

“Two-phase field”: for any average composition in here, a mixture of $\alpha$ phase and $\beta$ phase is most stable.

Liquid in which A atoms and B atoms can dissolve in any proportions at (almost) any temperature.

“Eutectic line” – at the lowest temperature at which liquid can be stable – even then only of a particular composition.
Lever rule

Single phase solid of composition $x_0$ is not thermodynamically stable at $T_1$. It decomposes into:
amount $f_\alpha$ of $\alpha$ phase of composition $x_\alpha$; + amount $f_\beta$ of $\beta$ phase of composition $x_\beta$.

\[
\begin{align*}
    f_\alpha &= \frac{x_\beta - x_0}{x_\beta - x_\alpha} \\
    f_\beta &= \frac{x_0 - x_\alpha}{x_\beta - x_\alpha}
\end{align*}
\]
Simple eutectic

Cooling from liquid of eutectic composition $x_e$ produces decomposition reaction at $T_e$ into solids $x_\alpha$ and $x_\beta$.

Usual form: interleaved plates of $\alpha$ and $\beta$.

More rapid cooling can “overshoot” $T_e$ and give slightly different $x_\alpha$ and $x_\beta$, but more importantly, a finer microstructure.

Two reasons:

1. Temperature is lower so diffusion is slower
2. Undercooling gives higher t’dynamic driving force $\Delta G$ needed to “pay for” the extra interfaces.
Simple eutectoid

Cooling from solid of eutectoid composition $x_e$ produces decomposition reaction at $T_e$ into solids $x_\alpha$ and $x_\beta$.

Usual form: *fine* interleaved plates of $\alpha$ and $\beta$.

Diffusion is very slow, as the “reject” atoms are diffusing through a *solid*.

Again, rapid cooling can “overshoot” $T_e$ and give slightly different $x_\alpha$ and $x_\beta$, but and a *finer microstructure*. 
More complicated phase diagram

Peritectic and eutectic.
(or similar)

γ is a compound, possibly an intermetallic compound of A and B. Possibly AB in this case. (It can dissolve extra A atoms, so the phase field is an area, not a vertical line).

γ is likely to be too brittle to use as the base for an alloy, but we can use it as a precipitate hardener in A- or B-based alloys, by exploiting the falling mutual solubilities with temperature.

The trick is to get fine, uniform, closely spaced precipitates of the γ phase.

Examples:
Al – Cu (approaches to CuAl₂)
Al – Mg – Si (MgSi₂)
Ni – Al (Ni₃Al)
Fe – C (Fe₃C)
Mg – Zn (MgZn)
What makes a metal suitable as a base for useful alloys?

- Readily available & cheap (bearing in mind the application)
- High melting point
  - first step in base for high temperature alloys
- Cubic crystal structure
  - large number of slip systems for good ductility
- Low density
  - for some applications, anyway.
- Readily dissolves a wide range of substitutional and interstitial solutes
  - allows strong solution hardening
- Solubility of some solutes varies strongly with temperature
  - allows use of precipitation reactions to form strong alloys
- Forms hard compounds with a range of elements
  - precipitation of these gives strong hardening
- Undergoes an allotropic phase change (e.g. Fe, Ti)
  - can cycle through phase change to produce “physically” complex microstructures
  - can use partitioning of solutes between the phases to produce “chemically” complex microstructures
  - can get martenstic (quenched) microstructures
- Chemically fairly stable
  - either in itself, or via a strong, tenacious oxide film
- Not hazardous
  - poisonous, explosive, inflammable, radioactive…. 
### “The big 3”

<table>
<thead>
<tr>
<th></th>
<th>Iron</th>
<th>Aluminium</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Available?</td>
<td>Plentiful</td>
<td>Useful ores (bauxite)</td>
<td>Useful ores fairly rare</td>
</tr>
<tr>
<td>Cheap? (£ / tonne 1997)</td>
<td>Extraction easy with C. ~£150</td>
<td>Needs cheap electricity to extract. ~£1000</td>
<td>Ores tend to be “thin”. Refining needed. ~£1500</td>
</tr>
<tr>
<td>M.P. (°C)</td>
<td>1538</td>
<td>660</td>
<td>1084</td>
</tr>
<tr>
<td>Density (kg m⁻³)</td>
<td>7874</td>
<td>2700</td>
<td>8920</td>
</tr>
<tr>
<td>Allotropy</td>
<td>bcc ⇒ fcc ⇒ bcc with rising T</td>
<td>fcc only</td>
<td>fcc only</td>
</tr>
<tr>
<td>Dissolves things?</td>
<td>good solvent for many elements. Solubility depends on allotropic form.</td>
<td>moderate solvent for many elements</td>
<td>good solvent for many elements</td>
</tr>
<tr>
<td>T-Variable solubility</td>
<td>can be strong – and affected by allotropic changes</td>
<td>strongly for many elements</td>
<td>not strongly for most elements</td>
</tr>
<tr>
<td>Compounds</td>
<td>forms compounds with many elements</td>
<td>forms compounds with many elements</td>
<td>forms compounds with many elements</td>
</tr>
</tbody>
</table>
# The “other 3”

<table>
<thead>
<tr>
<th></th>
<th>Nickel</th>
<th>Titanium</th>
<th>Magnesium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Available?</td>
<td>“Thin” ores in Canada and New Caledonia.</td>
<td>Useful ores not plentiful</td>
<td>Useful ores fairly common, also in seawater.</td>
</tr>
<tr>
<td>Cheap? (£ / tonne 1997)</td>
<td>Complicated, energy intensive extraction. ~£4700</td>
<td>Needs cheap electricity to extract. ~£10000</td>
<td>Needs electrolysis. ~£1500</td>
</tr>
<tr>
<td>M.P. (°C)</td>
<td>1455</td>
<td>1668</td>
<td>650</td>
</tr>
<tr>
<td>Density (kg m⁻³)</td>
<td>8908</td>
<td>4507</td>
<td>1738</td>
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