
1. Three types of metals.
3. Electrical resistance of metallic alloys.
4. Applications of metallic alloys.
Engine Materials

- Titanium
- Nickel
- Steel
- Aluminium
- Composites

Rolls-Royce
Three types of metals

Metals share common features that define them as a separate class of materials:

• Good thermal and electrical conductors (Why?).

• Electrical resistance increases with temperature (Why?).

• Specific heat grows linearly with temperature at low (Why?) temperatures.

• Good reflectivity in infrared and, for some metals, in visible light (Why?).

• High molar densities and structures with large number of nearest neighbors (Why?).
Properties of metals are largely defined by their electron structure.

For sp-bonded metals assuming one can assume that the macroscopic properties are the energy of electron gas (see lecture notes of the fall semester).

Energy of an electron gas with Fermi energy $E_F$:

$$U = \frac{3}{5} nE_F = \frac{3}{10} \frac{N\hbar^2}{m} \left( \frac{3\pi^2 N}{V} \right)$$

Pressure of electron gas:

$$P = - \left( \frac{\partial U}{\partial V} \right)_s$$

Bulk modulus:

$$B = -V \left( \frac{\partial P}{\partial V} \right)_s = -V \left( \frac{\partial^2 U}{\partial V^2} \right)_s = \frac{2nE_F}{3}$$

This derivation does not include the attraction force between the lattice and the electrons and coulomb repulsion.
**sp-bonded metals follow Sommerfeld model.**

### Properties of sp-Bonded Metals

<table>
<thead>
<tr>
<th>Element</th>
<th>Valence</th>
<th>Crystal</th>
<th>Cohesive Energy $E_{coh}$ (eV/atom)</th>
<th>Bulk Modulus $B$ (GPa)</th>
<th>Melting Temperature $T_m$ (K)</th>
<th>Debye Temperature $\Theta_D$ (K)</th>
<th>Coefficient of Thermal Expansion $\alpha$ ($10^{-6}$ K$^{-1}$)</th>
<th>Cutoff Radius $r_c$ (nm)</th>
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**sp-bonded metals are quite different:** Ia – metals are soft, IIa – metals are hard, IIIa and IVa – metals are soft. Most of these metals are good conductors.
**Transition metals.**

Properties of transition metals strongly depends on the number of d electrons!

Melting temperatures and elastic constant follow the same pattern.

The behavior reflects the strength of the d-orbital interactions.
**Rare Earth Metals.**

F-orbitals are localized and interaction between f-orbitals of different atoms is weak.

Most of the RE metals are trivalent (exception Ce$^{4+}$, Sm$^{2+}$, Eu$^{2+}$).

Most of RE metals are poor electrical conductors due to magnetic scattering (interaction of conducting electrons of with magnetic spin moments f-electrons). At low temperatures resistivity of RE metals increases with temperature (Kondo effect).

Melting points of RE metals are higher than those of sp-bonded ones but lower that the melting points of transition metals.

Effective electron mass in RE metals is 10-100 times larger than that of a free electron (Why?).

<table>
<thead>
<tr>
<th>Element</th>
<th>Crystal</th>
<th>$E_{coh}$ (eV/atom)</th>
<th>$T_m$ (K)</th>
<th>$\Theta_D$ (K)</th>
<th>n $(10^{28}$ m$^{-3}$)</th>
<th>$\rho$ $(10^{-8}$ $\Omega$ m)</th>
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Alloys.

Reminder: An alloy is a phase comprising of one or more components.

There distinguish three of alloys:
Substitutional: solute substitutes the solvent in the crystal lattice without structural changes.
Interstitial: solute does not occupy the sites in the lattice of the solvent but resides in crystallographic pores.
Transformational: A completely new lattice is formed. Usually occurs as a result of intermetallic compound formation.
Substitutional Solid Solution

In substitutional solid solution, the arrangement of the solute atoms may be disordered (random) or ordered.

Some alloy systems exhibit complete solid solubility (e.g. Cu-Ni, Cd-Mg), others show only limited solubility at any temperature.

Several factors determine the limits of solubility. These are expressed as a series of rules often called William Hume-Rothery Rules. These are:
Hume-Rothery Rule 1: Atomic Size Factor (the 15%) Rule.

Extensive substitutional solid solution occurs only if the relative difference between the atomic diameters (radii) of the two species is less than 15%. If the difference > 15%, the solubility is limited. Comparing the atomic radii of solids that form solid solutions, the empirical rule given by Hume-Rothery is given as:

\[
\text{Mismatch} = \left( \frac{r_{\text{solute}} - r_{\text{solvent}}}{r_{\text{solvent}}} \right) \times 100 \leq 15\%
\]
**Hume-Rothery Rule 2: Crystal Structure Rule.**

For appreciable solid solubility, the crystal structures of the two elements must be identical.

**Hume-Rothery Rule 3: Valency Rule.**

A metal will dissolve a metal of higher valency to a greater extent than one of lower valency. The solute and solvent atoms should typically have the same valence in order to achieve maximum solubility.

**Hume-Rothery Rule 4: The Electronegativity Rule.**

Electronegativity difference close to 0 gives maximum solubility. The more electropositive one element and the more electronegative the other, the greater is the likelihood that they will form an intermetallic compound instead of a substitutional solid solution. The solute and the solvent should lie relatively close in the electrochemical series.
Darken-Gurry maps.

High solubility is expected if the solute atom is within the first ellipse (<0.2 difference in $X$ and <7.5% difference in $r$) from the solvent.

$$\left(\frac{X - X_A}{0.2}\right)^2 + \left(\frac{r - r_A}{0.075r_A}\right)^2 = 1$$

Solubility of at least 5% is expected if the solute atom is within the second ellipse (<0.4 difference in $X$ and <15% difference in $r$) from the solvent.

$$\left(\frac{X - X_A}{0.4}\right)^2 + \left(\frac{r - r_A}{0.15r_A}\right)^2 = 1$$
Local stress in substitutional solid solution

Energy associated with the local strain can be approximated as:

\[ S = bB \left( \frac{r_{\text{solvent}} - r_{\text{solute}}}{r_{\text{solvent}}} \right)^2 \]

**b** is a constant, that depends on crystal crystal structure.

**Mixing energy for two components:**

\[ \Delta G_M = RT \left( n_1 \ln n_1 + n_2 \ln n_2 + \chi_{12} n_1 n_2 \right) \]

\( n_1 \) is molar fraction of solvent; \( n_2 \) is molar fraction of solvent; \( \chi \) is non-ideality constant (for ideal solution =0).

**For a solution to exist in a solid phase:**

\[ \Delta G_M + n_2 N_A S < 0 \]

Thus one can explain Hume-Rothery rules by local distortion of the lattice.
**Interstitial solid solution**

Similar to Hume-Rothery rules can be applied for interstitial solid solutions:

Interstitial solid solutions are formed if
1. a solute is smaller than pores in the lattice of a solvent;
2. a solute has approximately the same electronegativity as a solvent.

There are very few elements that create ions, small enough to fit in interstitial positions, therefore, appreciable solubility is rare for interstitial solid solutions.

Ions that often may be a solute in solid solutions are: H, Li, Na, B.

Most interstitial solid solutions have a strong tendency to spontaneous ordering (Why?).

Examples of ordered or partially interstitial solid solutions PdH$_n$, AlLi$_n$, BeLi.
Examples and applications.

Strictly speaking steel is not an alloy. It is a composite.

Classification scheme for the various alloys.
Phase diagrams.

Pseudo equilibrium

Most of type of steels are not at equilibrium. Their microstructure is defined by kinetics of phase transformation.
According to kinetics, phase transformations be divided into three categories:

1. **Diffusion-independent with no change in phase composition or number of phases present** (e.g. melting, solidification of pure metal, allotropic transformations, recrystallization, etc.).

2. **Diffusion-dependent with changes in phase compositions and/or number of phases** (e.g. eutectoid transformations).

3. **Diffusionless phase transformation** -produces a metastable phase by cooperative small displacements of all atoms in structure (so-called martensitic transformations).
In contrast other phase transformations, martensitic phase transformation has zero activation energy.

At equilibrium iron may exist in BCC (α-phase, = ferrite, low temperature form) and FCC (γ-phase, = austenite, high temperature form).

Martensite forms when austenite is rapidly cooled (quenched) to room temperature.

It forms nearly instantaneously when the required low temperature is reached. The austenite-martensite does not involve diffusion and no thermal activation is needed, this is called an athermal transformation.

Each atom displaces a small (sub-atomic) distance to transform FCC, γ-Fe (austenite) to martensite which has a Body Centered Tetragonal (BCT) unit cell (like BCC, but one unit cell axis is longer than the other two).

Martensite is metastable - can persist indefinitely at room temperature, but will transform to equilibrium phases on annealing at an elevated temperature.

Martensite can coexist with other phases and/or microstructures in Fe-C system. Since martensite is metastable non-equilibrium phase, it does not appear in phase Fe-C phase diagram.
The martensitic transformation begins at a well defined temperature called the martensite-start temperature or $M_S$. The fraction of martensite increases with the undercooling below $M_S$.

The martensite in steels is supersaturated with carbon. Carbon occupies octahedral interstices in the b.c.c. lattice; these are characterised by three principal axes $a < 0 0 1 >$, $a < 1 1 0 >$ and $a < 1 1 0 >$. There are three sub-lattices of octahedral holes, along directions parallel to the unit cell edges. Each carbon atom causes a tetragonal distortion since the principal axes of the octahedral sites are not equivalent. There is an expansion along $a < 1 0 0 >$ and small contractions along the other two axes. As a consequence, it is favorable for all the carbon atoms to lie on a single sub-lattice of octahedral interstices, giving rise to a body centered tetragonal structure for the martensite.
(a) Body-centered tetragonal austenite

(b) Body-centered tetragonal martensite

(c) STRAIN

(d)
**Microstructures in steels**

Two-dimensional morphology of pearlite, apparently consisting of alternating layers of cementite and ferrite.

Optical micrograph of Widmanstatten ferrite in an Fe-Ni-Si-C low-alloy steel

Martensite structure.
Intermetallic compounds.

Cu-Au resistivity vs. Au content.

Ordered intermetallic compounds are formed if the components have very different electronegativity.
Cu-La intermetallic compounds.
Superalloys

Superalloys is a name for a group of alloys that retain high strength at elevated temperatures.

The main strengthening mechanism is preventing grain boundaries from sliding via dislocation pinning (will consider it later).

Most of the superalloys are Substation solutions, where one of the components tends to form covalent bonds (Al in Ni$_3$Al, W in Ta or Nb.)
The blade is made out of a nickel-base superalloy with a microstructure containing about 65% of gamma-prime precipitates in a single-crystal gamma matrix. The blade is directionally-solidified via a spiral selector, which permits only one crystal to grow into the blade.
## Other alloys

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<th>Alloy Designation</th>
<th>Detail</th>
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<td>99% pure aluminium</td>
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<tr>
<td>2XXX</td>
<td>Cu containing alloy*</td>
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<tr>
<td>3XXX</td>
<td>Mn containing alloy</td>
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<td>4XXX</td>
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<td>Zn containing alloy*</td>
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<td>8XXX</td>
<td>Other alloys</td>
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Aluminium Beverage Can

Can End (5XXX Alloy – Mg rich)

Can Body (3XXX Alloy – Mn rich)
5XXX magnesium-containing
Aluminium Alloys in Aerospace

Despite competition from other materials, Al alloys still make up > 70% of structure of modern commercial airliner

2XXX (Cu-containing, 500 MPa)

7XXX (Zn+Mg+Cu-containing, 600 Mpa)
Ti-alloys: $\beta$-titanium, BCC, stable $>890\,^\circ{}C$.

$\alpha$-titanium, HCP, stable $<890\,^\circ{}C$.

Cu-strengthened $\alpha$-Ti: $\text{Ti}_2\text{Cu}$ plates in Ti

(Al-V)-strengthened $\beta$-Ti: $\text{Ti}_2\text{Cu}$ plates in Ti
Results of Ti-fire in jet turbine engine.

Homework: Why would you expect Ti to catch fire?

M. Hicks, Rolls-Royce