

# Materials Science

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## 1 Foreword

The following notes have been produced by me whilst following the 10 ECTS course “Materials Science” (STADS UVA-code: 290231U009) at Aarhus University in the spring of 2025. The course has been taught by Michal K. Budzik. The main literature used for the course is William D. Callister, ”Materials Science and Engineering - An Introduction” Ninth Edition International Student Version.

### Lecture 1: Introduction to Materials Science

27. Januar 2025

## 2 Introduction to Materials Science

### 2.1 Historical perspective

Materials development is a cornerstone in societal advancement. Many previous time-periods have even been classified based on the most “advanced” materials used in the period (think “the Stone Age”, “the Bronze Age”, “the Iron Age” and so on).

#### Discussion 2.1: What (material) age are we living in now?

The by-far most prominent and tone-setting material in the current age is *plastics*. For this reason we believe the most correct name for the current material age is “the Plastic Age”.

Other answers include: *the Composite Age, still the Iron Age, the Composite age, the Lithium Age, the Bio-materials Age, the Concrete Age, the Titanium Age, the Silicon Age, or the Carbon Age*. Michal Budzik seems to agree the most with the *the Plastics Age or the Silicon Age*.

### 2.2 Materials Science and engineering

It is important to note the small difference between *Materials Science* and *Materials Engineering*, both of which will be taught about during the course.

#### Definition 1: Materials Science

Materials Science seeks to investigate relationships between structures and properties of materials with the goal of designing or developing new materials.

#### Definition 2: Materials Engineering

Materials Engineering seeks to create new product from existing materials with the goal of developing materials processing techniques among other things.

### 2.3 Classification and properties of materials

We normally divide materials into 4 different categories:

1. Metals
2. Ceramics
3. Polymers
4. Composites

In general the densities of the four classes are arranged as follows:  $\rho_m > \rho_{cer} > \rho_p > \rho_{com}$  whereas for stiffness the ranking is more like  $Y_m = Y_{cer} \geq Y_{com} > Y_p$ .

## 2.4 Materials selection and Ashby diagrams

### 2.4.1 Ashby Diagrams

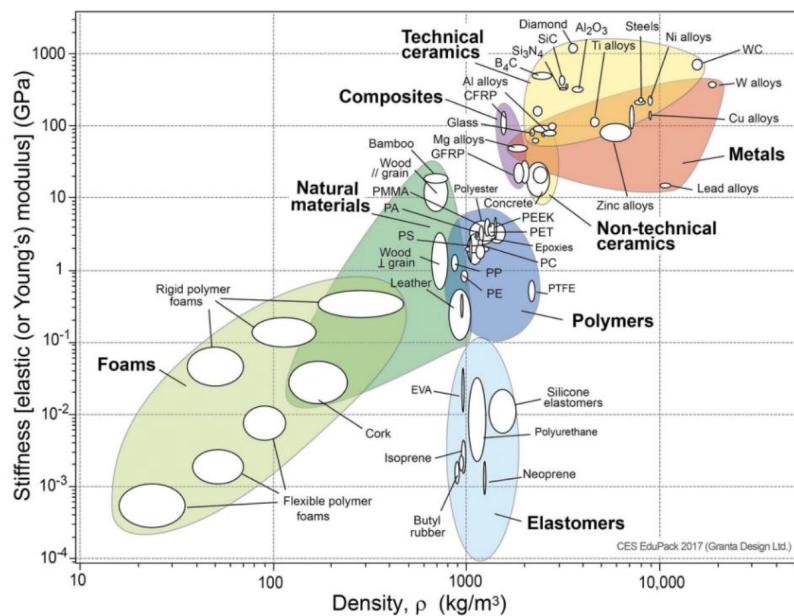


Figure 2.1: Ashby diagram for stiffness and density

To better be able to get an understanding of how different materials differ in terms of two (or more factors) these factors can be plotted on a log-log-scale – This is called an Ashby diagram. On Figure 2.1 an Ashby diagram comparing stiffness and density is shown.

The properties of materials fall into the following 6 different general categories. These are:

- Mechanical
- Electrical
- Thermal
- Magnetic
- Optical
- Deterioative

### 2.4.2 Materials selection

Whenever one has to select a material to use for a specific application one should stick to the following procedure.

1. First of all one needs to understand the application the material will be used in. This helps determine which material properties are important.
2. When the list of important properties have been made one needs to compare this list with known materials and see which aligns the best with the desired property.
3. When the best candidate-material has been found one can start to investigate the best way to process the material to bring out the desired qualities to the fullest.

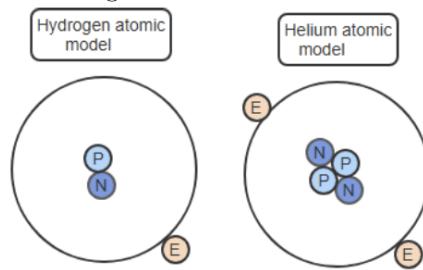
## Lecture 2: Atomic structure

29. Januar 2025

# 3 Introduction to atomic structure

An atom consists of positively charged protons, negatively charged electrons and neutrally charged neutrons. In Bohr's model of the atom (**Figure 3.1**) the electrons are modelled as orbiting a nucleus consisting of protons and neutrons. Bohr's model was for a long time the commonly accepted atomic model in the scientific

Figure 3.1: Bohr's model



community, however we have come to believe that Bohr's notion of electrons being small particles in neatly defined orbits is over-simplified and that one instead should talk about an “electron distribution”.

## 3.1 Electron structure

As mentioned in section 3 it turns out, that electrons have both particle-like and wave-like characteristics. Two of the wave like characteristics of electrons are that their position is given in terms of a Probability Density Function (PDF). The shape, size, and orientation of the PDF is given by the so called *quantum numbers* (see **Figure 3.2**). The four quantum numbers are

- $n$  = principal (shell) and is designated by  $K, L, M, N, O(1, 2, 3, 4, \text{etc.})$
- $l$  = azimuthal (subshell) and is designated by  $s, p, d, f, (0, 1, 2, 3, \dots n - 1)$ .

### 3 INTRODUCTION TO ATOMIC STRUCTURE

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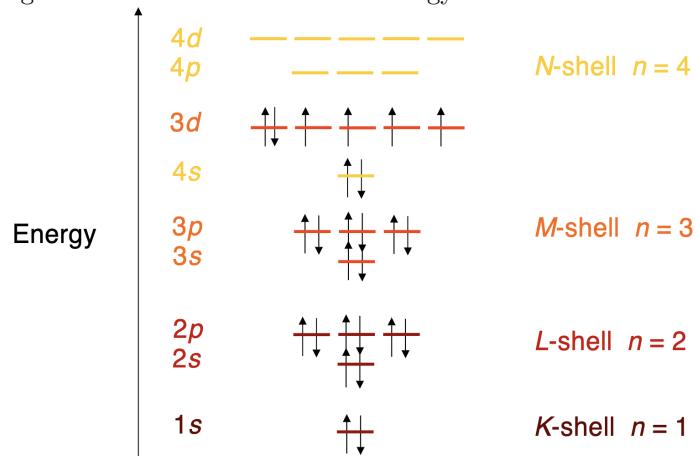
Figure 3.2: The quantum numbers and how they relate.

Value of n	Value of l	Values of $m_l$	Subshell	Number of Orbitals	Number of Electrons
1	0	0	1s	1	2
2	0	0	2s	1	2
	1	-1, 0, +1	2p	3	6
3	0	0	3s	1	2
	1	-1, 0, +1	3p	3	6
	2	-2, -1, 0, +1, +2	3d	5	10
4	0	0	4s	1	2
	1	-1, 0, +1	4p	3	6
	2	-2, -1, 0, +1, +2	4d	5	10
	3	-3, -2, -1, 0, +1, +2, +3	4f	7	14

- $m_l$  = magnetic (no. of orbitals) and is designated by  $-l$  to  $l$ .
- $m_s$  = spin and is either  $-\frac{1}{2}$  or  $\frac{1}{2}$ .

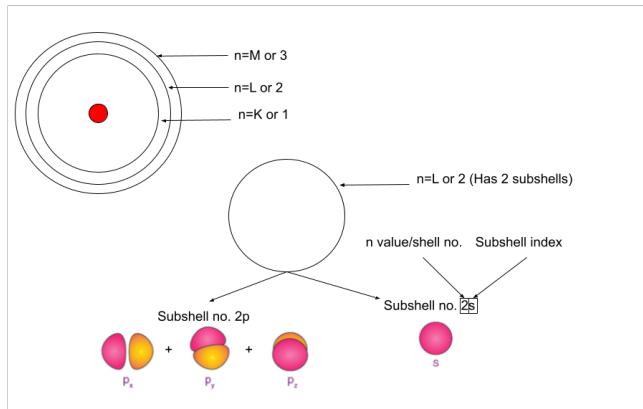
Two electrons in the same atom cannot have the same quantum numbers as this violates Pauli's exclusion principle (PEP). The different subshells (azimuthal quantum number) have discrete energy values and they tend to occupy the lowest available energy-states (see **Figure 3.3**). The electrons in the outer unfilled shells

Figure 3.3: Discretization of the energy levels of the subshells.



are called *valence electrons*. Valence electrons have a tendency to be more reactive than other electrons as it requires less energy to move an electron from an unfilled shell than from a filled shell. On **Figure 3.4** an illustration by Mikkel Klitgaard Nissen showcases how all of the above quantum numbers relate.

Figure 3.4: Illustration showcasing how the quantum numbers relate visually. By Mikkel Klitgaard Nissen.



## 3.2 Trends in the periodic table

Elements in each column of the periodic table have similar valence electron structure. In general the elements in the first column have 1 valence electron, the elements in the second column have 2 valence electrons and so on. Similarly the elements in the second-to-last column only need to gain 1 valence electron to fill their valence shell, whilst the elements in the last column already has a filled valence shell (the filled valence shell is the reason noble gasses are inert).

A quantified measure for the qualitative phenomenon above is *electronegativity*. A small electronegativity translates to a tendency to lose electrons and a large electronegativity translates to a tendency to acquire electrons. All the elements and their electronegativity is shown in **Figure 3.5**.

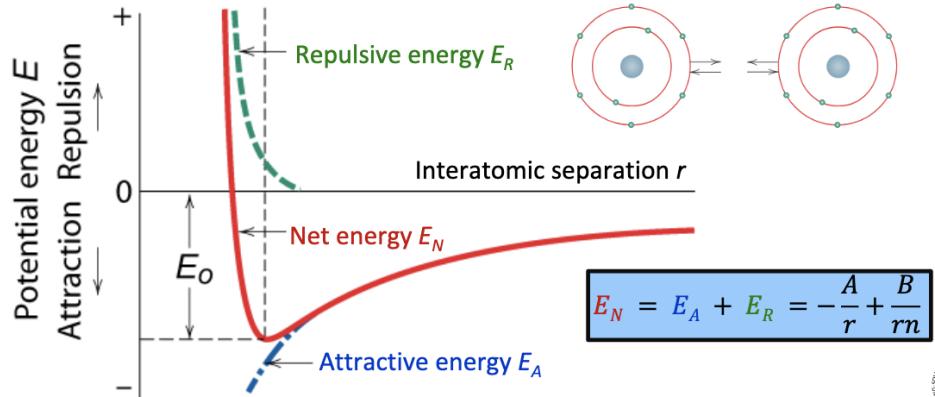
Figure 3.5: The periodic table with electronegativity of each element shown.

Group	Element	Electronegativity
IA	H	2.1
IIA	Be	1.5
Na	Mg	0.9 1.2
IIIIB	Sc	1.3
IVB	Ti	1.5
VB	V	1.6
VIB	Cr	1.6
VIIIB	Mn	1.5
VIII	Fe	1.8
	Co	1.8
	Ni	1.8
	Cu	1.9
	Zn	1.6
	Ga	1.6
	Ge	1.8
	As	2.0
	Se	2.4
	Br	2.8
	Kr	-
Rb	Sr	0.8 1.0
	Y	1.2
	Zr	1.4
	Nb	1.6
	Mo	1.8
	Tc	1.9
	Ru	2.2
	Rh	2.2
	Pd	2.2
	Ag	1.9
	Cd	1.7
	In	1.7
	Sn	1.8
	Sb	1.9
	Te	2.1
	I	2.5
	Xe	-
Cs	Ba	0.7 0.9
	La-Lu	1.1-1.2
	Hf	1.3
	Ta	1.5
	W	1.7
	Re	1.9
	Os	2.2
	Ir	2.2
	Pt	2.2
	Au	2.4
	Hg	1.9
	Tl	1.8
	Pb	1.8
	Bi	1.9
	Po	2.0
	At	2.2
	Rn	-
Fr	Ra	0.7 0.9
	Ac-No	1.1-1.7

## 4 Bonding

The interaction energy (potential energy) is shown as a function of separation on **Figure 4.1**. This is also called the Coulomb interaction. As energy is the integral of the force a negative energy translates to an attractive force and vice-versa. The net potential energy is the sum of the repulsive and attractive energies. The repulsive energy has an asymptote at some  $r > 0$  due to the PEP.

Figure 4.1: Potential energy as a function of separation. Note  $rn$  should be  $r^n$ , where  $n \approx 6$ .



### 4.1 Ionic bonding

Elements with dissimilar electronegativities gives rise to the phenomenon of *ionization*. If one of the elements has a much larger “interest” in the electrons than the other then the other element will “transfer” one/some electron(s) to the first element. When the two elements have gained/lost an electron they have opposite charges and therefore an attractive electromagnetic interaction between them happens. A bond between atoms formed in this way is called an *ionic bond*.

Ionic bonds are most off the time very strong and ionic bonding is the main bonding mechanism in ceramics.

### 4.2 Covalent bonding

Elements with similar electronegativities cannot pass electrons between them as easily as was the case for ionic bonding. Instead they have to “share” electrons. This is done in a way such that the two atoms each share one/some electron(s) so that the given electron(s) are in the valence shells of both atoms “at once”. Normally it is the *s* or *p* orbitals that are involved. This bonding mechanism is called *covalent bonding*.

### 4.3 Metallic bonding

In metals the electronegativity is normally rather low and therefore metals do not “want” to keep their valence electrons. Instead the electrons in a metal will form a de-localized electron “cloud”. All of these free electrons are the reason metals are such good electrical conductors.

## 4.4 Secondary bonding

Other types of bonds than the above three also exist. These are called *secondary bonds*. These are the weakest bonds but they are rather important as they give rise to phenomena such as adhesion. These types of bonds generally arise due to attractive forces between dipoles.

*Van der Waal's bonds* is the name for the bonding mechanism that happens due to randomly induced dipoles that come and go within the material at a rapid speed.

*Hydrogen bonds* is the name for the phenomena that hydrogen covalently bound to a very electronegative atom has a tendency to bond make secondary bonds to other hydrogen atoms covalently bound to very electronegative atoms. This is for example the case in water where hydrogen is bound to the electronegative oxygen ( $\sim 3.5$ ).

## 4.5 The relationship between bonding type, melting temperature and thermal expansion

It is generally true, that the higher the bonding energy the higher the melting temperature. This is because more energy (heat) is required to break up a stronger bond (e.g. metallic) whereas less energy (heat) is required to break a weaker bond (e.g. polymer).

It is also generally true that the higher the bonding energy the lower the coefficient of thermal expansion. This is because an increase in the bond length ( $\sim$ coefficient of thermal expansion) leads to an asymmetry in the attractive/repulsive energy curves and as the bonding energy increases this asymmetry decreases.

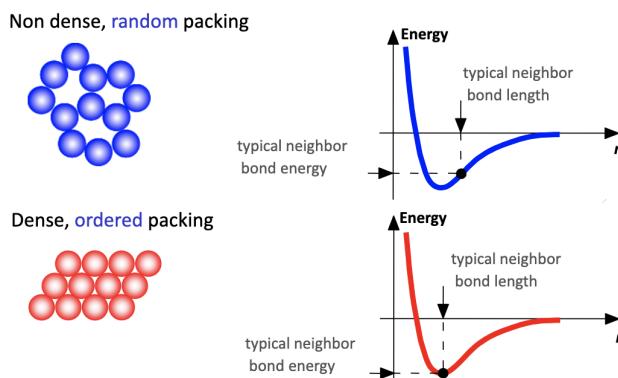
# Lecture 3: Crystalline solids

3. Februar 2025

## 5 Crystalline solids

### 5.1 Atomic arrangements and packing

Figure 5.1: Atomic bonding energy as a function of bonding length



As everything else, atoms tend to organize themselves in a manner that minimizes the energy – in the case

of atoms the energy in question is bonding energy. As we learned last week bonding energy is a function of length and thus the atoms will tend to keep some “optimal” distance between themselves. This leads to orderly packing. An atomic structure with long-range periodicity is called *crystalline* and an atomic structure without this periodicity is called *noncrystalline* or *amorphous*. Most noncrystalline materials are formed as a result of rapid cooling. This is shown in **Figure 5.1**.

#### Definition 3: Crystalline

“A *crystalline* material is one in which the atoms are situated in a repeating or periodic array over large atomic distances – that is, long range order exists, such that upon solidification, the atoms will position themselves in a repetitive three-dimensional pattern, in which each atom is bonded to its nearest neighbor atom.”

#### Definition 4: Crystal structure

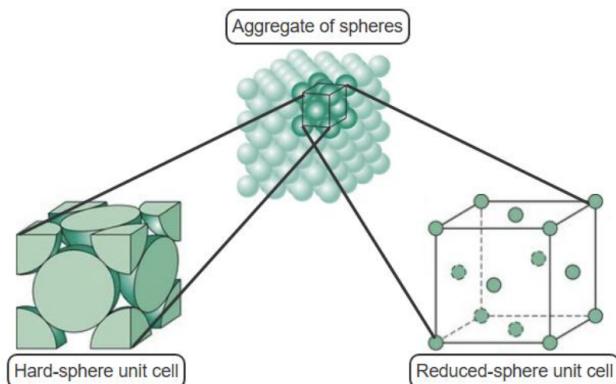
“A *crystal structure* is the manner in which atoms, ions, or molecules are spatially arranged.”

#### Definition 5: Lattice

“A *lattice* means a three-dimensional array of points coinciding with atom positions (or sphere centers)”

## 5.2 Unit cell

Figure 5.2: The two representations of unit cells.



#### Definition 6: Unit cell

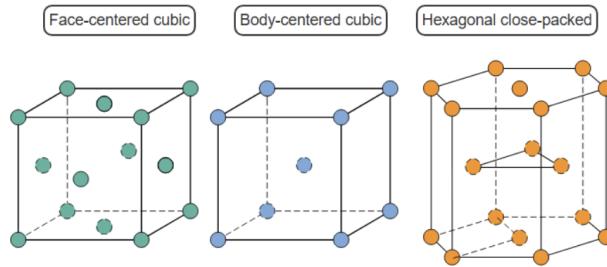
A unit cell is the most basic structural building block of a material. The unit cell completely defines the material's structure based on its geometry. For some materials multiple unit cells can be chosen but we usually choose the unit cell with the highest level of geometrical symmetry. These are typically shown either with the “hard sphere model” or with the “reduced sphere model” as shown in **Figure 5.2**.

## 5.3 Crystal structures for metals

Most metals have 1 of 3 different crystal structures. These are

- Face-centered cubic (FCC)
- Body-centered cubic (BCC)
- Hexagonal close-packed (HCP)

Figure 5.3: Examples of common crystal structures for metals.



These common metallic crystal structures are shown in **Figure 5.3**. In **Figure 5.4** a table of metals and their corresponding crystal structure is shown.

Figure 5.4: Metals and their crystal structure.

Metal	Crystal Structure <sup>a</sup>	Atomic Radius <sup>b</sup> (nm)	Metal	Crystal Structure	Atomic Radius (nm)
Aluminum	FCC	0.1431	Molybdenum	BCC	0.1363
Cadmium	HCP	0.1490	Nickel	FCC	0.1246
Chromium	BCC	0.1249	Platinum	FCC	0.1387
Cobalt	HCP	0.1253	Silver	FCC	0.1445
Copper	FCC	0.1278	Tantalum	BCC	0.1430
Gold	FCC	0.1442	Titanium ( $\alpha$ )	HCP	0.1445
Iron ( $\alpha$ )	BCC	0.1241	Tungsten	BCC	0.1371
Lead	FCC	0.1750	Zinc	HCP	0.1332

## 5.4 Atomic packing factor

To calculate the number of atoms within a unit cell  $N$  one can use the formula

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8}.$$

Where  $N_i$  is the number of interior atoms,  $N_f$  is the number of face atoms and  $N_c$  is the number of corner atoms.

The atomic packing factor (APF) can then be calculated as

$$\text{APF} = \frac{\text{volume of atoms in unit cell (hard spheres)}}{\text{Volume of unit cell}}.$$

Another related concept is that of the *coordination number*.

**Definition 7: Coordination number**

The coordination number is the number of atoms that “touches” any given atom in the unit cell. That is the amount of atoms sharing the smallest distance to a given atom.

## 5.5 Theoretical density of a material

The theoretical density of a material can be calculated solely based on the geometry of the unit cell and material-specific values. The formula is

$$\rho = \frac{\text{Mass of atoms in UC}}{\text{Volume of UC}} = \frac{nA}{V_c N_a}.$$

Where  $n$  is the number of atoms per unit cell,  $A$  is the atomic weight,  $V_c$  is the volume of the unit cell and  $N_a$  is avogadro's constant.

## 5.6 Crystal systems

Any crystal structure can be described based on 6 parameters relating to the unit cells. These are called the *lattice parameters* and consist of edge lengths and interaxial angles.

**Definition 8: Crystal systems**

A *crystal system* is a scheme in which crystal structures are classified based on the geometry of the UC. This geometry is specified in terms of the *lattice parameters*. The 7 different crystal systems are shown in **Figure 5.5**.

## 5.7 Point coordinates

For a general cubic structure there are three different specific edge-lengths. Any position within the UC can be represented by a so-called *point coordinate*. Point coordinates are given as a *fractional multiple* of  $a$ ,  $b$ , and  $c$  – the edge lengths of the UC. A Point coordinate is given as a list of the fractional multiples without commas. That is for the outer upper corner – which is placed at 1 on both the  $a$ ,  $b$ , and  $c$ -axis we get a point coordinate of 111 (1, 1, 1 – but without commas). The general algorithm is:

- Determine your lattice position (for outer upper corner this is 1, 1, 1.)
- Divide by edge lengths of UC

$$\frac{a}{a} \frac{b}{b} \frac{c}{c} = 111.$$

- Concatenate the numbers to get 111

## 5.8 Crystallographic directions

Not just positions in the UC can be represented numerically. The same is true for directions. The general algorithm for this is

Figure 5.5: The 7 different crystal systems and their axial relationships and interaxial angles.

Crystal System	Axial Relationships	Interaxial Angles	Unit Cell Geometry
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Monoclinic	$a \neq b \neq c$	$\alpha = 90^\circ \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	

- Determine the coordinates of the vector tail  $p_1$  and vector head  $p_2$ .
- Subtract tail coordinates from head coordinates.
- Normalize coordinate differences in terms of lattice parameters  $a$ ,  $b$ , and  $c$ . (Divide by  $a$ ,  $b$ , and  $c$ ).
- Reduce to smallest integer values.
- Enclose indices in square brackets without commas like  $[uvw]$ .
- Note: Negative values are written as  $\bar{x}$  where  $\bar{x} = -x$ .

### Example: Crystallographic direction

We want to determine the crystallographic direction from pt. 1:  $x_1 = 0, y_1 = 0, z_1 = 0$  to pt. 2:  $x_2 = a, y_2 = 0, z_2 = \frac{c}{2}$ .

Firstly we get the three indices as

$$\begin{aligned}\Delta x &= 1 \\ \Delta y &= 0 \\ \Delta z &= \frac{1}{2}.\end{aligned}$$

This gives  $[1, 0, \frac{1}{2}]$ . This is then reduced to integer values as  $[2, 0, 1]$ . Commas can now be removed and we get  $[201]$ . If the  $z$ -direction had been negative the crystallographic direction would instead be  $[20\bar{1}]$ .

**Definition 9: Linear density of atoms**

The *linear density of atoms* is defined as the number of atoms *centered* on a direction vector divided by the length of the direction vector.

## 5.9 Crystallographic planes

Parallel to the notion of crystallographic points and crystallographic direction is *crystallographic planes*. These are defined in terms of the so-called *miller-indices* of the plane. The general algorithm for this is

- Choose an origin and a plane.
- If the chosen plane passes through the origin choose a new plane or a new origin.
- Read off the values of intercept with the  $x$ ,  $y$  and  $z$  axes in terms of  $a$ ,  $b$ , and  $c$ .
- Take the reciprocals of the intercepts.
- Normalize the reciprocals of intercepts by multiplying by lattice parameters  $a$ ,  $b$  and  $c$ .
- Reduce to smallest integer values.
- Enclose the resulting *miller indices* in parenthesis with no commas like  $(hkl)$ . If any values are negative these can be shown as  $\bar{x}$  where  $\bar{x} = x$

Examples of this algorithm are shown in **Figure 5.6**, **Figure 5.7** and **Figure 5.8**.

	$x$	$y$	$z$
1. Relocate origin – not needed			
2. Intercepts	$a$	$b$	$\infty c$
3. Reciprocals	$1/a$	$1/b$	$1/\infty c$
4. Normalize	$a/a$	$b/b$	$c/\infty c$
5. Reduction	1	1	0
6. Miller Indices	(110)		

Figure 5.6: Example 1 of a crystallographic plane.

	$x$	$y$	$z$
1. Relocate origin – not needed			
2. Intercepts	$a/2$	$\infty b$	$\infty c$
3. Reciprocals	$2/a$	$1/\infty b$	$1/\infty c$
4. Normalize	$2a/a$	$b/\infty b$	$c/\infty c$
5. Reduction	2	0	0
6. Miller Indices	(200)		

Figure 5.7: Example 2 of a crystallographic plane.

	$x$	$y$	$z$
1. Relocate origin – not needed			
2. Intercepts	$a/2$	$b$	$3c/4$
3. Reciprocals	$2/a$	$1/b$	$4/3c$
4. Normalize	$2a/a$	$b/b$	$4c/3c$
5. Reduction (x3)	2	1	$4/3$
6. Miller Indices	(634)		

Figure 5.8: Example 3 of a crystallographic plane.

**Definition 10: Planar density of atoms**

As was the case for the linear density a planar density of atoms can also be defined. This is defined as the number of atoms centered on a plane divided by the area of the plane.

## Lecture 4: Imperfections in solids

5. Februar 2025

## 6 Solidification

The subject of today is imperfections in solids and therefore it is important to also mention solidification. A typical solidification follows this process

### 1. Molecular motion in the liquid

In the liquid state, molecules and/or atoms have relatively high kinetic energies and they move freely in a disordered manner. The high kinetic energy of the atoms/molecules keeps them from settling into position and establishing long-range order.

### 2. Cooling and reduction in kinetic energy

As the liquid cools the kinetic energy of the atoms/molecules decreases. This smaller amount of energy means that the attractive intermolecular/interatomic forces can begin to dominate. This slowly pulls the atoms/molecules more together and slowly establishes order.

### 3. Nucleation:

When the kinetic energy of the atoms/molecules has become small enough small clusters of atoms or molecules will start to come together. Sometimes these form spontaneously in the bulk liquid – a process referred to as *homogeneous nucleation*. Often, impurities, container walls or other surfaces provide a point of nucleation – this is referred to as *heterogeneous nucleation*. It should also be noted that not all small clusters will grow into a solid crystal. Each nucleus must reach a size where it is thermodynamically stable, meaning that the amount of energy gained from forming a solid outweighs the energy cost of creating a new interface between the solid and the liquid.

### 4. Crystal growth

Once a stable nucleus has formed, additional molecules/atoms from the liquid will start to attach to it. Molecules/atoms will approach the nucleus and if their orientation and energy is correct they will attach to the nucleus. This process is highly directional as molecules will align themselves in a pattern that reflects the symmetry and spacing of the crystal lattice. This process will (always?) release some latent heat, which can raise the temperature of the crystal and the surrounding liquid if the heat, for some reason, is not effectively removed.

### 5. Role of impurities

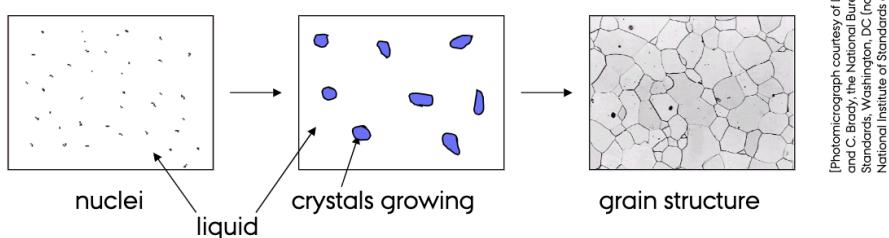
During the solidification process impurities can be introduced. Impurities are either incorporated or rejected from the crystal lattice based on their chemical compatibility with the host lattice. If an impurity does not fit well inside the lattice, it will tend to accumulate at an interface between the liquid and solid phases. If too much impurity accumulates here it can affect the growth of the crystals.

### 6. Completion of solidification

As more and more molecules are organized into a crystal lattice the entire volume of the liquid will soon have turned solid. Many of the final properties of the solid – such as grain size, defect density, and impurity distribution – are determined by the conditions during solidification.

This entire process is also shown briefly in **Figure 6.1**. As mentioned in part 6. of the solidification process

Figure 6.1: Solidification process



[Photomicrograph courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC (now the National Institute of Standards and Technology, Gaithersburg, MD).]

explanation some of the properties of the solidified solid are determined by the conditions of the solidification process. This is explained a bit below.

- **Types of Grains:**

- **Equiaxed Grains:**

These grains are approximately equal in all directions. They typically form under rapid cooling conditions, where many nuclei form simultaneously. The fast extraction of heat limits their growth, resulting in a fine, isotropic grain structure (see **Figure 6.2**).

- **Columnar Grains:**

These are elongated grains that grow predominantly in one direction, often aligned with the heat flow. When cooling is slower, nucleation is limited and existing grains have more time to grow directionally, resulting in a columnar structure (see **Figure 6.2**).

- **Heat Flow and Cooling Rate:**

- **Rapid Cooling Near the Walls:**

The outer regions of a casting, for example, cool more quickly due to heat extraction toward the mold walls. This rapid cooling promotes a high nucleation rate and the formation of many small, equiaxed grains.

- **Slower Cooling in the Center:**

The interior of the material cools more slowly, allowing directional solidification. This slower rate favors the growth of fewer, larger columnar grains aligned with the heat flow.

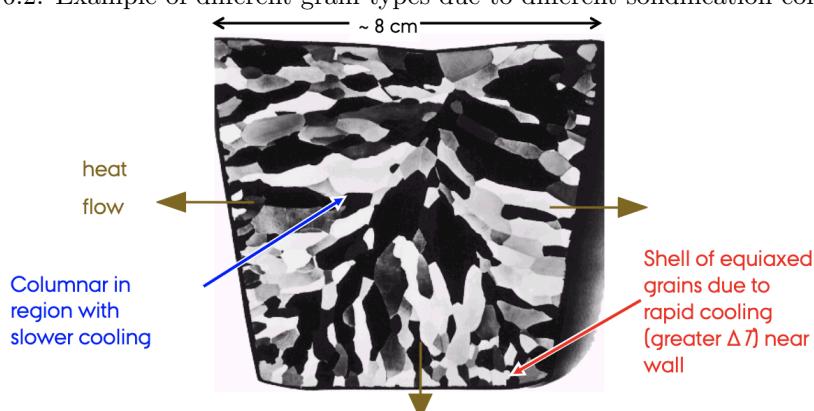
- **Role of Grain Refiners:**

Additives known as grain refiners can be used to promote the formation of smaller, more uniform equiaxed grains. These refiners provide additional nucleation sites and help disrupt the growth of large columnar grains, which is often desirable for improving isotropy and mechanical properties. In many ways one can think of the fact that it is easier to make it “random” each time and thus rely on the law of large numbers to determine the properties than to rely on making exactly the same type of large columnar grains each time.

- **Real-World Implications:**

In cast metals and alloys, the combination of equiaxed and columnar grains can have a significant impact on mechanical properties. Equiaxed grains typically enhance toughness and isotropy, while columnar grains may introduce anisotropy that is either beneficial or detrimental depending on the application.

Figure 6.2: Example of different grain types due to different solidification conditions.



## 7 Imperfections

There is no such thing as a perfect crystal – crystalline imperfections (or *defects*) are always present. This detail is not merely trivial as many important properties of materials are rather sensitive to defects.

### 7.1 Types of imperfections

A few common types of imperfections will be explained in the next few paragraphs. These are

- Point defects (0-dimensional)
  - Vacancies
  - Interstitial atoms
  - Substitutional impurity atoms
- Linear defects (1-dimensional)
  - Dislocations
- Interfacial defects (2-dimensional)
  - Grain boundaries

### 7.2 Point defects

#### 7.2.1 Vacancies

- **Definition:**

A vacancy is a point defect where an atom is missing from one of the regular lattice sites. Imagine the perfect crystal lattice as a grid of atoms—if one atom is absent, a vacancy is created (see **Figure 7.1**).

- **Formation:**

Vacancies can form during the crystallization process or be introduced thermally when atoms gain enough energy to leave their lattice sites. The equilibrium concentration of vacancies increases with temperature. The equilibrium concentration of vacancies for a given material and temperature is given by

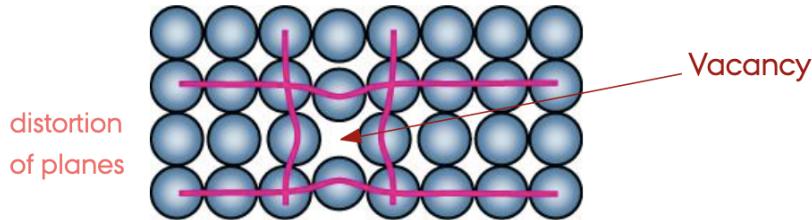
$$\frac{N_v}{N} = e^{-\frac{Q_v}{kT}}.$$

Where  $N_v$  is the amount of vacancies,  $N$  is the amount of lattice positions (maximum amount of vacancies),  $Q_v$  is the activation energy for forming a vacancy,  $k$  is Boltzmann's constant and  $T$  is the absolute temperature. The activation energy for forming a vacancy  $Q_v$  is material and crystal structure specific and must be determined experimentally.

- **Effects on Material Properties:**

- **Diffusion:** Vacancies facilitate atomic diffusion. Atoms can "jump" into adjacent vacant sites, allowing mass transport through the lattice.
- **Mechanical Properties:** A high concentration of vacancies can weaken the material by providing sites for crack initiation or influencing creep behavior
- **Electrical Properties:** In semiconductors, vacancies can act as electron traps, affecting conductivity.

Figure 7.1: Vacancy in a crystal lattice



### 7.2.2 Interstitials

- **Definition:**

An interstitial defect occurs when an extra atom occupies a space (an interstice) between the regular lattice sites. These positions are normally empty in an ideal crystal (see **Figure 7.2**).

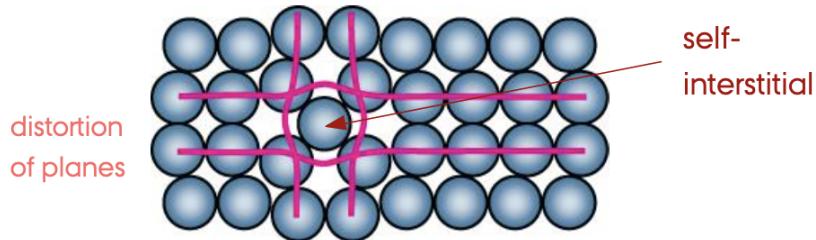
- **Types of Interstitial Atoms**

- **Host atoms:** Sometimes atoms from the same element may become interstitials if they are displaced from their normal lattice sites.
- **Impurity atoms:** Foreign atoms, often smaller than the host atoms, can fit into the interstitial spaces.

- **Effects on Material Properties:**

- **Strain and Distortion:** Because an interstitial atom does not fit perfectly into the lattice, it can distort the surrounding atomic arrangement, leading to local stress.
- **Hardening:** In some metals, interstitial impurities (such as carbon in iron to form steel) increase the material's hardness by impeding dislocation movement.
- **Diffusion:** Similar to vacancies, interstitial atoms can enhance diffusion; however, their movement mechanisms and activation energies differ from those of vacancies.

Figure 7.2: Interstitial defect in a crystal lattice



### 7.2.3 Substitutional Impurity Atoms

- **Definition:**

A substitutional impurity occurs when an atom of a foreign element takes the place of a host atom in the crystal lattice. This defect is "substitutional" because the impurity substitutes for a lattice atom (see **Figure 7.3**).

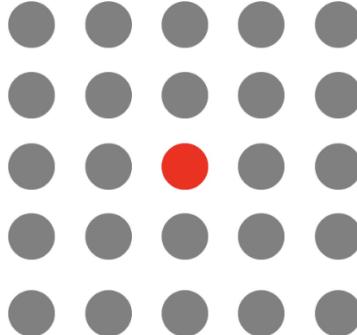
- **Formation:**

- **During Solidification:** Substitutional impurities can become incorporated into the lattice as the material solidifies from the liquid state if the impurity atoms are present in the melt.
- **Doping Processes:** In semiconductors, substitutional doping is intentionally carried out to modify electrical properties by replacing some host atoms with impurity atoms that have different valence electron configurations.

• **Effects on Material Properties:**

- **Mechanical Properties:** The presence of substitutional impurities can distort the lattice due to differences in atomic size compared to the host atoms. This distortion can either strengthen the material (by impeding dislocation movement) or weaken it if excessive strain is introduced.
- **Electrical Properties:** In semiconductors, substitutional impurities are crucial for controlling conductivity. For example, replacing a silicon atom with a phosphorus atom (which has five valence electrons) creates an excess of electrons (*n*-type doping), whereas using boron (with three valence electrons) results in *p*-type doping by creating holes.
- **Thermal Properties:** The lattice distortion and scattering of phonons by impurity atoms can affect the thermal conductivity of the material.
- **Chemical properties:** The chemical reactivity may also be altered if the impurity atoms interact differently with the environment compared to the host atoms.

Figure 7.3: Substitutional impurity in a crystal lattice



**Example: Equilibrium number of vacancies in 1 cubic meter of copper at 1000 degrees celsius**

We want to determine the equilibrium number of vacancies in 1 m<sup>3</sup> Cu at 1000 °C.

We start by finding the total amount of lattice sites using the formula

$$N = \frac{N_A \rho}{A}.$$

Where  $N_A$  is Avogadro's constant,  $\rho$  is the density of the material and  $A$  is the atomic weight. By substituting in known values we get

$$N = \frac{6,022 \cdot 10^{23} \text{ mol}^{-1} \cdot 8,4 \frac{\text{g}}{\text{cm}^3}}{63,5 \frac{\text{g}}{\text{mol}}} = 8,0 \cdot 10^{28} \text{ mol}^{-1}.$$

We can now determine the equilibrium number of vacancies as

$$N_v = N e^{-\frac{Q_v}{kT}}.$$

$Q_v$  has experimentally been found to be  $Q_v = 0,9 \text{ eV}$  for Cu and thus we get

$$N_v = N e^{-\frac{0,9 \text{ eV}}{8,62 \cdot 10^{-5} \frac{\text{eV}}{\text{K}} \cdot 1273 \text{ K}}} = (2,7 \cdot 10^{-4}) N = 2,2 \cdot 10^{25} \text{ m}^{-3}.$$

I.e. we expect there to be  $2,2 \cdot 10^{25} \text{ m}^{-3}$  vacancies in  $1 \text{ m}^3$  of Cu.

### Example: Calculation of fraction of vacancies

For some hypothetical metal the equilibrium number of vacancies at  $900^\circ\text{C}$  is  $2,3 \cdot 10^{25} \text{ m}^{-3}$ . If the density and atomic weights are  $7,40 \text{ g/cm}^3$  and  $85,5 \text{ g/mol}$ , respectively, calculate the fraction of vacancies for this metal at  $900^\circ\text{C}$ .

We can use the same formula for the amount of lattice positions as we did above

$$N = \frac{N_A \rho}{A} = \frac{6,022 \cdot 10^{23} \text{ mol}^{-1} \cdot 7,40 \frac{\text{g}}{\text{cm}^3}}{85,5 \frac{\text{g}}{\text{mol}}} = 5,21 \cdot 10^{28} \text{ m}^{-3}.$$

Now we can find the fraction as

$$\frac{N_v}{N} = \frac{2,3 \cdot 10^{25} \text{ m}^{-3}}{5,21 \cdot 10^{28} \text{ m}^{-3}} = 4,41 \cdot 10^{-4}.$$

### 7.2.4 Impurities in metals

If impurity atoms are added to a solid composed of host atoms then the impurities will start to dissolve into the host lattice. Until the impurity concentration exceeds the solubility limit the impurities will simply dissolve into the main metal. After exceeding the solubility limit no more impurity can be dissolved into the main metal. Instead a “secondary phase” is formed which can have a different structure than the main metal. This secondary phase will also build grains in the same way the primary phase (main metal) does.

A few different rules dictate how impurities can be added to metals. These are known as the Hume-Rothery rules. There are two sets of Hume-Rothery rules – one for substitutional solid solutions and one for interstitial solid solutions. These are

#### Hume-Rothery Rules for Substitutional Solid Solutions

1. The atomic radius of the solute and solvent must differ by no more than 15%.
2. The crystal structures of the solvent and solute must be similar.
3. Complete solubility occurs when the solvent and solute have the same valency. A metal is more likely to dissolve a metal of higher valency, than vice versa.
4. The solute and solvent should have similar electronegativity. If the electronegativity difference is too great, the metals tend to form intermetallic compounds instead of solid solutions.

#### Hume-Rothery Rules for Interstitial Solid Solutions

1. Solute atoms should have a smaller radius than 59% of the radius of solvent atoms.
2. The solute and solvent should have similar electronegativity.
3. The solute and solvent should have the same valence. The greater the difference in valence between solute and solvent atoms, the lower the solubility.

#### Example: Application of the Hume-Rothery Rules

We want to determine whether Al or Ag is more likely to form a substitutional solid solution in Zn.

The atomic radii are  $r_{Zn} = 0,1332 \text{ nm}$ ,  $r_{Al} = 0,1431 \text{ nm}$  and  $r_{Ag} = 0,1445 \text{ nm}$ . It can be observed, that in terms of difference of atomic radii, Al is slightly favoured compared to Ag.

The crystal structures for both Al and Ag are FCC, whereas it is HCP for Zn. This means Al and Ag are tied for this criterion.

The valence of Ag is +1, for Al it is +3 and for Zn it is +2. As the valence of Al > Ag this criterion favors Al.

The electronegativity of Zn is 1,6, whilst it is 1,9 and 1,5 for Ag and Al, respectively. As the electronegativity of Al is closer to Zn than the electronegativity of Ag is, Al must be favored in this criterion as well.

Based on the above it seems more likely that Al will form a substitutional solid solution in Zn than that Ag will.

## 7.3 Linear defects

All linear defects are examples of *dislocations*. These are 1-dimensional defects around which atoms are misaligned. However to really understand these we first need to introduce the concept of *Burger's vector*,  $\vec{b}$ .

### 7.3.1 Burger's vector

The Burger's vector,  $\vec{b}$ , is a vector that represents both the magnitude and the direction of the lattice distortion caused by a dislocation. It essentially quantifies the “missing” or “extra” displacement in the crystal lattice due to the dislocation. To determine the magnitude and direction of Burger's vector one must follow this procedure:

1. Visualize the crystal structure without the defect, i.e. the *perfect* crystal structure.
2. Construct a rectangle encompassing the site of the dislocation with side lengths that are integer multiples of  $a$  (the edge length of the UC). This rectangle is known as a *Burger's circuit*-
3. Reintroduce the dislocation in the visualization.
4. The, previously closed, Burger's circuit will now have been deformed along with the crystal lattice underneath. The “missing” vector that is needed to close the loop is then the Burger's vector.

### 7.3.2 Edge Dislocations

- **Definition:**

An edge dislocation is a line defect in a crystal lattice characterized by the presence of an extra half-

plane of atoms that terminates within the crystal. This extra half-plane creates a localized distortion of the surrounding lattice (see **Figure 7.4**).

- **Formation:**

Edge dislocations can form during processes such as plastic deformation, where the crystal is subjected to stresses that force an extra half-plane of atoms into the lattice, or due to thermal stresses. The introduction of these dislocations helps accommodate the strain imposed on the crystal.

- **Burgers Vector:**

The magnitude and direction of the lattice distortion are described by the Burgers vector. For an edge dislocation, the Burgers vector is perpendicular to the dislocation line, quantifying the shift of atomic planes relative to each other.

- **Effects on Material Properties:**

- **Plastic Deformation:**

The movement of edge dislocations under applied stress allows layers of atoms to slip past each other, which is the primary mechanism for permanent (plastic) deformation in crystalline materials.

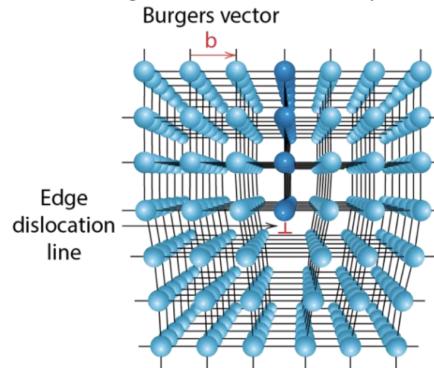
- **Work Hardening:**

As deformation progresses, the density of dislocations increases and they interact with one another. These interactions can impede further dislocation movement, thereby increasing the strength of the material through work hardening.

- **Stress Concentration:**

The localized lattice distortion around an edge dislocation creates regions of high internal stress. These stress concentrations can act as initiation sites for cracks, influencing the material's fracture behavior.

Figure 7.4: Edge dislocation in a crystal lattice



### 7.3.3 Screw Dislocations

- **Definition:**

A screw dislocation is a line defect in a crystal lattice characterized by a helical arrangement of the atomic planes around the dislocation line. Unlike an edge dislocation, a screw dislocation does not have an extra half-plane of atoms; instead, the lattice shifts in a spiral manner around the defect (see **Figure 7.5**).

- **Formation:**

Screw dislocations are commonly formed during plastic deformation when shear stresses are applied to

the crystal. These stresses cause the atomic planes to shift relative to one another in a helical path, creating the screw dislocation.

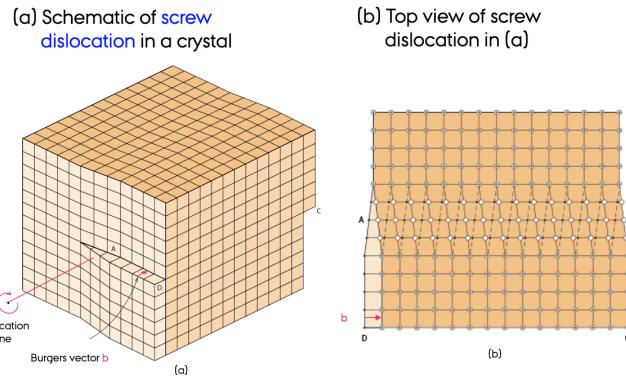
- **Burgers Vector:**

In the case of a screw dislocation, the Burgers vector is parallel to the dislocation line.

- **Effects on Material Properties:**

- **Plastic Deformation:** The motion of screw dislocations under applied stress enables shear deformation of the crystal, contributing to the material's overall ductility.
- **Dislocation Mobility:** Screw dislocations can move through the lattice via a process called *glide* (along specific crystallographic planes) or *climb* (perpendicular to the glide plane, often assisted by diffusion), affecting the rate and mode of deformation.
- **Interaction with Other Defects:** The presence of screw dislocations influences the interaction with other dislocations and defects, which can either facilitate or impede further movement and thus impact the work hardening and strength of the material.

Figure 7.5: Screw dislocation in a crystal lattice



#### 7.3.4 Mixed Dislocations

- **Definition:**

Mixed dislocations are line defects in the crystal lattice that possess both edge and screw components. The dislocation line in these cases does not lie entirely in the plane of the extra half-plane (as in a pure edge dislocation) nor is it completely parallel to the Burgers vector (as in a pure screw dislocation) (See **Figure 7.6**).

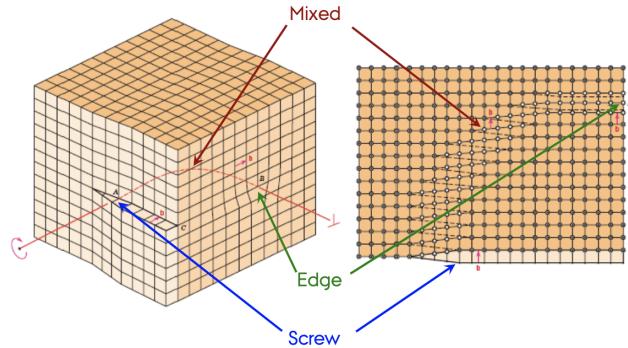
- **Characteristics:**

The local character of a mixed dislocation may vary along its length, with certain segments behaving more like edge dislocations and others more like screw dislocations.

- **Importance:**

Most dislocations in real materials are mixed, and their complex behavior influences the material's plastic deformation, work hardening, and interaction with other defects.

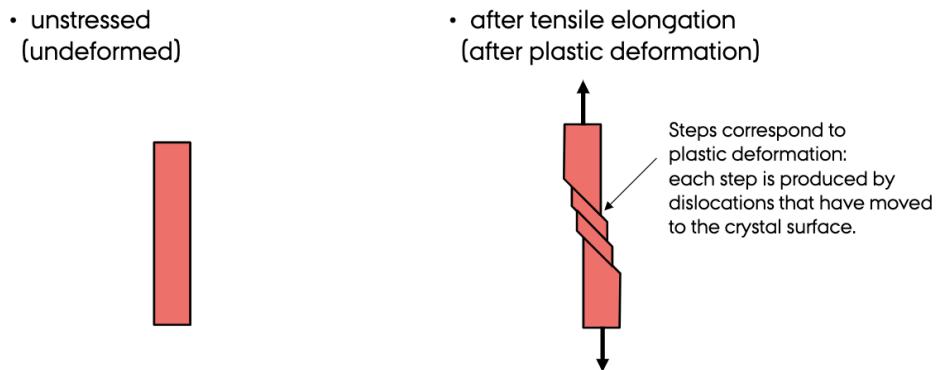
Figure 7.6: Mixed dislocation in a crystal lattice



### 7.3.5 Plastic deformation and dislocations

When an external stress is applied to a material dislocations will begin to move. As these dislocations move through the material they allow layers of atoms to slip relatively to each other. This is what leads to plastic deformation. The fact that dislocations can move under applied stress is central to the idea of ductility in many materials. In a single crystal metal, when dislocations move to the surface, they leave behind small steps. Each step corresponds to a dislocation slip event. These incremental steps collectively account for the overall plastic deformation of the material. This mechanism is shown in **Figure 7.7**. Based on the above it is clear that plastic deformation is not a smooth, continuous process but rather the accumulation of many discrete events. Each time a dislocation moves and reaches the surface, it produces a step. Over time, these steps add up, leading to a measurable change in shape of the material.

Figure 7.7: Plastic deformation in a single-crystal metal



## 7.4 Planar defects

### 7.4.1 Twin Boundaries

- **Definition:**

A twin boundary is a planar defect where two adjacent regions of a crystal are mirror images of each other across a specific crystallographic plane. This mirror symmetry distinguishes twin boundaries from other types of interfaces in the crystal (see **Figure 7.8**).

- **Formation:**

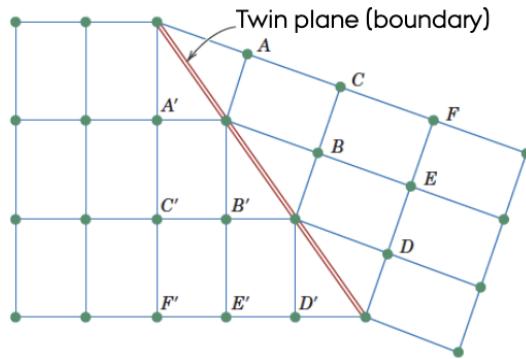
Twin boundaries can form during:

- **Crystal Growth:** During solidification or annealing, certain conditions may favor the formation of twin domains.
- **Plastic Deformation:** Under high strain rates or low temperatures, deformation twins may form as a mechanism to accommodate plastic deformation.

- **Effects on Material Properties:**

- **Strengthening Mechanism:** Twin boundaries can impede dislocation motion, which may enhance the material's strength.
- **Toughness:** In some cases, twin boundaries can increase ductility and toughness by providing additional pathways for deformation.
- **Anisotropy:** The mirror symmetry may influence the directional properties of the material, leading to anisotropic behavior.

Figure 7.8: Twin boundary in a crystal lattice



#### 7.4.2 Grain Boundaries

- **Definition:**

A grain boundary is the interface between two individual grains within a polycrystalline material, where the crystal lattice orientation changes abruptly. This boundary represents a discontinuity in the crystallographic arrangement (see **Figure 7.9**).

- **Formation:**

Grain boundaries form during:

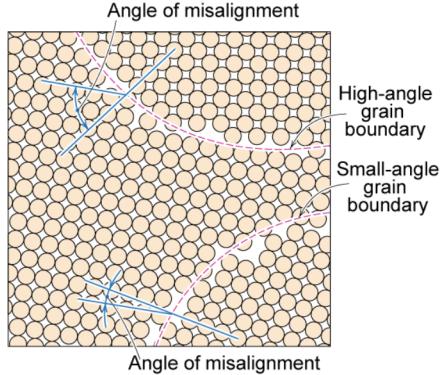
- **Solidification:** As a polycrystalline material cools, different grains nucleate and grow in various orientations. When these growing grains impinge upon one another, grain boundaries form.
- **Recrystallization:** During thermomechanical processing, new strain-free grains can nucleate within a deformed microstructure, resulting in new grain boundaries.

- **Effects on Material Properties:**

- **Strengthening:** Grain boundaries act as barriers to dislocation motion, which increases strength. However, very small grains can also lead to a reduction in ductility.
- **Diffusion:** The less ordered structure at grain boundaries allows for enhanced diffusion compared to the crystal interior.

- **Corrosion and Creep:** Grain boundaries can serve as preferred sites for corrosion attack or creep deformation due to their higher energy and susceptibility to impurity segregation.

Figure 7.9: Grain boundary in a polycrystalline material



#### 7.4.3 Stacking Faults

- **Definition:**

A stacking fault is a planar defect that occurs when there is a disruption in the regular stacking sequence of atomic planes in a crystal. In close-packed structures, atoms are arranged in a specific order (e.g., ABCABC... in face-centered cubic (FCC) crystals or ABAB... in hexagonal close-packed (HCP) crystals). A stacking fault introduces a deviation from this ideal sequence (see **Figure 7.10**).

- **Understanding Stacking:**

- In FCC metals, the close-packed planes follow an *ABC* stacking sequence. Each letter represents a distinct position of the plane relative to the one below it. For example, if the ideal stacking is ...ABCABCABC..., a fault might produce a sequence like ...ABC~~A~~ACABC..., where the normal progression is interrupted.
- In HCP metals, the ideal stacking sequence is *ABAB*.... A fault in this sequence might result in a local deviation, such as an extra A or B layer, leading to a disrupted stacking order.
- The stacking sequence is critical because it determines the overall symmetry and slip systems available in the crystal, thereby influencing the mechanical properties.

- **Formation:**

Stacking faults can be formed during:

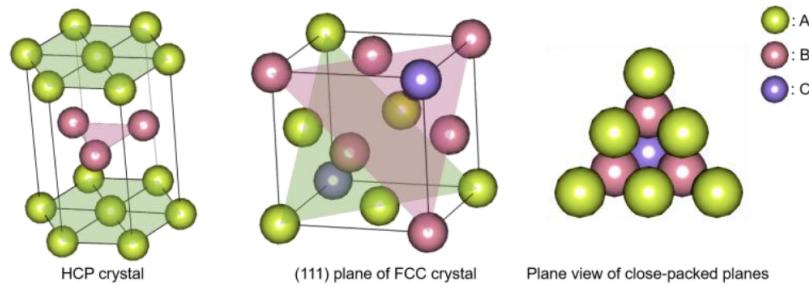
- **Crystal Growth:** Imperfections during the deposition of atomic layers can lead to errors in the stacking sequence.
- **Plastic Deformation:** Dislocation movement, especially partial dislocations, can create stacking faults. For example, in FCC metals, the motion of a partial dislocation leaves behind a stacking fault in the slip plane.
- **Phase Transformations:** Changes in temperature or pressure may induce stacking faults during transformations between different crystal structures.

- **Effects on Material Properties:**

- **Influence on Dislocation Motion:** Stacking faults can modify the way dislocations move through a crystal. In some cases, they can act as barriers that impede dislocation glide, contributing to strengthening. In other cases, they may facilitate the splitting of dislocations into partials.

- **Planar Defect Energy:** The energy associated with a stacking fault depends on the degree of disruption in the stacking order. Lower stacking fault energies tend to promote the formation of extended partial dislocations, which can enhance ductility by allowing more cross-slip.
- **Twining and Deformation Mechanisms:** In certain materials, stacking faults are precursors to deformation twinning—a process that can contribute to plastic deformation. The local reordering of the stacking sequence may lead to twin formation, which influences the material’s mechanical response.

Figure 7.10: Ideal stacking for HCP and FCC crystals.



## Lecture 5: Diffusion in solids

10. Februar 2025

Before talking about diffusion it is important to have a few general definitions.

## 8 Diffusion

### Definition 11: Diffusion

Diffusion is the process of transporting mass by atomic motion.

### Definition 12: Diffusion mechanisms

The main diffusion mechanism for liquids and gasses is *random* Brownian motion, whereas the main diffusion mechanism for solids is vacancy and interstitial diffusion.

### Definition 13: Interdiffusion

Diffusion of atoms of one material into another material.

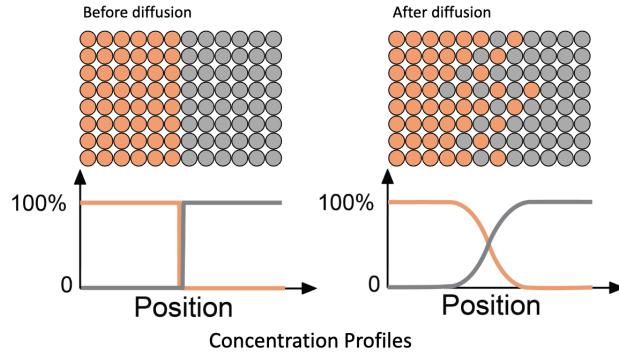
### Definition 14: Self-diffusion

Atomic migration in a pure metal.

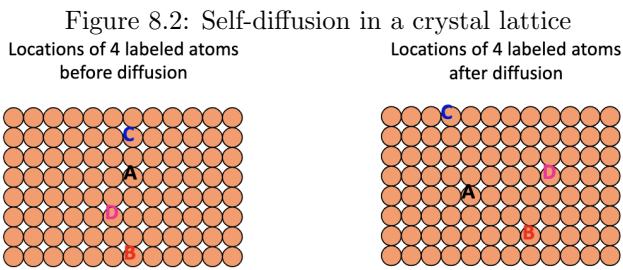
## 8.1 Mechanisms of diffusion

Atoms tend to migrate from regions of high concentration to regions of low concentration. This is shown in **Figure 8.1**.

Figure 8.1: Diffusion between materials at the interface of the materials



It is however not only different materials that diffuse into each other. If one labels a few different atoms in the crystal lattice of a solid, then at some later point these atoms will be in new positions due to self-diffusion. This is shown on **Figure 8.2**.



### 8.1.1 Vacancy diffusion

Atoms and vacancies are always exchanging positions. This applies to both the host atoms of a lattice and the substitutional impurity atoms. In short the diffusion rate depends on the number of vacancies and the activation energy to exchange. This is the most energy-expensive form of diffusion. This process is shown in **Figure 8.3**.

### 8.1.2 Interstitial diffusion

Through the process of interstitial diffusion, (relatively) small (often C or H) atoms are able to move from one interstitial position to another. This process requires less energy and happens much more rapidly than vacancy diffusion. This process is shown in **Figure 8.4**.

Figure 8.3: Vacancy diffusion in a crystal lattice

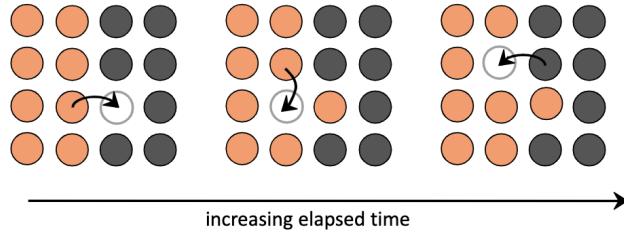
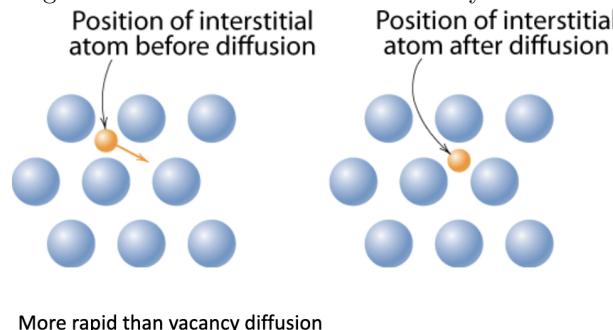


Figure 8.4: Interstitial diffusion in a crystal lattice



## 8.2 Diffusion rate

Diffusion is a time-dependent process. The rate of diffusion is expressed as the diffusion flux,  $J$ .

$$J = \text{flux} = \frac{\text{mass of diffused species}}{(\text{area})(\text{time})} = \frac{M}{At} \left[ \frac{\text{kg}}{\text{m}^2 \text{s}} \right] = \frac{I}{A} \frac{\text{d}M}{\text{dt}}.$$

This is typically measured experimentally by finding a thin sheet (membrane) with cross-sectional area  $A$ . Then one imposes a concentration gradient across the membrane and measures the mass of the diffusion species  $M$  that passes through the sheet over a time period  $t$ .

## 8.3 Steady-state diffusion and Fick's 1st law

Steady state diffusion (or flux) is any diffusion (or flux) that is independent of time. The flux ( $J$ ) will then be proportional to the concentration gradient, as

$$J \propto \frac{\text{d}C}{\text{d}x}$$

where  $C$  is the concentration and  $x$  is the diffusion direction. Fick's first law of diffusion states that

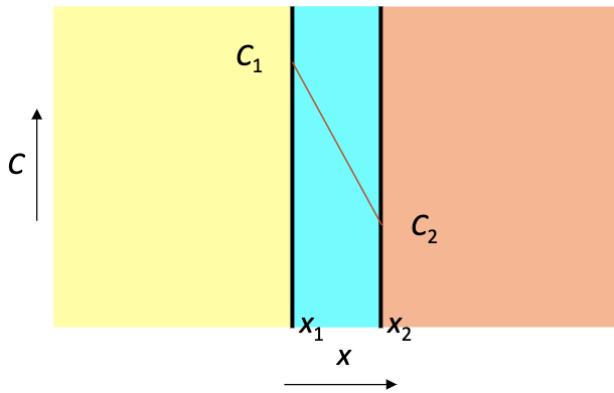
$$J = -D \frac{\text{d}C}{\text{d}x}$$

where  $D$  is the diffusion coefficient. If the concentration gradient is linear then

$$\frac{\text{d}C}{\text{d}x} \approx \frac{\Delta C}{\Delta x} = \frac{C_2 - C_1}{x_2 - x_1}$$

this is also shown in **Figure 8.5**.

Figure 8.5: Linear concentration gradient

**Example: Chemical protective clothing (CPC)**

Methylene chloride is a common ingredient of paint removers. Besides being an irritant, it also may be absorbed through the skin. When using this paint remover, protective gloves should be worn. We want to investigate whether butyl rubber gloves (0,04 cm thick) commonly found in the kitchen can be used as protective gloves. It should be noted that the maximum allowable flux for a 150 lbs person is less than  $3,5 \cdot 10^{-7} \text{ g cm}^{-2} \text{ s}^{-1}$ . Our goal is thus to calculate the diffusion flux of methylene chloride through the gloves. We have that

$$J = -D \frac{dC}{dx} = -D \frac{C_2 - C_1}{x_2 - x_1}.$$

We know that

$$\begin{aligned} D &= 110 \cdot 10^{-8} \frac{\text{cm}^2}{\text{s}} \\ C_1 &= 0,44 \frac{\text{g}}{\text{cm}^3} \\ C_2 &= 0,02 \frac{\text{g}}{\text{cm}^3} \\ x_1 - x_2 &= 0,04 \text{ cm}. \end{aligned}$$

We thus have

$$J = -110 \cdot 10^{-8} \frac{\text{cm}^2}{\text{s}} \cdot \frac{0,02 \frac{\text{g}}{\text{cm}^3} - 0,44 \frac{\text{g}}{\text{cm}^3}}{0,04 \text{ cm}} = 1,16 \cdot 10^{-5} \frac{\text{g}}{\text{cm}^2 \text{ s}}.$$

We thus have that  $J = 1,16 \cdot 10^{-5} \frac{\text{g}}{\text{cm}^2 \text{ s}} > 3,5 \cdot 10^{-7} \frac{\text{g}}{\text{cm}^2 \text{ s}}$  and therefore the butyl gloves are not good enough to be able to use with the paint remover.

## 8.4 Effect of temperature

The diffusion coefficient  $D$  increases with increasing temperature  $T$ . We have that

$$D = D_0 e^{-\frac{Q_d}{RT}} \quad (1)$$

where  $D_0 \left[ \frac{\text{m}^2}{\text{s}} \right]$  is the *theoretical* diffusion coefficient at  $T = 0 \text{ K}$ ,  $Q_d \left[ \frac{\text{J}}{\text{mol}} \right]$  is the activation energy for diffusion,  $R$  is the gas constant and  $T$  [K] is the absolute temperature. A general graph of this is shown in **Figure 8.6**,

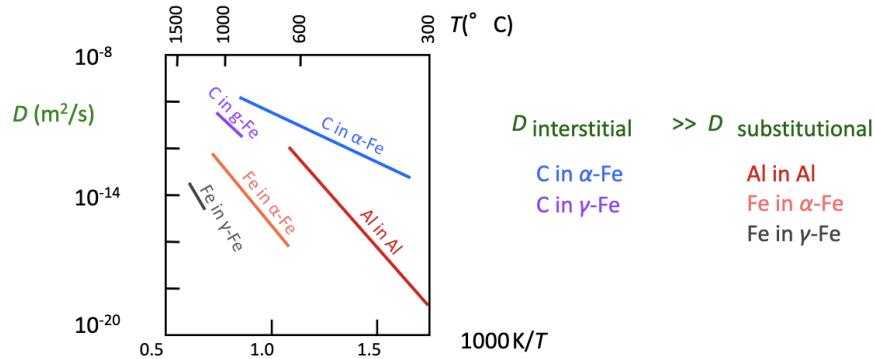
whilst some different diffusion coefficients for some common material combinations are shown on **Figure 8.7**. A parallel to **Equation 1**, which would allow one to calculate the diffusion coefficient at one temperature

Figure 8.6: Graph of diffusion coefficient as a function of temperature



$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right) \xrightarrow{\text{take natural log of both sides}} \ln D = \ln D_0 - \frac{Q_d}{RT}$$

Figure 8.7: Common material combinations and their diffusion coefficients  
*D has exponential dependence on T*



if one knows the diffusion coefficient at another, can be found by first knowing the diffusion coefficients  $D_1$  and  $D_2$  at two temperatures  $T_1$  and  $T_2$ . We then have that

$$\begin{aligned} \ln D_2 &= \ln D_0 - \frac{Q_d}{R} \left( \frac{1}{T_2} \right) \\ \ln D_1 &= \ln D_0 - \frac{Q_d}{R} \left( \frac{1}{T_1} \right). \end{aligned}$$

We can now subtract the second equation above from the first as

$$\ln D_2 - \ln D_1 = \ln \frac{D_2}{D_1} = -\frac{Q_d}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right).$$

And if we take the exponential on both sides we get

$$D_2 = D_1 e^{-\frac{Q_d}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)}.$$

**Example: Finding the diffusion coefficient at another temperature**

Suppose we known that the diffusion coefficient and activation energy for Cu in Si are

$$D_1(300\text{ }^{\circ}\text{C}) = 7,8 \cdot 10^{-11} \frac{\text{m}^2}{\text{s}}$$

$$Q_d(300\text{ }^{\circ}\text{C}) = 41,5 \frac{\text{kJ}}{\text{mol}}.$$

We now want to calculate the diffusion coefficient at 350 °C .

We can use the formula for calculating the diffusion coefficient at another temperature as

$$D_2 = D_1 e^{-\frac{Q_d}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)}$$

$$= 7,8 \cdot 10^{-11} \frac{\text{m}^2}{\text{s}} e^{-\frac{41,5 \frac{\text{kJ}}{\text{mol}}}{R} \left( \frac{1}{623\text{ K}} - \frac{1}{573\text{ K}} \right)}$$

$$= 1,569 \cdot 10^{-10} \frac{\text{m}^2}{\text{s}}.$$

## 8.5 Non-steady-state diffusion and Fick's 2nd law

For non-steady-state systems the concentration depends not only on position but also on time  $C = C(x, t)$ . For these kinds of systems we seek solutions to Fick's 2nd law, which can be stated as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2)$$

It should be noted that this form of the equation assumes  $D$  is independent of the concentration. If this is not the case the above becomes

$$\frac{\partial C}{\partial t} = \frac{\partial D}{\partial x} \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2}$$

however in this course we will mostly (only?) be working with the first form ( $D$  is independent of the concentration).

If we consider the case of copper diffusing into a bar of aluminum one might get something along the lines of **Figure 8.8**.

The solution to **Equation 2** is of the form

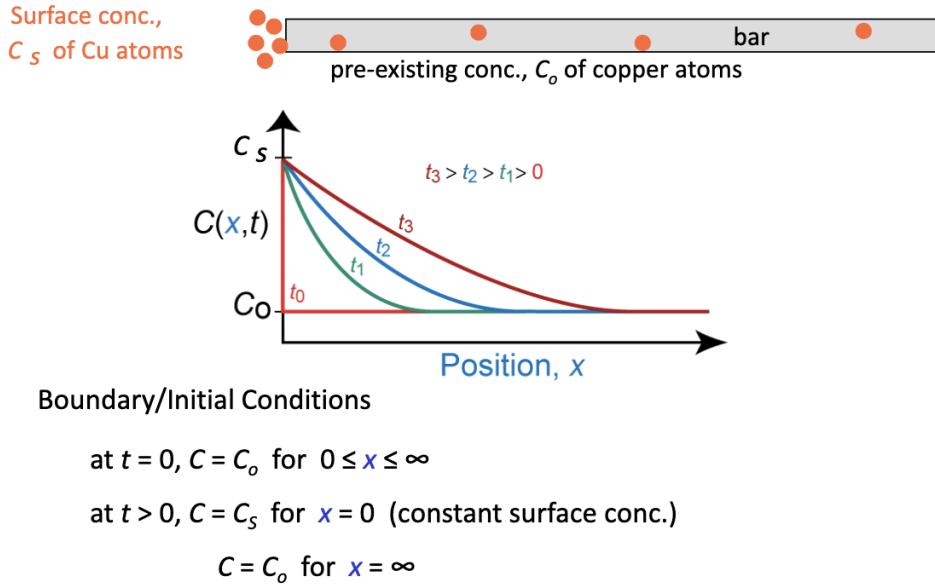
$$\frac{C(x, t) - C_0}{C_s - C_0} = 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$

where  $x$  is the position,  $t$  is the time,  $C_0$  is the bulk concentration,  $C_s$  is the surface concentration,  $D$  is the diffusion coefficient and  $\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt$  is the error function.

**Example: Calculating the temperature of a diffusion process**

An FCC iron-carbon alloy initially containing 0,20 wt% C is carburized at an elevated temperature and in an atmosphere in which the surface carbon concentration is maintained at 1,0 wt%. If, after 49,5 h, the concentration of carbon is 0,35 wt% at a position 4,0 mm below the surface, determine the temperature at which the treatment was carried out.

Figure 8.8: Copper diffusing into aluminum



We start with the solution to Fick's 2nd law

$$\frac{C(x, t) - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right).$$

The data needed for the problem can be found in table 5.2 of the book.

$$t = 49,5 \text{ hr}$$

$$C_x = 0,35\%$$

$$C_0 = 0,20\%$$

$$x = 4,0 \cdot 10^{-3} \text{ m}$$

$$C_s = 1,0\%.$$

Thus we have that

$$\frac{0,35 - 0,2}{1 - 0,2} = 1 - \operatorname{erf}(z)$$

with  $z = \frac{x}{2\sqrt{Dt}}$ . We thus have that

$$\operatorname{erf}(z) = 0,8125.$$

We can now determine that  $z = 0,93$  by using the solution table to the error function found in the book. We get

$$0,93 = \frac{x}{2\sqrt{Dt}} \implies D = \frac{x^2}{40,93^2 t} \implies D = 2,6 \cdot 10^{-11} \frac{\text{m}^2}{\text{s}}.$$

We also have the formula

$$D = D_0 e^{-\frac{Q_d}{RT}} \implies T = \frac{Q_d}{R(\ln D_0 - \ln D)}.$$

From table 5.2 in the book we have that

$$D_0 = 2,3 \cdot 10^{-5} \frac{\text{m}^2}{\text{s}}$$

$$Q_d = 148\,000 \frac{\text{J}}{\text{mol}}.$$

By plugging in the values we get that

$$T = 1300 \text{ K} = 1027^\circ\text{C}.$$

## Lecture 6: Mechanical Properties, Pt. 1: Elasticity

12. Februar 2025

From physics we are already familiar with the concept of springs. These are defined in terms of a so-called Spring constant that measures the “stiffness” of a spring. For general notes on spring systems please see the lecture-notes for “Physics and Mechanics” from the 1st semester.

# 9 Elasticity

## 9.1 Force-displacement relation

A Force-displacement relation is the relation between the applied force and the resulting displacement for a given material. This is, however, a rather ungeneralized notion as it does not take into account the thickness or general dimensionality of the test-specimen meaning the result is only true for a given material with a given shape/size. Instead we will seek to define stress and strain as an internal and relative measure of the force and displacement, respectively.

## 9.2 Strain

Strain  $\epsilon$  is a relative measurement of displacement. It is given by

$$\epsilon = \frac{d}{L_0}.$$

Where  $d$  is the measured displacement and the gauge length,  $L_0$  is the *original* length of the material – it should be noted that for the common “wishbone”-geometry of Tensile test-specimens  $L_0$  is typically taken to be a length slightly shorter than the length of the narrow section in the middle as the thick ends will not expand as much (the error goes to zero as the geometry goes to infinitely crazy). Strain is a unit-less scalar, although the unit of strain is sometimes given as  $[\epsilon] = \frac{\text{mm}}{\text{m}}$  to compensate for (often) very small numbers.

## 9.3 Stress

Stress  $\sigma$  is a relative measurement of force. It is given by

$$\sigma = \frac{F}{A_0}.$$

Where  $F$  is the applied force and  $A_0$  is the cross sectional area of the specimen. Stress has units of Pa or N/m<sup>2</sup> and it is therefore commensurable to pressure. Stresses are often in an order of about  $1 \cdot 10^6$  Pa and therefore  $[\sigma]$  is often given as MPa.

## 9.4 Stress-strain relations

We will now seek to find a relation between the two quantities of stress and strain. We start by imagining a rod subject to a force. It is a reasonable expectation that the rod will act sort of in the same way as a spring. We will therefore use the formula for the force in a spring as

$$F = kd.$$

We can now rewrite this as

$$\frac{F}{A_0} A_0 = k \frac{d}{l_0} l_0.$$

And it becomes obvious the above is just

$$\sigma A_0 = k \epsilon l_0.$$

This can be written as

$$\sigma = \frac{k l_0}{A_0} \epsilon.$$

By introducing the Modulus of Elasticity (Young's modulus)  $E = \frac{k l_0}{A_0}$  we can write the above as

$$\sigma = E \epsilon \implies E = \frac{\sigma}{\epsilon}.$$

Now we have found a constitutive equation between stress  $\sigma$  and strain  $\epsilon$  only depending on the (*material-specific*) elastic modulus  $E$ .

## 9.5 Elatic deformation

*Elastic deformation* is non-permanent and reversible. It is generally the type of deformation happening at small deformations and the stress/strain curve is approximately linear (with the elastic modulus  $E$  as its slope). On a microscopical scale elastic deformation can be thought about as a “stretching” of the interatomic bonds – this “stretching” will stop when the applied force is removed.

### 9.5.1 Elastic modulus and interatomic bonding forces

The elastic modulus  $E$  depends on the strength of the interatomic forces in the material. Actually, the modulus of elasticity is proportional to the slope of the interatomic force-interatomic separation curve as shown in **Figure 9.1** – also it is true that in general we get that  $E \propto r_0^{-2}$ , where  $r_0$  is the equilibrium interatomic spacing. Elastic moduli for different common materials are shown in **Figure 9.2**.

## 9.6 Shear stress

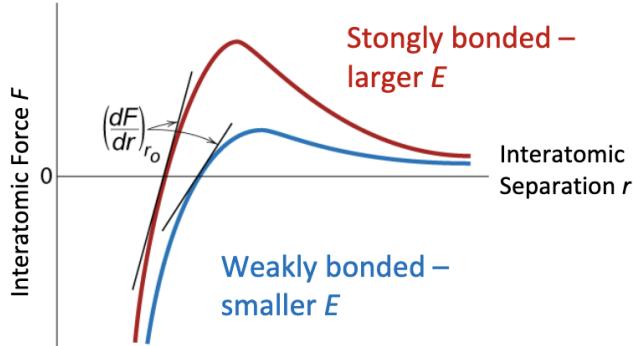
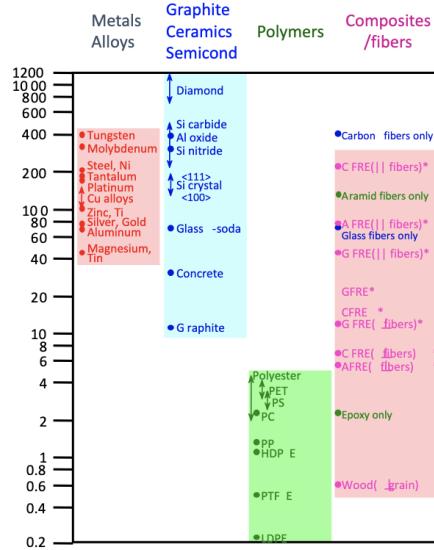
Not always the *tensile* version of stress is wanted. Sometimes one instead seeks to find a solution to a problem involving a “bending” of the material. This is known as shear stress  $\tau$ . Shear stress is also given as

$$\tau = \frac{F_{\perp}}{A_0}.$$

As was the case for tensile stress we also want to find a constitutive equation for shear stress. We once again start as

$$F = kd.$$

Figure 9.1: Relationship between EM and interatomic interactions


 Figure 9.2: EM for common materials ( $y$ -axis is given in MPa)


And follow the same steps as was the case for the tensile stress until we get

$$\tau = \frac{kl_0}{A_0} \gamma.$$

Where  $\gamma = \frac{d}{l_0}$  is the shear strain and  $\tau$  is the shear stress. We now define  $G = \frac{kl_0}{A_0}$  as the shear modulus and get

$$\tau = G\gamma.$$

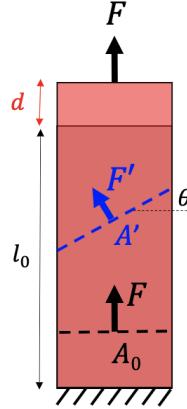
The tensile modulus  $E$  is always larger than the shear modulus  $G$ .

$$E > G.$$

### 9.6.1 Stresses on different planes

To compute a stress, a specific plane needs to be defined. This is shown in **Figure 9.3**. For the case on

Figure 9.3: Stresses on different planes



**Figure 9.3** we actually get the two relations for the tensile stress

$$\sigma_0 = \frac{F}{A_0}$$

$$\sigma' = \frac{F'}{A'}.$$

These two tensile stresses are related by

$$\sigma' = \frac{F \cos \theta}{A_0 / \cos \theta} = \sigma_0 \cos^2 \theta = \sigma_0 \left( \frac{1 + \cos 2\theta}{2} \right).$$

And the shear stresses are related as

$$\tau' = \frac{F \sin \theta}{A_0 / \cos \theta} = \sigma_0 \sin \theta \cos \theta = \sigma_0 \left( \frac{\sin 2\theta}{2} \right).$$

## 9.7 Bulk modulus

The *bulk modulus*  $K$  is a measurement of how resistant a material is to compression and it is defined as the ratio of the pressure increase to the resulting relative decrease of the volume.

$$\Delta p = K \frac{\Delta V}{V_0}.$$

## 9.8 Poisson's ratio

To define the so-called Poisson's ratio we will first define the axial strain  $\epsilon_z$  and the transverse strain  $\epsilon_x$  as

$$\epsilon_z = \frac{d_z}{l_{0z}}$$

$$\epsilon_x = \frac{d_x}{l_{0x}}.$$

That is the strain in a given direction is defined as the strain measured solely in that direction.

Poisson's ratio  $\nu$  is then defined as

$$\nu = -\frac{\epsilon_x}{\epsilon_z}.$$

The Poisson's ratio is thus a measurement of the Poisson effect, which is the deformation (expansion or contraction) of a material in the directions perpendicular to the applied load.

### 9.8.1 The relationship between Poisson's ratio and moduli

It can be shown that

$$G = \frac{E}{2(1+\nu)} \quad \text{and} \quad K = \frac{E}{3(1-2\nu)}.$$

That means the shear and bulk moduli ( $G$  and  $K$ ) can be found in terms of the Poisson ratio  $\nu$  and Youngs modulus  $E$ . This also means that the Poisson's ratio of a stable, isotropic, linear elastic material must be between  $-1$  and  $+0.5$ , because of the requirement for Young's, shear and bulk modulus to have positive values. A negative Poissons ratio indicate that the material expands when a perpendicular force is applied and therefore most materials have positive Poissons ratio – All materials with negative Poissons ratios are known under the name *Auxetics*.

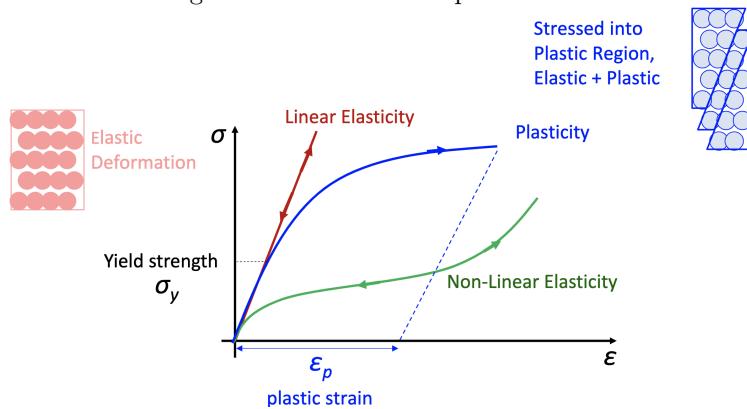
## Lecture 7: Mechanical properties, pt. 2: Plasticity

17. Februar 2025

# 10 Plasticity

Opposed to *elastic deformation*, when a material undergoes *plastic deformation* the process is irreversible and dissipates energy. If we compare *elasticity* with springs, *plasticity* is a breaking of these “springs” and instead the lattice will start changing, such as by getting narrower and longer if the material is pulled in a given direction. Plastic deformation is nonlinear, whereas elastic deformation is oftentimes linear. This is shown along with a small model of a lattice undergoing elastic and plastic deformation is shown on **Figure 10.1**

Figure 10.1: Elastic and plastic strain

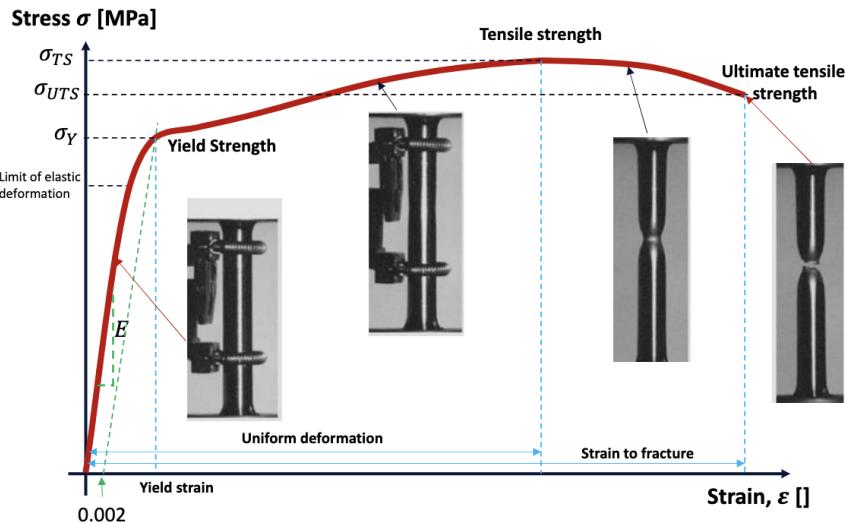


### 10.1 Stress-strain curves

To get an understanding of how materials behave under increasing loads the following will provide a short explanation of a so-called *stress-strain curve* (in this case for steel). The stress-strain curve can be seen on

**Figure 10.2.**

Figure 10.2: Stress-strain curve for steel



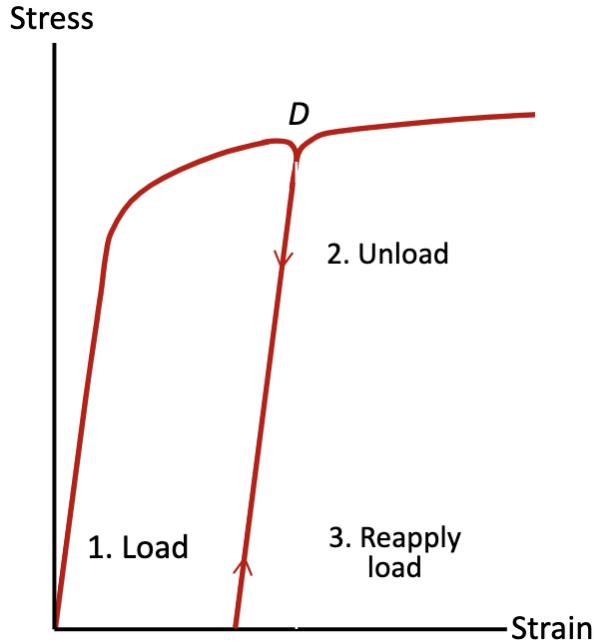
- When the load is applied (and has a relatively low size) the steel undergoes plastic deformation. During this phase of the process the stress increases linearly with the strain with a slope equal to Young's modulus for the material.
- When the stress-strain curve stops being linear we have reached the limit of elastic deformation. Hereafter the material will (in theory) start to deform permanently.
- After increasing the load even more we reach the yield strength which is defined as having *noticeable* deformation even after the stress is removed (this is often defined to 0,2 %). The corresponding stress and strain (without removed load) at this point are known as the *yield strength* and the *yield strain*.
- Hereafter the material will start to heavily deform and the stress-strain curve becomes “flatter”, meaning less stress is required to produce additional strain.
- When the stress-strain curve reaches a maximum the tensile strength has been reached. For metals this point occurs right at the onset of visible “necking” (the metal becomes thinner and thinner around the point it is going to break).
- After passing the tensile strength the stress will actually become lower again before reaching the ultimate tensile strength right at the point of fracture.

## 10.2 Elastic strain recovery and ductility

As mentioned above, a material loaded beyond the elastic limit will start to deform permanently. After removing the load from the material the stress will return to zero along with the elastic strain. The plastic strain, however, will remain. This can actually be used to harden materials through the process of *strain-hardening*. A graph of this is shown on **Figure 10.3**.

The maximum amount of plastic deformation (amount of plastic deformation at failure) of a material is known as the material's *ductility*. Ductility is normally measured in percent elongation or percent reduction in cross-sectional area. A material with high ductility will deform more before breaking than a material with lower ductility.

Figure 10.3: Elastic strain recovery



### 10.3 Resilience

A materials *resilience* is its ability to absorb energy during elastic deformation – in other words it is the area underneath the stress-strain curve from 0 to the yield strain. This also corresponds to the amount of energy released when the load is removed (the potential energy in all the small springs that make up intermolecular bonds). Resilience is given by the *modulus of resilience*,  $U_r$ . If we assume a linear stress-strain curve up till the yield strength we get a strain curve given by

$$\sigma = E\epsilon$$

which simplifies to

$$U_r = \frac{1}{2}\sigma_y\epsilon_y = \frac{\sigma_y^2}{2E}.$$

### 10.4 Toughness

A materials *toughness* is a measurement of its ability to absorb energy before failure – in other words it is equal to the area under the stress-strain curve. Materials with a smaller toughnesses will either break with little strain or strain with little stress – think ceramics (break under small strain) or polymers (strain under small stress). Materials with high toughness will however both require a lot of stress before straining and strain for a long distance before breaking – think many metals.

It should be noted that it is a common misconception that the toughness of a material inherently is related to whether a material is brittle or not. A small toughness does not necessarily mean a material is more brittle (e.g. will many polymers often have low toughness but still not be brittle, as they have the ability to plastically deform).

## 10.5 Hardness

A materials *hardness* is a measure of the materials ability to withstand plastic deformation on its surface – this can be either via indentation or scratches. A large hardness means a material is more resistant to compressive loads and oftentimes a harder material will have better wear properties.

### 10.5.1 Hardness measurements

Hardness is oftentimes measured on the qualitative *Moh's scale*. This scale is determined by a materials ability to scratch another material – in this way the Moh's scale is a comparative scale. The scale goes from 1 (talc) to 10 (diamond) and after making these two definitions one can place all other materials on the scale from 1-10 depending on which other materials a material can scratch.

However, different types of quantitative tests have also been designed to combat the qualitativeness og the Moh's scale. These generally all work by pressing an indenter (with specified material and size) into a sample with a given load before measuring the amount of plastic (permanent) deformation after removing the load. An example of such a quantitative test is the so-called *Brinell Hardness scale*, which gives a hardness reading HB. The Brinell test works by pressing a  $D = 10$  mm sphere of steel or tungsten carbide into the material with a load of  $P$  [kg], which will leave a circular mark with diameter  $d$ . Thereafter the hardness (HB-value) can be found as

$$\text{HB} = \frac{2P}{\pi D(D - \sqrt{D^2 - d^2})}.$$

In general there is a relationship between a materials Brinell hardness (HB) and its tensile strength ( $TS$ ) given by

$$TS \text{ MPa} \approx 3,45 \cdot \text{HB}.$$

Using the *Vicker's microhardness scale* or the *Knoop microhardness scale* instead of the Brinell scale, one would get an HV or HK value respetively. These can be found with

$$\begin{aligned} \text{HV} &= 1,854 \frac{P}{d_1^2} \\ \text{HK} &= 14,2 \frac{P}{l^2}. \end{aligned}$$

*Note:* For the Vicker's scale  $d_1$  is the sidelength of the pyramid-shaped indenter and for Knoop's scale  $l$  is the length of the longest diagonal in the skew-pyramid-shaped indenter.

## 10.6 Variability in materials properties

Material properties always have some inherent randomness – you cannot expect two different lumps of the same material to have exactly the same grain structure and so on. This means that a lump of a given material can have rather different properties. For this reason one needs to use a bit of statistical modelling when trying to measure a property. One can find the typical value,  $\bar{x}$ , by averaging all of ones  $n$  different measurements,  $x_i$ , as

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n}.$$

This can then be used to find the *sample standard deviation*,  $s$ , as

$$s = \sqrt{\frac{\sum(x_i - \bar{x})}{n - 1}}.$$

### 10.6.1 Safety factor

Because of the inherent variability of a material's properties one must compensate for possibly getting a bad material to protect against unexpected failure. This is simply done by using the working stress  $\sigma_w$  instead of the yield strength  $\sigma_y$ . To find this  $\sigma_w$  one must also define a factor of safety  $N$ . Then the formula is

$$\sigma_w = \frac{\sigma_y}{N}.$$

The value of  $N$  is typically between 1.2 and 4 depending on the application.

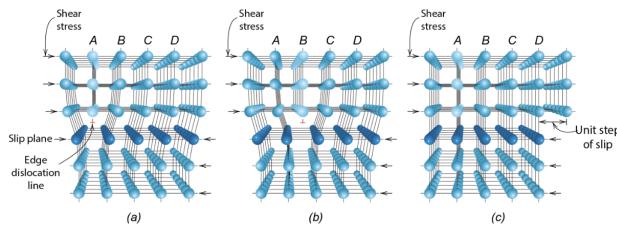
## Lecture 8: Dislocations and strengthening mechanisms

19. Februar 2025

# 11 Slipping

Plastic deformation occurs by motion of dislocations in a process known as *slip*. An applied shear stress can e.g. cause an edge dislocation (half plane of atoms) to move as shown in **Figure 11.1**. During this process,

Figure 11.1: Motion of an edge dislocation due to shear stress



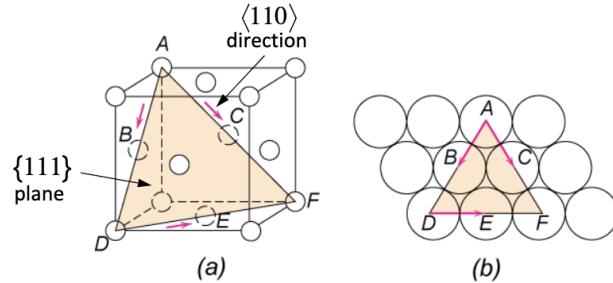
atomic bonds are broken and reformed along the slip plane as the dislocation moves.

### 11.1 Slip systems

A *slip system* is a combination of a *slip plane* and a *slip direction*. A slip plane is a crystallographic plane on which slip occurs most easily – this is the plane with the highest planar density. A slip direction is the crystallographic direction along which slips occur most easily – this is the direction with the highest linear density.

For the FCC crystal structure the slip system is  $\{111\} \langle 110 \rangle$ . This means the dislocation motion is on the  $\{111\}$  plane and in the  $\langle 110 \rangle$  direction. This family of slip systems contains 12 “different” independent slip systems for FCC. The slip system for FCC is shown in **Figure 11.2**. For BCC and HCP other slip systems exist.

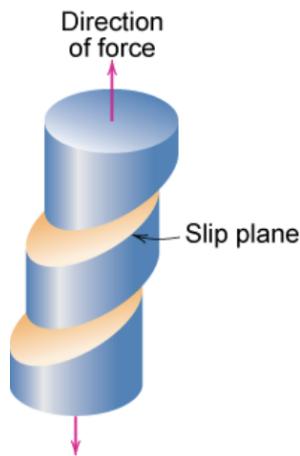
Figure 11.2: Slip system for FCC



## 11.2 Slipping in single crystals

When looking at a single crystal we do not have any grain boundaries. The slipping will happen along the slip planes, which can lead to “stepping”, as a large number of dislocations will move along the same line. This is shown in **Figure 11.3**

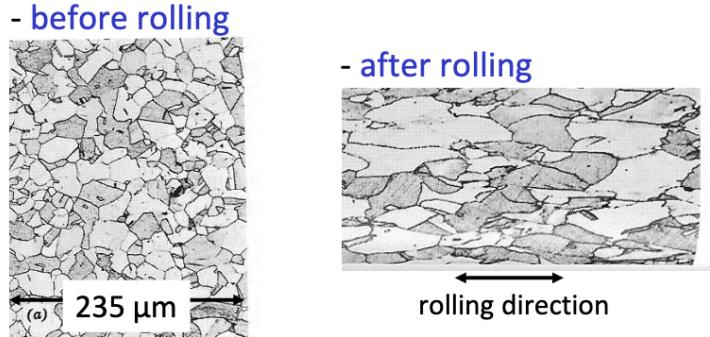
Figure 11.3: Slipping in a single crystal



## 11.3 Slipping in polycrystalline materials

Polycrystalline materials have many grains and with (often) random crystallographic orientation of the grains. The slipping will therefore also happen pretty “randomly” on a microscopic scale, as the system will always slip in the most favourable direction. However, looking at the material macroscopically, one is able to draw some general conclusions. In general, individual grains will become distorted in a manner similar to the gross plastic deformation. On **Figure 11.4** a picture of the grains in a metal is shown before and after rolling – it is easy to see that the grains have become distorted and have expanded in the horizontal direction. After this process, the material will often become somewhat anisotropic as the grains no longer are “equal” in all directions.

Figure 11.4: Distortion of grains due to slipping



## 12 Strengthening mechanisms in metals

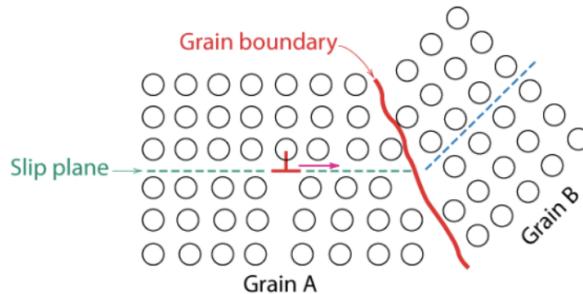
For a metal to plastically deform dislocations must move. The quantities of strength and hardness are related to the mobility of dislocations – if one decreases the dislocation mobility the metal will become stronger/harder and vice versa. All mechanisms for strengthening/hardening metals work by decreasing the mobility of dislocations. In this course we will focus on the following three methods of hardening.

- Grain size reduction
- Solid solution strengthening
- Strain hardening (cold working)

### 12.1 Grain size reduction

Grain boundaries act as barriers of dislocation motion. This is because right at the boundary the slip plane changes direction (see **Figure 12.1**) which makes the slip plane discontinuous and therefore slipping will be inhibited. By reducing the grain size the total area of the grain boundaries will increase which provides more barriers to slipping and thus increasing the hardness and strength of the material.

Figure 12.1: Slip planes across grain boundaries



If ones grains are not too coarse or too fine one can approximate the yield strength of a material using the *Hall-Petch equation*.

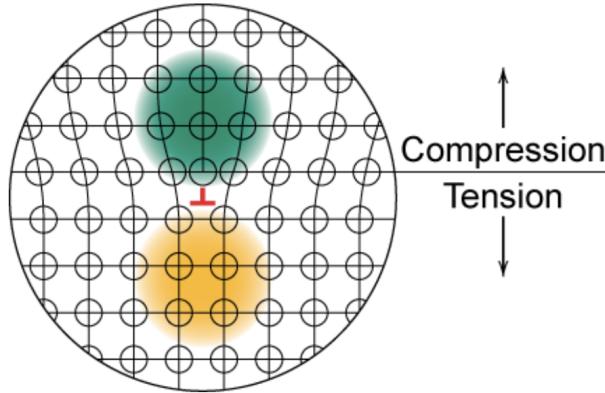
$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}$$

where the constant  $k$  and the “original” yield strength  $\sigma_0$  are material-dependent constants and  $d$  is the average grain diameter.

## 12.2 Solid-solution strengthening

A solid solution occurs when one or more types of solute atoms (impurity atoms) dissolve into a host lattice (the solvent) without forming a separate phase. These solute atoms either occupy the substitutional or interstitial spots in the lattice (see subsubsection 7.2.2 and subsubsection 7.2.3). Substitutional atoms that are smaller than the atoms in the host lattice produce tensile strain and vice versa. Interstitial atoms (like carbon in iron) produce significant lattice distortions because they sit in the spaces between host atoms, pushing them apart and generally creating compressive strain fields around themselves.

Figure 12.2: Tensile and compressive strains around an edge dislocation



Around dislocations the lattice structure is strained. On **Figure 12.2** is an illustration of the tensile and compressive strains around an edge dislocation. Dislocations carry around these strain fields. If a solute atom also introduces a strain in the lattice, the interaction between the solute atom’s strain field and the dislocation’s strain field can either:

- Reduce the overall strain energy if they have opposite “signs” (e.g., a solute that produces tensile strain is attracted to a region of compressive strain around the dislocation).
- Increase the strain energy if they have the same sign (e.g., both produce compressive strain).

But because nature tends to minimize energy, a solute atom will be attracted to the region of the lattice around a dislocation that best accommodates (i.e., partially cancels) its own strain. In this way, the solute atoms sort of “pin” the dislocations because they want to maintain the minimized strain energy – if the dislocations start moving the solute atoms will also want to move but moving a solute atom is much harder than moving a dislocation.

In general, introducing more solute atoms (up to a solubility limit) increases the strength and hardness of the metal even more. A mathematical empirical relationship for the yield stress in a solid solution is

$$\sigma_y = \sigma_0 + kC^n$$

where  $\sigma_0$  is the yield strength of the pure metal,  $C$  is the solute concentration, and  $k$  and  $n$  are constants that depend on the specific alloy system. It should be stressed that the above expression only is empirical and it should mostly be used to get an idea of how the effect changes with changing amounts of solute.

### 12.3 Strain hardening (Cold working)

Strain hardening is the process of plastically deforming a metal at a temperature below the metals recrystallization temperature (you often just use room-temperature for most metals), which in turn makes the metal stronger. This deformation often reduces the cross-sectional area of the metal (e.g. a metal sheet will become thinner when rolled).

As you deform a metal you will increase the dislocation density as new dislocations are formed and already existing dislocations multiply (can go from  $10^6$  -  $10^8$  dislocations/m<sup>2</sup> in an annealed metal to  $10^{10}$  -  $10^{12}$  dislocations/m<sup>2</sup> in a metal that has undergone significant cold working). When many dislocations are present at once they will start to interact with each other and entangle. Along the same line of thought as in **subsection 12.2** these dislocations will try to organize themselves in a way that minimizes energy. When the dislocations start to entangle they also “pin” each other in place as moving through another dislocation or too close to another dislocation introduces significant lattice strain.

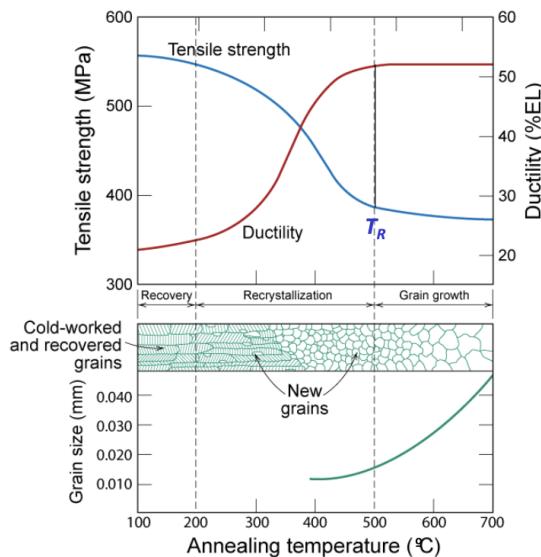
The degree of strain hardening is measured in %CW (percent cold work) which is a way to quantify the amount of plastic deformation introduced. This is

$$\%CW = \frac{A_0 - A_d}{A_0} \times 100\%$$

where  $A_0$  is the original cross section of the metal and  $A_d$  is the cross section of the metal after deformation. A higher %CW means there is a higher dislocation density and therefore that the metal is stronger.

If one chooses to heat treat a strain hardened metal one changes the structure of the cold worked metal. More precisely, if a strain hardened metal is heated to a temperature above its recrystallization temperature (a process known as annealing) the dislocation density will fall and the metal will become more and more like it was before strain hardening. This is shown in **Figure 12.3**, where the effect of cold working is almost completely gone in the “grain growth” part of the annealing diagram.

Figure 12.3: Effect of annealing on temperature



**Lecture 9: Failure Mechanisms, pt. 1: Static Loading and Fracture** 24. Februar 2025

## 13 Fundamentals of Fracture

**Discussion 13.1:** Cite two situations in which the possibility of failure is part of the design of a component or product

Lots of products are made in such a way that them failing is central to their function. Examples include:

- Electrical fuses
- Pull tabs on soda cans
- The metal fencing between driveways in opposite directions on highways
- Many sprinkler systems inside homes
- and much more

Before delwing into a discussion about fracturing it is very important to have some basic definitions in place.

**Definition 15: Fracture**

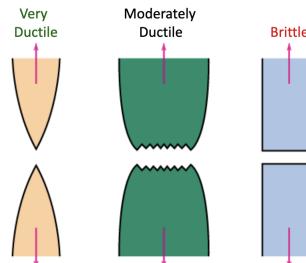
A *fracture* is the separation of a body into two or more pieces in response to a stress. A fracture can either be *cohesive*, if the fracture happens within the material itself or *adhesive* if it happens at the intersection between two materials or phases.

In general there are two types of fractures. These are split into

**Definition 16: Ductile fractures**

A *ductile fracture* is characterized by rather slow crack propagation and ductile fracturing is accompanied by significant plastic deformation – It *fails with warning* so to say. For examples of this please refer to **Figures 13.1 to 13.3**.

Figure 13.1: Fracture profiles for 3 different materials ranging from *Very Ductile* to *Brittle*



**Definition 17: Brittle fractures**

A *brittle fracture* is characterized by very rapid crack propagation – often in the order of the speed of sound. Brittle fracturing happens with little or no plastic deformation at all – It “fails without warning” so to say. For examples of this please refer to **Figures 13.1 to 13.3**.

In general ductile fracturing is more desirable than brittle fracturing but it of course depends on the application.



Figure 13.2: Fracture surfaces for a *moderately ductile* and a *totally brittle* material.

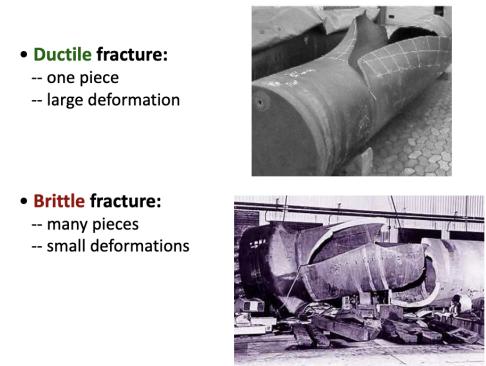


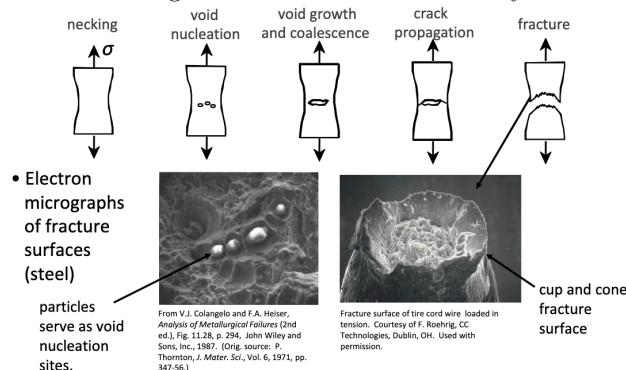
Figure 13.3: *Ductile* and *brittle* fracturing in pipes.

The *cup-and-cone* fracture as seen on **Figure 13.2** is a rather characteristic fracture type for moderately ductile materials. In general the process of a moderately ductile fracture are

- 1. Necking:** When a moderately ductile material is exposed to a strong tensile stress it will start to *neck*, meaning it will start to get smaller (plastically deform) around the part of the sample that is later going to break.
- 2. Void nucleation:** Within the necked region, microscopic voids will start to form. These voids often originate at imperfections, such as inclusions or second-phase particles, which act as stress concentrators. To see this please refer to **Figure 13.4**.
- 3. Void growth and coalescence:** As deformation continues, these nucleated voids grow in size. Eventually, adjacent voids merge (coalesce) forming microcracks within the material.
- 4. Crack propagation and Fracture:** Once a critical level of void coalescence is reached, a crack begins to propagate rapidly through the material, leading to separation into two or more pieces.

All of these stages are shown graphically on **Figure 13.4**.

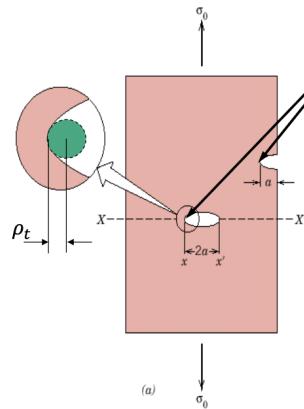
Figure 13.4: The stages of fracture of a moderately ductile material



## 14 Failure Mechanics

Both the Titanic and many of the so-called Liberty ships built in the second world war failed in a brittle manner. This stands in sharp contrast to the ductility of steel one had found in tension tests in laboratories. It was for a long time a mystery why so many ships were suddenly becoming brittle rather than ductile and it took quite a while until we figured out that steel becomes brittle under the so-called *ductile-brittle transition temperature*. This real-life example highlights the importance of understanding fracture mechanics and gaining an understanding about how the use-case of a material might affect its properties. In short, the measured fracture strength of materials is lower than that predicted by theory. This is due to inherent flaws (in the form of microscopic cracks) in the material. These cracks act as stress-amplifiers as an applied stress will become many times bigger in magnitude around these cracks. This is shown on **Figure 14.1**.

Figure 14.1: Concentration of stress around flaws



### 14.1 Stress concentration

We are actually able to form a mathematical expression for the amount of stress measured exactly at the tip of the flaw ( $\sigma_m$ ) just using the dimensions shown in **Figure 14.1**. This is

$$\sigma_m = 2\sigma_0 \sqrt{\frac{a}{\rho_t}}$$

where  $\sigma_0$  is the applied bulk stress,  $\rho_t$  is the radius of curvature of the tip of the flaw and  $a$  is the half length of the elliptical (or crack-like) flaw. Thus even a small crack with a very sharp tip can amplify the stress many times. Analog to this we can define the *stress concentration factor*  $K_t$ , as the ratio of the peak stress at the crack/hole boundary  $\sigma_m$  to the nominal far-field stress  $\sigma_0$ :

$$K_t = \frac{\sigma_m}{\sigma_0}.$$

In real life the amplified stress is not only concentrated at the tip or edge of the defect but but most of the additional stress will be seen in an area very close to the defect as seen on **Figure 14.2**. The amplification of stress at edges of defects is also the reason that samples with sharp corners tend to fail more easily than samples with filleted edges. The effect of material dimensions and the corresponding change in strength is shown on **Figure 14.3**.

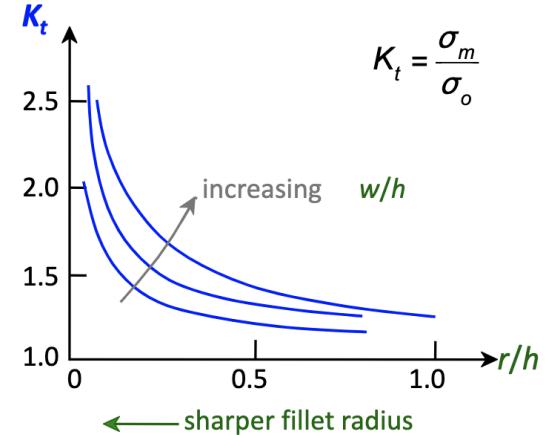
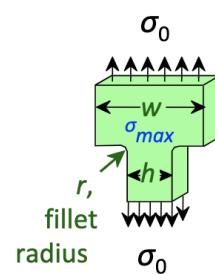
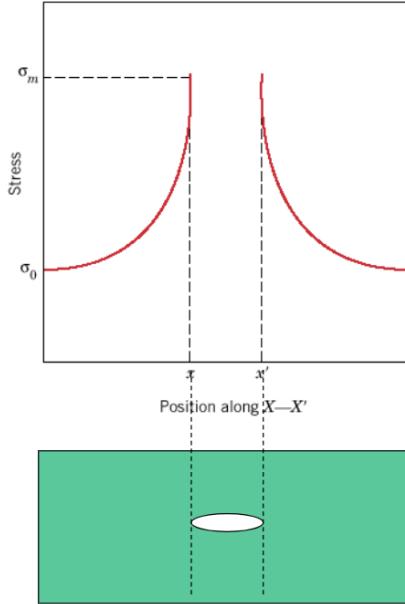


Figure 14.3: Implication of dimensions on fracture properties

Figure 14.2: Increase in stress concentration close to the edges of defects

## 14.2 Crack propagation

As explained in **subsection 14.1** an applied external stress is concentrated and amplified at the edges of cracks, defects or other imperfections. Sharper edges of these imperfections leads to more amplification of the applied stress and if the edges are too sharp or the bulk stress is too high the cracks will start to expand and propagate. Ductile materials will experience this effect to a lesser degree than an otherwise similar but ductile material as the ductile material will deform around the edges of the imperfections in such a way that it minimizes the stress (in this case the edge of the crack will deform and become more blunt).

Assuming you are working with a brittle material it is possible to determine the critical stress for crack propagation  $\sigma_c$  as

$$\sigma_c = \sqrt{\frac{2E\gamma_s}{\pi a}}$$

Where  $E$  is Young's modulus,  $\gamma_s$  is the specific surface energy and  $a$  is the half length of an internal crack. For brittle materials the specific surface energy  $\gamma_s$  should be replaced with  $\gamma_s + \gamma_p$  where  $\gamma_p$  is the plastic deformation energy. It is important to note that materials have numerous crack with different lengths and orientations. Crack propagation (and fracture) occurs when  $\sigma_m > \sigma_c$  for the crack with the lowest  $\sigma_c$  – this also means that the largest and most stressed cracks will grow first.

## 15 Fracture Toughness

The *fracture toughness* of a material is a measure of its resistance to brittle fracture when a crack is present. The fracture toughness is defined as

$$K_{Ic} = Y\sigma_c\sqrt{\pi a}.$$

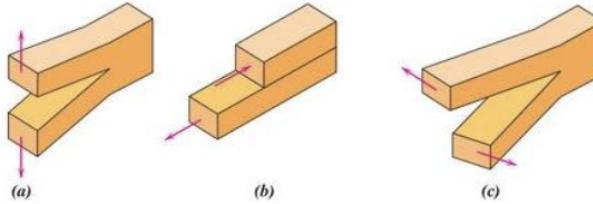
Where  $Y$  is a dimensionless parameter often written as  $f(a/W)$  which accounts for the specimen's geometry and the crack's position,  $\sigma_c$  is the critical stress for crack propagation and  $a$  is the crack length. The fracture toughness  $K_c$  is essentially the critical stress intensity beyond which a crack will rapidly propagate.

### 15.1 Fracture modes

Fractures can be split loosely into 3 categories:

1. **Opening/Tensile Mode:** The crack faces are pulled apart directly away from each other. This is the most common (and often most severe) mode, where the crack “opens up” under tensile stress. This is the mode labelled (a) on **Figure 15.1**.
2. **Sliding/In-Plane Shear Mode:** The load is applied parallel to the crack front, causing the two crack faces to slide relative to each other in the plane of the crack. This is the mode labelled (b) in **Figure 15.1**.
3. **Tearing/Anti-Plane Shear Mode:** The load is, again, parallel to the crack front, but in a direction out of the crack plane. You can think of one crack face “twisting” relative to the other. This is the mode labelled (c) in **Figure 15.1**.

Figure 15.1: The three main fracture modes



## 16 Design Implications

The above considerations can be summarised in the so-called *crack growth condition*:

$$K_{Ic} < Y\sigma_c\sqrt{\pi a}.$$

This can then be used in some different ways. For example

- If you are given the materials fracture toughness  $K_{Ic}$  and the flaw size  $a$  you are able to find the maximum design (critical) stress as

$$\sigma_c = \frac{K_{Ic}}{Y\sqrt{\pi a}}.$$

- If you know the fracture toughness of the material  $K_{Ic}$  and the applied stress  $\sigma$  you can find the maximum allowable flaw size as

$$a_c = \frac{1}{\pi} \left( \frac{K_{Ic}}{Y\sigma} \right)^2.$$

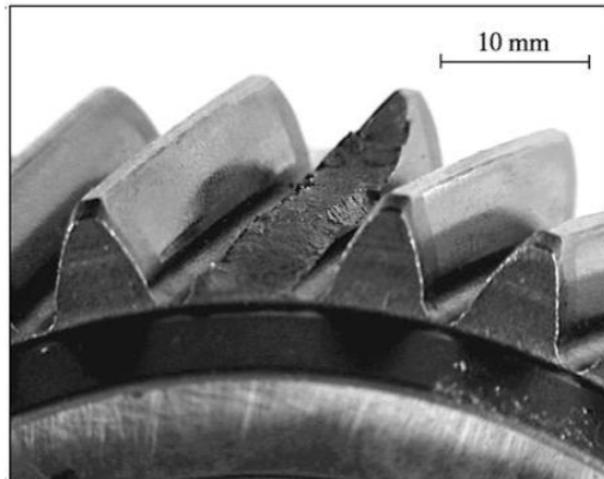
## 17 Fatigue

### Definition 18: Fatigue

*Fatigue* is a form of failure that occurs in materials subjected to cyclic (repeated) stress over an extended period. Even if the peak stress in each cycle is below the yield strength cracks will gradually initiate and propagate until sudden fracture occurs. In this way fatigue is not about one-time overloading but rather a cumulative effect of repeated (often variable) stresses that eventually lead to crack growth and failure.

The typical mechanism for a fatigue failure like explained above is that sharp edges of cracks or other defects act as stress concentrators and as such relatively small stresses are required to start growing the cracks that amplify the stress the most. When these cracks start growing they will accelerate in growth speed and at some point these cracks reach a critical size where the cross-section of the uncracked metal can no longer sustain the load and sudden fracture occurs. This is the case for the fractured gear on **Figure 17.1**.

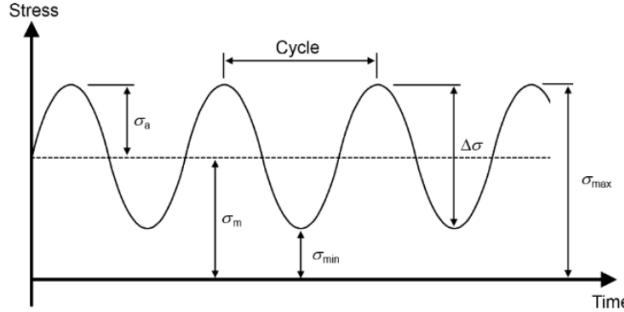
Figure 17.1: Gear fractured due to fatigue



### 17.1 Rotating bending test

To test how a material behaves under cyclic loading (the type of loading that produces fatigue) you often employ a *rotating bending test* where a cylindrical specimen is clamped at both ends and rotated by a motor. The test specimen will also be pulled down by a fixed load. As the specimen rotates different parts of the outer surface of the test specimen will be in compression and tension due to the bending load. This makes one able to standardize the test by fixing the rpm and or amount of rev's such that one can compare the fatigue data from the test across different materials. The cycle of such a test is often sinusoidal like shown in **Figure 17.2**. This also means it is rather easy to calculate the mean stress  $\sigma_m$ , the stress range  $\sigma_r$ , the

Figure 17.2: Sinusoidal behaviour of fatigue tests



stress amplitude  $\sigma_a$  and the stress ratio  $R$  as

$$\sigma_m = \frac{\sigma_{\max} - \sigma_{\min}}{2}$$

$$\sigma_r = \sigma_{\max} - \sigma_{\min}$$

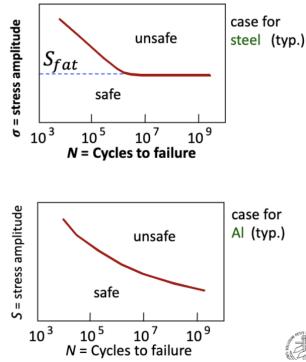
$$\sigma_a = \frac{\sigma_r}{2} = \frac{\sigma_{\max} - \sigma_{\min}}{2}$$

$$R = \frac{\sigma_{\min}}{\sigma_{\max}}.$$

## 17.2 S-N Curves

The data from e.g. a rotating bending test is often plotted on an  $S \log N$ -plot (an SN curve) as shown on **Figure 17.3**. These curves generally look pretty alike for most materials (plus minus some scaling of

Figure 17.3: SN curve for steel and Al



course), however, there is one point where materials can differ – namely in terms of the fatigue limit  $S_{\text{fat}}$ . Not all materials have a fatigue limit (I believe most do not) but for the materials that do have a fatigue limit fatigue will not accumulate if the applied stress is smaller than the fatigue limit. That is there will be no stress accumulation for  $\sigma < S_{\text{fat}}$ . This is the case for e.g. steel, whereas aluminum does not have a fatigue limit and it will therefore accumulate fatigue even for very small applied stresses.

Based on the results from e.g. the rotating bending test a so-called *fatigue limit*  $N_f$  can also be calculated. The fatigue limit refers to the total number of stress cycles to cause fatigue failure at a specified stress amplitude.

### 17.3 Improving fatigue life

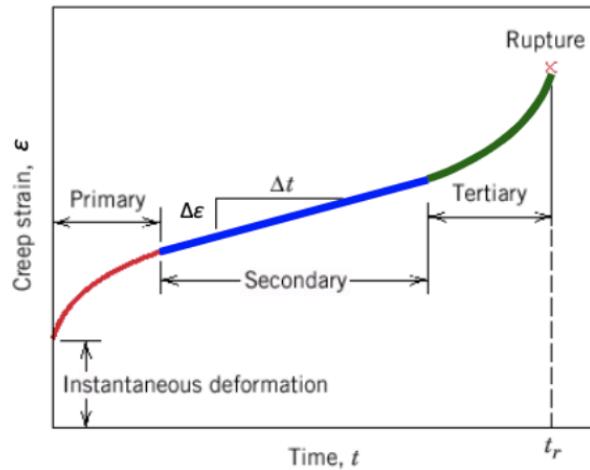
There are three main techniques to enhance the fatigue life of a component

- **Reducing the magnitude of mean stress:** This is the obvious answer, of course if you want your material to have a longer lifetime you should stress it less.
- **Surface treatments:** Fatigue cracks often initiate at or near the surface, so introducing compressive residual stresses at the surface can help prevent or delay crack initiation. This can be done in many ways. Two popular methods work by either shot peening where hard spheres are blasted into the surface of the material which creates compressive stresses due to plastic deformation or by carburizing where C-atoms are diffused into the surface layer of the material (creating compressive stresses and hardening the surface).
- **Design changes:** By eliminating sharp corners and other stress concentrators you can also improve the lifespan of your material.

## 18 Creep

Creep is (on top of the name of a hit radio single by Radiohead) a measurement of the deformation (strain) vs. time at a constant stress. Simply put, if you apply a constant stress to something it will deform a bit initially but if you do not remove the stress immediately again the material will start to *creep* and deform (strain) even more even if not changing the applied stress.

Figure 18.1: The three stages of creep



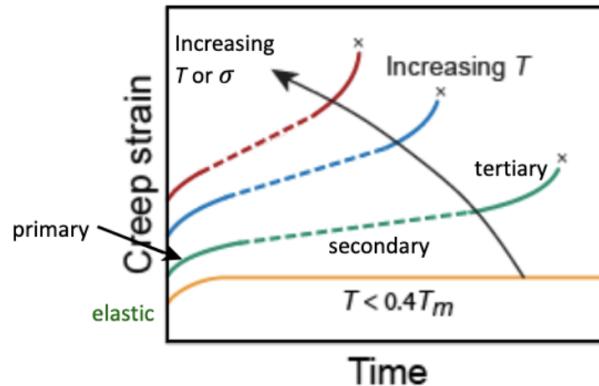
Creep generally happens in three phases

- **Primary creep:** The first phase. Here the creep rate (slope of creep strain vs. time plot) is decreasing with time (creeps a lot at the start and then “settles in”)
- **Secondary creep:** The second phase. Here the creep is steady-state, meaning the creep rate is increasing linearly with time, i.e.  $\frac{\Delta\epsilon}{\Delta t} = \text{const.}$

- **Tertiary creep:** The third phase. Here the creep rate starts accelerating until fracture happens.

The above three phases are also shown on **Figure 18.1**. The steady state creep rate  $\dot{\epsilon}_s$  (secondary phase creep rate) increases with increasing temperature  $T$  or stress  $\sigma$ . Parallel to this is that the rupture lifetime  $t_r$  (the amount of time until rupture with a constant stress) decreases with increasing temperature  $T$  and stress  $\sigma$ . This is shown in **Figure 18.2**.

Figure 18.2: The temperature dependence of creep



## 18.1 Steady-state creep

The steady-state creep rate  $\dot{\epsilon}_s$  (secondary phase creep) is constant for constant temperature  $T$  and stress  $\sigma$ . The steady-state creep rate  $\dot{\epsilon}_s$  can be calculated as

$$\dot{\epsilon}_s = K_2 \sigma^n e^{-\frac{Q_c}{RT}}.$$

Where  $K_2$  is a material constant,  $Q_c$  is the activation energy for creep,  $R$  is the universal gas constant and the stress exponent  $n$  is a material parameter. The equation can also be written as

$$\dot{\epsilon}_s = K_1 \sigma^n.$$

Where  $K_1$  and  $n$  are material parameters.

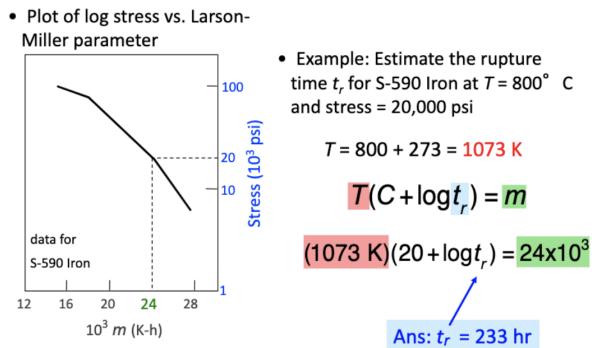
## 18.2 Creep life time

The time to rupture  $t_r$  is a measurement of the amount of time a specimen can handle a given (constant) load before rupturing. It is difficult to gather creep data for a prolonged time (e.g. years) and instead you extrapolate from data collected for a shorter time at higher  $T$  using the Larson-Miller parameter  $m$ , defined as

$$T(C + \log t_r) = m.$$

Where  $T$  is the temperature,  $C$  is a constant (normally  $\approx 20$ ,  $t_r$  is the time to rupture and the Larson-Miller parameter  $m$  is a function of the applied stress. An example of how this can be used is shown in **Figure 18.3**.

Figure 18.3: Example of how to calculate the creep life time using the Larson-Miller parameter



Lecture 11: Introduction to Polymer Science – By guest-lecturer Simon Mckie 3. Marts 2025

## 19 Polymer Chemistry

Polymers are long chains of covalently bonded monomers. The interactions between these polymers define the characteristics of the polymer. Two common monomers you will find in nature is cellulose (fibers in plants and grasses) and isoprene (found in the sap of rubber trees). The same monomers does not necessarily give the same properties of the polymer – e.g. nitrocellulose and camfer makes billiard balls whereas nitrocellulose and octasulfur gives tire-rubber.

The process of converting a bunch of monomers into polymers one must normally let the monomers be in a high-temperature high-pressure environment for the reaction to occur.

### Definition 19: Polymer

A polymer is the main ingredient in *plastics*. Polymers are long chains of monomers (small “unit”-atoms). The word “polymer” comes from greek *polús* meaning “many” and greek *mérōs* meaning “parts”. Plastics are made up of polymers and additives.

To make ABS – such as at LEGO. One needs to combine the monomers of *acrylonitrile*, *butadiene*, and *styrene*. To make polyethylene you just need the monomer “ethylene”.

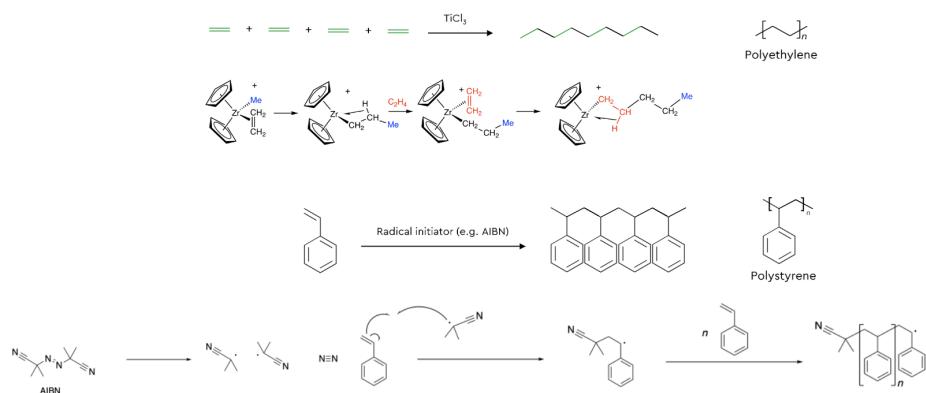
### 19.1 Polymerisation

To make plastics, one needs to polymerize some monomers, as mentioned above. There is broadly two types of polymerisation, i.e. addition and condensation polymerisation.

#### 19.1.1 Addition polymerisation

On **Figure 19.1** two different addition polymerisations are shown. These are all characterized by an addition reaction being the main reaction type driving the polymerisation.

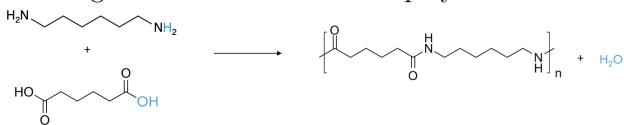
Figure 19.1: Two different addition polymerisations



### 19.1.2 Condensation polymerisation

On **Figure 19.2** a condensation polymerisation is shown. These are characterized by condensation reactions and therefore small amounts of additional “product” is made during the reaction – this can be but is not necessarily water.

Figure 19.2: A condensation polymerisation



## 19.2 Polymer lengths and length distribution

There are a few definitions that we need to get under our belt before continuing.

### Definition 20: Average molecular weight

The average molecular weight in a polymer is the average mass of the polymer chains.

### Definition 21: Molecular weight distribution

The molecular weight distribution is how the molecular weights of the polymer chains are distributed.

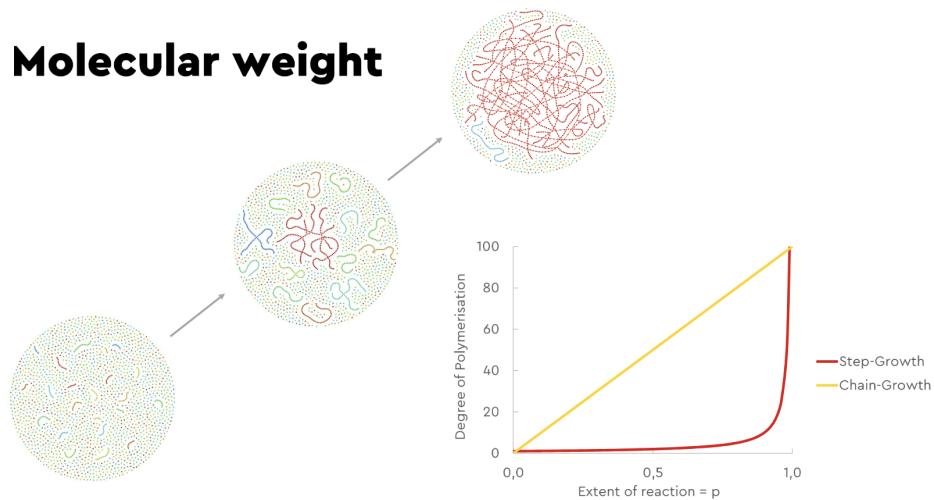
### Definition 22: Degree of polymerisation

The degree of polymerisation is a measurement for the number of monomeric units in the polymer chains.

### 19.2.1 Molecular weight and reaction speed

On **Figure 19.3** the difference in reaction speed between the step growth type polymerisation and chain-growth polymerisation.

Figure 19.3: Difference between step-growth and chain-growth



### 19.2.2 Molecular weight distribution

When polymerising a bunch of monomers you cannot expect all monomers to react exactly the same. Instead one might imagine a normally-distributed mass-distribution around some average value. This is shown on **Figure 19.4** and **Figure 19.5** (the molecular weight of the monomer is around 28 g/mol in this case). The difference between **Figure 19.4** and **Figure 19.5** is that on **Figure 19.4** the “number average” molecular weight has been found using the formula

$$M_n = \sum x_i M_i$$

whereas the “weight average” molecular weight on **Figure 19.5** has been found using

$$M_w = \sum w_i M_i.$$

These are in many ways equivalent, although the weight average will be skewed towards heavier molecules compared to the number average.

The relationship between the number average molecular weight and the weight average molecular weight is given by the index of dispersity, PDI (disperisty factor). This is given by

$$\text{PDI} = \frac{M_w}{M_n}.$$

Figure 19.4: Number average molecular weight distribution

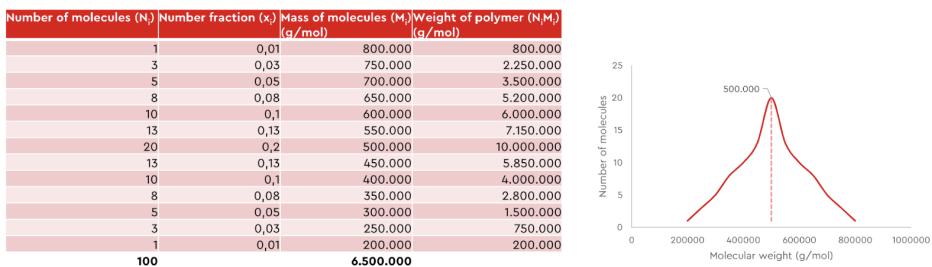


Figure 19.5: Weight average molecular weight distribution



### 19.2.3 Degree of polymerisation

The degree of polymerisation can simply be found as

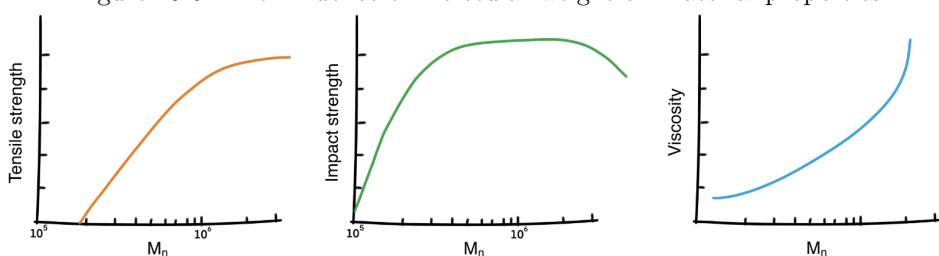
$$\frac{M_n}{M_0}$$

where  $M_0$  is the molecular weight of the monomer.

### 19.2.4 Material properties and molecular weight

In general the tensile strength, impact strength and viscosity are all increasing for increasing molecular weights. This is shown on **Figure 19.6**.

Figure 19.6: The influence of molecular weight on material properties



**Example: Index of dispersity and molecular weights**

We want to determine the degree of polymerisation in a sample of polyethylene with a mass-average molecular mass of 196 400 g/mol. We know that  $\text{PDI} \leq 1,2$ .

To start we use the dispersity to calculate the number average molecular mass as

$$\begin{aligned}\text{PDI} &= \frac{M_w}{M_n} \\ M_n &= \frac{M_w}{\text{PDI}} \\ &= \frac{196\,400 \frac{\text{g}}{\text{mol}}}{1,2} \\ &= 163\,666,66 \frac{\text{g}}{\text{mol}}.\end{aligned}$$

We can now find the degree of polymerisation as

$$\begin{aligned}\text{deg. polym.} &= \frac{M_n}{M_0} \\ &= \frac{163\,666,66 \frac{\text{g}}{\text{mol}}}{28,06 \frac{\text{g}}{\text{mol}}} \\ &= 5832,7.\end{aligned}$$

### 19.3 Mixing polymers

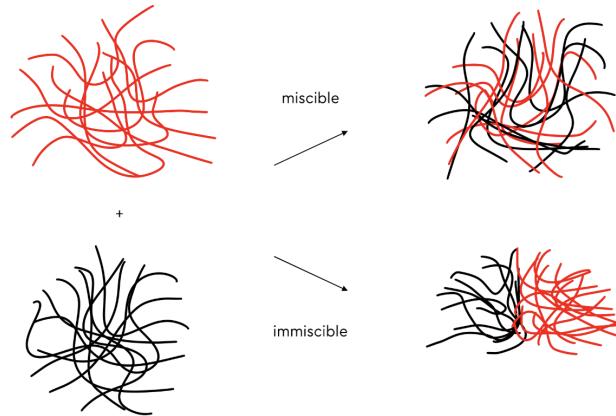
Until now we have only focused on polymers consisting of only one polymer. A *blend* or a *compound* is a mixture between two or more polymers. Long large macromolecules have a rather low entropy and therefore blending two polymers is thermodynamically often rather hard (as the Gibbs free energy is not negative for low entropy) – but sometimes it can give desired effects. Blends or compounds are also often known as *co-polymers*.

When mixing two polymers they can either be miscible (rare) or immiscible (common) as shown on **Figure 19.7**. To combat this one can add an emulsifier or an “emulsifying polymer” to help with the blending. An example of the “emulsifying polymer” described above is used when mixing polybutadiene and styrene acrylonitrile to make ABS. These are normally immiscible and therefore something must be done for the two polymers to mix and not just form a two-phase mix. What is done in practise is that one can “graft” styrene acrylonitrile chains to the polymer chain of polybutadiene chemically. This means that the acrylonitrile and the polybutadiene are bonded together chemically and the acrylonitrile polymers can now grow from the grafted “nucleation points”.

## 20 Polymer Processing and Conversion

When wanting to make a polymer you typically start with oil, which you refine into monomers and then polymerize into polymers. For condensation polymerisation one needs to keep in mind, that it is an equilibrium reaction – therefore it is important to drive off the biproduct formed during the reaction (e.g. with a vacuum to suck away water). This however is not only a bad thing. The fact that the reaction is reversible means that one can break down the polymers in a condensation polymer by adding the biproduct back again

Figure 19.7: Miscible and immiscible polymers



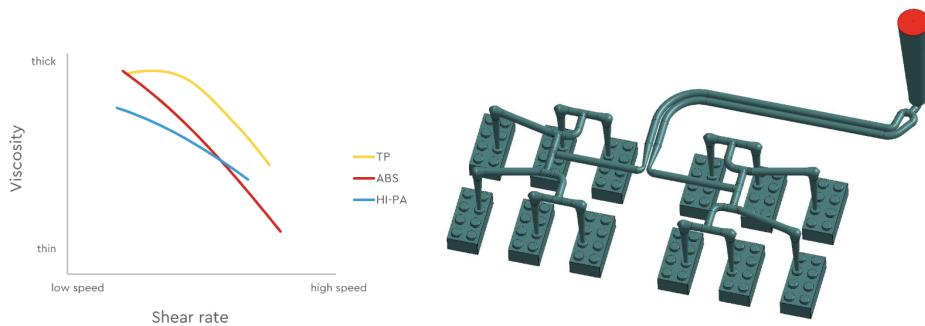
and this way one can recycle used condensation polymers easier than addition polymers.

#### Definition 23: Glass transition temperature

The *glass transition temperature* is the equivalent of a melting point for an amorphous material.

Polymers are (often) non-newtonian meaning that their viscosity changes with the flow speed – polymers are shear thinning, meaning that the more you shear (the faster you try to make it flow) the thinner the polymer will become. This is shown on **Figure 20.1**. This happens because the high temperature decreases the influence of e.g. Van der Waals-interactions between the polymer chains.

Figure 20.1: Shear thinning of polymers



## Lecture 12: Composites, Pt. 1 – Materials and general rules

5. Marts 2025

# 21 Composites

The following lectures are going to be focused on composites.

### Definition 24: Composites

A *composite* is a combination of two or more individual materials. The hope of combining materials like this is that the combined properties of the material fit better for the desired use case than either of the individual materials would individually.

Composites are used in a wide range of materials. E.g. polymer based carbon fiber is used in the fields of:

- Acoustics
- Textile and Paper industry
- Aerospace and Aircraft industry
- Portable power sources
- Energy production
- Sports equipment
- Civil engineering
- Automotive industry

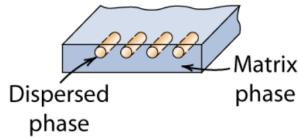
## 21.1 The architecture of composites

A composite can be thought of as an artificially made (as composites do not exist in nature) multiphase material. The phases in a composite are normally split into the two categories:

- **Matrix:** The continuous phase
- **Dispersed:** Is discontinuous and surrounded by the matrix

These two different phases that exist in all composites are shown on **Figure 21.1**.

Figure 21.1: The architecture of a composite

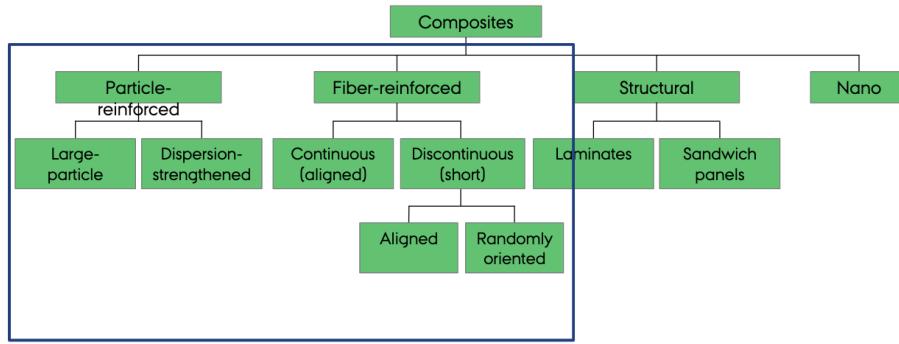


The purpose of the matrix phase is to transfer stress to the dispersed phase and generally protect the dispersed phase from the environment. These mainly come as either metals (MMC), ceramics (CMC) or polymers (PMC). The dispersed phase is normally either made of particles or fibers (although it is sometimes made from structural components such as sandwich panels or nanoparticles as well) and its purpose depends a bit on the type of matrix:

- MMC: The purpose of the dispersed phase is often to increase the yield strength  $\sigma_y$ , increase the creep resistance and to increase the tensile strength.

- CMC: The purpose of the dispersed phase is often to boost fracture toughness  $K_{Ic}$
- PMC: The purpose of the dispersed phase if to enhance stiffness  $E$ , yield strength  $\sigma_y$  and creep resistance.

Figure 21.2: Classification of composites with the part mentioned in this lecture encased in a blue rectangle.

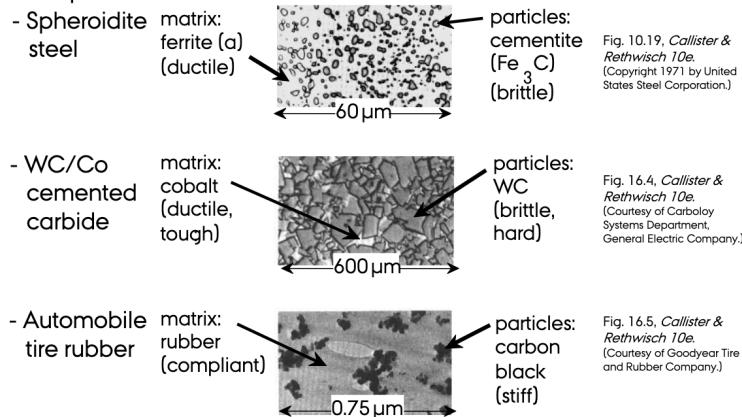


On **Figure 21.2** the most common way to classify composites is shown. This lecture will focus on particle- and fiber-reinforced composites (the part encased in the blue rectangle).

## 21.2 Particle-reinforced composites

On **Figure 21.3** three examples of particle reinforced composites in common usage are shown. The top

Figure 21.3: Examples of particle reinforced composites



picture is of Spheroidite steel. In spheroidite steel the matrix is ferrite (which is relatively ductile) and the dispersed phase is particles of cementite ( $\text{Fe}_3\text{C}$ ; which is hard and brittle). Here the cementite particles strengthen the steel, while the ferrite matrix provides overall toughness.

The second picture is of WC/Co (Tungsten Carbide in Cobalt). Here the matrix is made of cobalt, which is a ductile and tough metal. The dispersed phase is particles of tungsten carbide, which is extremely hard and brittle. The Tungsten Carbide provides high hardness and wear resistance, whilst the Cobalt helps the material retain some toughness. This mixture is a part of a larger group of “cemented carbides” which are commonly used for cutting tools and other high-wear applications. The last picture is of Automobile Tire

Rubber. In this case, the matrix is rubber, which is compliant and elastic. The dispersed phase consists of particles of carbon black which is stiff and enhances wear resistance and mechanical strength.

Common for all the three above examples is that the *matrix* phase is generally more ductile or compliant, while the *particles* are stiffer or harder. This is true for most composites.

### 21.2.1 Elastic modulus of Particle-Reinforced Composites

To predict an overall elastic modulus for a composite material  $E_c$  two extreme bounds known as *rules of mixture* are commonly used.

**Voigt Model (Upper Bound)** The Voigt model assumes that both of the phases in the material experience equal strain (i.e. they elongate the same under load). This is typically thought of as the “best case” scenario for stiffness. The predicted stiffness from the Voigt model can be found as

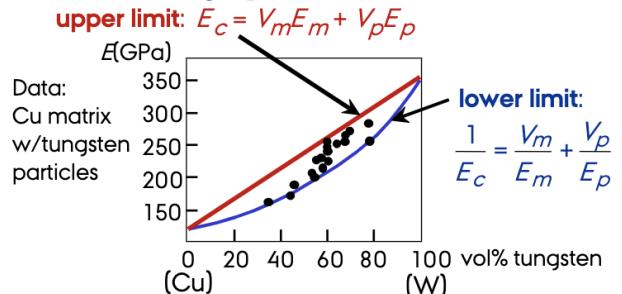
$$E_c = V_m E_m + V_p E_p.$$

**Reuss Model (Lower Bound)** The Reuss model assumes that both of the phases in the composite experience the same stress under a load (also called the *isostress condition*). This represents the “worst-case” scenario for stiffness and the predicted stiffness can be calculated as

$$\frac{1}{E_c} = \frac{V_m}{E_m} + \frac{V_p}{E_p}.$$

Real composites typically fall between these two bounds as shown on **Figure 21.4**.

Figure 21.4: Determining a predicted elastic modulus of a composite



## 21.3 Fiber-reinforced composites

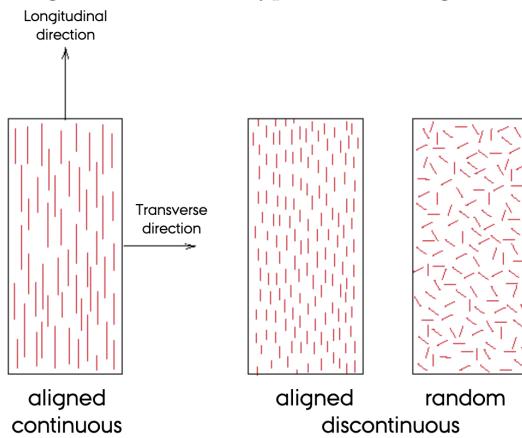
Fibers are very strong in tension and are therefore often used in composites – This can provide a significant strength-boost to the composite. A few different fiber types are in common use these include (but are not limited to):

- **Whiskers:** Extremely strong single crystals (e.g. silicon carbide, silicon nitride, or graphite). These crystals have high crystal perfection and are therefore extremely strong but also expensive and they can be difficult to disperse.

- **Fibers:** Usually polycrystalline or amorphous (e.g. alumina, aramid, boron, UHMWPE) polymers or ceramics. These are typically used in polymer-matrix composites.
- **Wires:** Metallic wires (e.g. steel, tungsten) can be used where high temperature or electrical conductivity is important.

### 21.3.1 Fiber alignment

Figure 21.5: Three types of fiber alignment



In general three types of fiber alignment are in use. These are shown on **Figure 21.5**. If you use continuous (long) fibers these are typically aligned within the matrix. This gives great strength and stiffness when the load is parallel to the fibers but very low strength in the direction transverse to the fibers as the fibers do not carry load effectively sideways.

If you instead use discontinuous (short) fibers you can choose to either align these or have them in random directions. When aligned some of the benefits from the continuous fibers are retained. When random the properties of the material are more isotropic (similar in all directions) but the composite does not reach the same peak strength as aligned fibers.

### 21.3.2 Critical fiber length

For effective stiffening and strengthening the fiber length in the composite should surpass the critical fiber length  $l_c$  given by

$$l_c = \frac{\sigma_f d}{2\tau_c}$$

Where  $\sigma_f$  is the ultimate tensile strength of the fibers,  $d$  is the fiber diameter and  $\tau_c$  is the shear-strength of the fiber-matrix interface. This is a result of the fact that longer fibers transfer the stress from the matrix much more efficiently than short fibers.

### 21.3.3 Estimating the elastic modulus and strength for fiber reinforced composites

For continuous and aligned fibers it is reasonable to assume that the fibers and the matrix experience the same strain (isostrain; Voigt model). That is

$$\sigma_c = \sigma_m V_m + \sigma_f V_f \quad \text{and} \quad \epsilon_c = \epsilon_m = \epsilon_f.$$

These can be combined to find the longitudinal modulus for a composite with continuous fibers as

$$E_{cl} = E_m V_m + E_f V_f.$$

In transverse loading the fibers carry less of the load and in this case we instead assume isostress (Reuss model). That is

$$\epsilon_c = \epsilon_m V_m + \epsilon_f V_f \quad \text{and} \quad \sigma_c = \sigma_m = \sigma_f = \sigma.$$

These can be combined to give the transverse modulus for a continuous fiber reinforced composite as

$$\frac{1}{E_{ct}} = \frac{V_m}{E_m} + \frac{V_f}{E_f} \implies E_{cf} = \frac{E_m E_f}{V_m E_f + V_f E_m}.$$

Empirically we have also been able to make estimates of  $E_{cd}$  for discontinuous fibers. This is however only valid for fiber lengths  $< 15 \frac{\sigma_f d}{\tau_c}$ . If this is respected the elastic modulus in the fiber direction is

$$E_{cd} = E_m V_m + k E_f V_f.$$

Where  $k$  is the “efficiency factor”, which is:

- Aligned:
  - Aligned parallel  $k = 1$
  - Aligned perpendicular  $k = 0$
- Random:
  - Random 2D  $k = \frac{3}{8}$
  - Random 3D  $k = \frac{1}{5}$

The estimated strength  $\sigma_{cd}^*$  for a fiber-reinforced composite with discontinuous fibers is:

- When  $l > l_c$ :

$$\sigma_{cd}^* = \sigma_f^* V_f \left( 1 - \frac{l_c}{2l} \right) + \sigma_m' (1 - V_f).$$

- When  $l < l_c$ :

$$\sigma_{cd'}^* = \frac{l \tau_c}{d} V_f + \sigma_m' (1 - V_f).$$

**Lecture 13: Composites, Pt. 2 – Laminates and sandwich panels**

10. Marts 2025

**21.4 Structural composites**

In this course we will focus on two types of structural composites. These are

- Laminates
- Sandwich Panels

**21.4.1 Laminates**

Laminates are created by stacking and bonding multiple layers (laminae) of fiber-reinforced material on top of each other. This can be done in a variety of ways but a common manner of stacking is a  $0^\circ/90^\circ$  stacking sequence in which the laminae are stacked such that the fibers are perpendicular to the layer above and below each laminae. This helps achieve a balanced in-plane stiffness and helps mitigate some of the anisotropy that can arise when making composites. Because the fibers in each layer can be oriented differently, laminates can be designed to carry loads efficiently in one or more directions. In general one wants to orient the fibers as much in the direction that will experience stress as possible (multiple stresses from different directions will often require different fiber orientations).

For  $0^\circ$  lamina the lamina's stiffness is dominated by the properties of the fibers themselves. The Voigt model (isostrain) typically applies best in this scenario meaning the combined modulus is close to that of the fibers themselves. For  $90^\circ$  lamina the matrix carries the most of the load (as the fibers are in the wrong direction). In this case the Reuss model (isostress) best captures the relationship leading to a modulus much closer to that of the matrix itself. For a combination of lamina directions the end result will fall somewhere in-between these two extremes. One can (with reasonable success) approximate the modulus of the composite by using the different rules of mixture (the Reuss and Voigt model) for the respective lamina and then combine the result at the end on basis of the volume fraction or thickness fraction of each lamina direction.

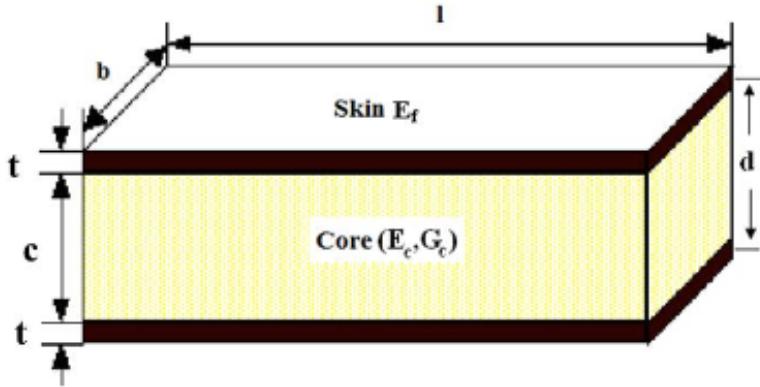
**21.4.2 Sandwich Panels**

Sandwich Panels consist of a lightweight core (often honeycomb or foam) placed between two stiff, strong face sheets (often made from fiber-reinforced composite or metal). The face sheets carry the bending load, while the core provides shear strength and prevents the face sheets from buckling. This helps achieve a high bending stiffness at a low weight. An adhesive layer is often utilized to secure the face sheets to the honeycomb.

On **Figure 21.6** an illustration of a Sandwich Panel composite is shown. On this illustration the elastic modulus and shear modulus of the core are labelled  $E_c$  and  $G_c$  respectively. The thickness of the lamina and the core are  $t$  and  $c$  respectively. The thickness of the combined composite is  $d$ , its length is  $l$  and its width is  $b$ . From these we can write some expressions for the material properties of a sandwich panel under bending. The bending stiffness  $EI_{eq}$  can be approximated as

$$EI_{eq} = \underbrace{\frac{E_f b t^3}{6}}_{\text{top face sheet}} + \underbrace{\frac{E_c b c^3}{12}}_{\text{Core}} + \underbrace{\frac{E_f b t d^3}{2}}_{\text{bottom face sheet}} .$$

Figure 21.6: Illustration of a Sandwich Panel composite



In typical Sandwich Panels, the face sheets have a much higher modulus  $E_f$  than the core  $E_c$  and their thickness  $t$  is small compared to the core thickness  $c \approx d$ . Under these assumptions the dominant term simplifies to:

$$EI_{eq} \approx \frac{E_f b t c^2}{2}.$$

This indicates that the most of the bending stiffness comes from the face sheets separated by the thick lightweight core.

The shear stiffness of the Sandwich Panels  $AG_{eq}$  can be predicted by

$$AG_{eq} = \frac{bd^2G_c}{c}.$$

And because  $d \approx c$  this can simplify to

$$AG_{eq} \approx bcG_c.$$

All in all it is clear that the sandwich panels achieve their high overall stiffness by placing the strong face sheets far apart (large  $c$ ), thereby increasing the moment of inertia for bending, while the core provides shear rigidity.

The deflection of a Sandwich Panel  $\delta$  subject to a stress  $P$  is the sum of the bending deflection  $\delta_b$  and the shear deflection  $\delta_s$  as:

$$\delta = \delta_b + \delta_s = \frac{Pl^3}{B_1 EI_{eq}} + \frac{Pl}{B_2 AG_{eq}}.$$

Here  $B_1$  and  $B_2$  are coefficients for different loading modes. These coefficients account for boundary conditions (e.g. free vs. built-in ends) and load distributions (point load vs. uniform load). These values can be found in **Figure 21.7**.

The compliance (the reciprocal of stiffness) can be estimated with the formula:

$$\frac{\delta}{P} = \frac{2l^3}{B_1 E_f b t c^2} + \frac{1}{B_2 b c G_c^*}.$$

Also here are the coefficients from **Figure 21.7** used.

Figure 21.7: Coefficients for different loading modes

Mode of loading	$B_1$	$B_2$	$B_3$	$B_4$
Cantilever, $P$	3	1	1	1
Cantilever, $q = \frac{P}{l}$	8	2	2	1
3 point bending, $P$	48	4	4	2
3 point bending, $q = \frac{P}{l}$	384/5	8	8	2
Ends built in, central $P$	192	4	8	2
Ends built in, $q = \frac{P}{l}$	384	8	12	2

**Example: Wind turbine blade**

A wind turbine blade is exposed to lots of different stresses through its life. The wind exerts a shearing force on the blades and any variation in wind speed or direction will make this shearing force even bigger. On top of this gravity influences the material in a cyclic way meaning the material will be subject to lots of fatiguing stress.

To combat this one utilizes composites in the wind turbine blades. The aeroshells themselves are made of a sandwich-panel composite. On top of this a load-carrying spear-beam is bonded to the middle of the blade. This spar is often made of a combination of a thick monolithic composite and a sandwich composite.

**Lecture 15: Phase diagrams, Pt. 1**

31. Marts 2025

**22 Phase diagrams**

A phase diagram is a simple diagram showcasing which *phase* a material will be in at a given combination of two of temperature, pressure and concentration.

**22.1 Solubility limit**

For many alloy systems and at some specific temperature, there is a maximum concentration of solute atoms that may dissolve in the solvent to form a solid solution; this is called a *solubility limit*. The addition of solute in excess of this solubility limit results in the formation of another solid solution or compound that has a distinctly different composition. E.g. for the addition of sugar to water, first a syrup forms. As more sugar is introduced, the solution becomes more concentrated, until the solubility limit is reached or the solution becomes saturated with sugar. At this time the solution is not capable of dissolving more sugar, and further additions will simply settle to the bottom. Therefore the system now consists of two separate substances: A sugar-water syrup liquid solution and solid crystals of undissolved sugar.

This solubility limit depends on the temperature of the system. It can be represented in graphical form on a plot of temperature vs. composition. This is shown for sugar in water on **Figure 22.1**. The solubility limit is the nearly vertical line in the figure. For compositions and temperatures to the left of the solubility limit only the syrup-phase exists. For systems on the right of the solubility limit, solid sugar will settle to the bottom.

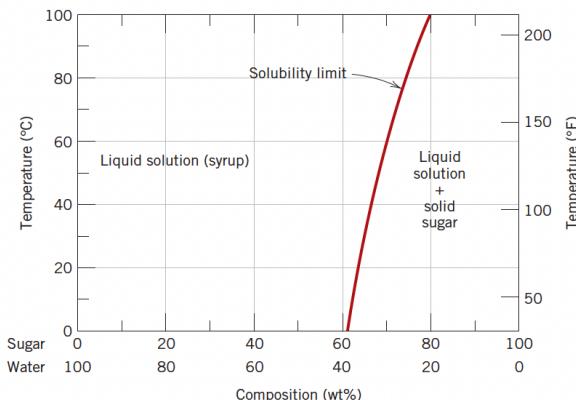


Figure 22.1: Solubility limit of sugar in water

## 22.2 Phases

Another critical term when talking about phase diagrams is the concept of a *phase*.

### Definition 25: Phases

A phase is a homogeneous portion of a system that has uniform physical and chemical characteristics.

Every pure material is considered to be a phase; so also is every solid, liquid, and gaseous solution. E.g. the water-sugar syrup phase discussed before is a phase and so is solid sugar. Each phase has different physical properties (one is a liquid and the other is a solid in the aforementioned example). Furthermore, each is chemically different (i.e. the different chemical compositions of water and sugar in the aforementioned example). If more than one phase is present in a given system, each will have its own distinct properties, and a boundary separating the phases will exist, across which there will be a discontinuous and abrupt change in physical and/or chemical characteristics.

Sometimes, a single-phase system is termed *homogeneous*. Systems composed of two or more phases, are termed *mixtures* or *heterogeneous systems*. Most metallic alloys and, for that matter, ceramic, polymeric, and composite systems are heterogeneous. Typically, the phases interact in such a way that the property combination of the multiphase system is different from, and more desirable than, either of the individual phases.

## 22.3 Microstructure

The physical properties and, in particular, the mechanical properties of a material often depend on the microstructure. Microstructure is subjected to direct microscopic observation using optical or electron microscopes. In metal alloys, microstructure is characterized by the number of phases present, their proportions, and the manner in which they are distributed or arranged. The microstructure of an alloy depends on such variables as the alloying elements present, their concentrations, and the heat treatment of the alloy).

## 22.4 Phase equilibria

*Equilibrium* is another essential concept, it is best described in terms of a thermodynamic quantity called the *free energy*. In brief, *free energy* is a function of the internal energy of a system and also the randomness or disorder of the atoms or molecules (the sum of enthalpy and entropy). A system is at equilibrium if its free energy is at a minimum under some specified combination of temperature, pressure, and composition. In a macroscopic sense, this means that the characteristics of the system do not change with time, but persist indefinitely – that is, the system is stable. A change in temperature, pressure and/or composition for a system in equilibrium results in an increase in the free energy and in a possible spontaneous change to another state by which the free energy is lowered.

The term *phase equilibrium*, often used in the context of this discussion, refers to equilibrium as it applies to systems in which more than one phase may exist. Phase equilibrium is reflected by a constancy with time in the phase characteristics of a system.

It is often the case, especially in solid systems, that a state of equilibrium is never completely achieved because the rate of approach to equilibrium is extremely slow; such a system is said to be in a *nonequilibrium* or *metastable* state. A metastable state or microstructure may persist indefinitely, experiencing only extremely slight and almost imperceptible changes as time progresses. Often, metastable structures are of more practical significance than equilibrium ones.

## 22.5 One-component (unary) phase diagrams

Much of the information about the control of the phase structure of a particular system is conveniently and concisely displayed in what is called a *phase diagram*, also often termed an equilibrium diagram. Three externally controllable parameters affect phase structure – temperature, pressure and composition – and phase diagrams are constructed when various combinations of these parameters are plotted against one another.

Perhaps the simplest and easiest type of phase diagram to understand is that for a one-component system, in which composition is held constant (i.e., the phase diagram is for a pure substance); this means that pressure and temperature are the variables. This one-component phase diagram is represented as a two-dimensional plot of pressure versus temperature. Most often the pressure axis is scaled logarithmically.

On **Figure 22.2** a phase diagram for pure water is shown. Regions for three different phases – solid, liquid, and vapor – are delineated on the plot. Each of the phases exist under equilibrium conditions over the temperature-pressure ranges of its corresponding area.

## 22.6 Binary phase diagrams

Another type of extremely common phase diagram is one in which temperature and composition are variable parameters and pressure is held constant – normally 1 atm. There are several different varieties; in the present discussion, we will concern ourselves with binary alloys. If more than two components are present, phase diagrams become extremely complicated and difficult to represent. An explanation of the principles governing and the interpretation of phase diagrams can be demonstrated using binary alloys even though most alloys contain more than two components.

Binary phase diagrams are maps that represent the relationships between temperature and the compositions and quantities of phases at equilibrium, which influence the microstructure of an alloy. Many microstructures

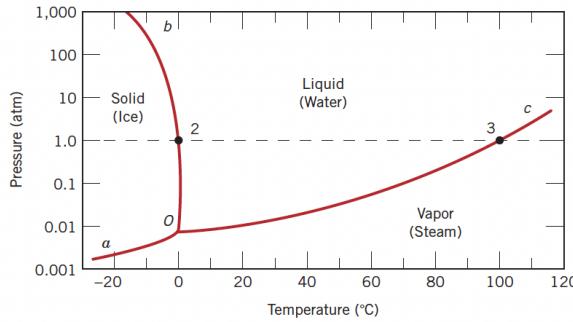


Figure 22.2: Phase diagram for pure water

develop from *phase transformations*; the changes that occur when the temperature is altered. This may involve the transition from one phase to another or the appearance or disappearance of a phase.

## 22.7 Binary isomorphous systems

Possibly the easiest type of binary phase diagram to understand and interpret is the type that is characterized by the copper-nickel system shown on **Figure 22.3**. The composition ranges from 0 wt% Ni (100 wt% Cu) on the far left and 100 wt% Ni (0 wt% Cu) on the right. Three different phase regions, or *fields*, appear on the diagram: An alpha ( $\alpha$ ) field, a liquid ( $L$ ) field, and a two-phase  $\alpha + L$  field. Each region is defined by the phase or phases that exists over the range of temperatures and compositions delineated by the phase boundary lines.

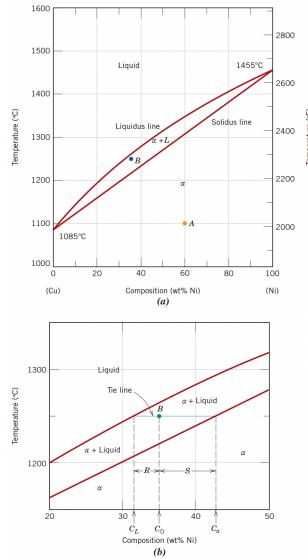


Figure 22.3: Copper-nickel phase diagram

The liquid  $L$  is a homogeneous liquid solution compound of both copper and nickel. The  $\alpha$  phase is a substitutional solid solution consisting of both Cu and Ni atoms and has an FCC crystal structure. At temperatures below about 1080 °C, copper and nickel are mutually soluble in each other in the solid state for all compositions. This complete solubility is explained by the fact that both Cu and Ni have the same

crystal structure, nearly identical atomic radii and electronegativities, and similar valences. Therefore the copper-nickel system is termed *isomorphous* because of the complete liquid and solid solubility of the two components.

For metallic alloys, solid solutions are commonly designated by lowercase Greek letters ( $\alpha, \beta, \gamma$ , etc.). With regard to phase boundaries, the line separating the  $L$  and  $\alpha + L$  phase fields is termed the *liquidus line*. The *solidus line* is located between the  $\alpha$  and  $\alpha + L$  regions. On **Figure 22.3** the *liquidus* and *solidus* lines intersect at the two composition extremes; these correspond to the melting temperatures of the pure components. For any temperature between these two extremes the solid-to-liquid transformation takes place at the melting temperature, meaning some of the heat energy will be stored as latent energy over this interval (in this way the interval corresponds to the single melting temperature of a pure substance).

## 22.8 Interpretation of phase diagrams

For a binary system of known composition and temperature at equilibrium, at least three kinds of information are available:

1. The phases that are present
2. The compositions of these phases
3. The percentages or fractions of the phases

### 22.8.1 Phases present

The establishment of what phases are present is relatively simple. One just locates the temperature-composition point on the diagram and notes the phase(s) with which the corresponding phase field is labeled.

### 22.8.2 Determination of phase compositions

The first step in the determination of phase compositions (in terms of the concentrations of the components) is to locate the temperature-composition point on the phase diagram. Different methods are used for single- and two-phase regions. If only one phase is present the procedure is trivial: The composition of this phase is simple the same as the overall composition of the alloy.

For an alloy having a composition and temperature located in a two-phase region, the situation is more complicated. In all two-phase regions (and in two-phase regions only), one may imagine a series of horizontal lines, one at every temperature; each of these is known as a *tie line*, or sometimes an *isotherm*. These tie lines extend across the two-phase region and terminate at the phase boundary lines on either side. To compute the equilibrium concentrations of the two phases, the following procedure is used:

1. A tie line is constructed across the two-phase region at the temperature of the alloy
2. The intersections of the tie line and the phase boundaries on either side are noted
3. Perpendiculars are dropped from these intersections to the horizontal composition axis, from which the composition of each of the respective phases is read.

### 22.8.3 Determination of phase amounts

The relative amounts (as fractions or as percentages) of the phases present at equilibrium may also be computed with the aid of phase diagrams. Again, the single- and two-phase situations must be treated separately. The solution is obvious in the single-phase region. Because only one phase is present, the alloy is composed entirely of that phase – that is, the phase fraction is 1,0.

If the composition and temperature position is located within a two-phase region, things are more complex. The tie line must be used in conjunction with a procedure that is often called the *lever rule* (or the *inverse lever rule*), which is applied as:

1. The tie line is constructed across the two-phase region at the temperature of the alloy
2. The overall composition is located on the tie line
3. The fraction of one phase is computed by taking the length of tie line from the overall alloy composition on the phase boundary for the *other phase* and dividing by the total tie line length.
4. The fraction of the other phase is determined in the same manner
5. If phase percentages are desired, each phase fraction is multiplied by 100. When the composition axis is scaled in weight percent, the phase fractions computed using the lever rule are *mass fractions* – the mass (or weight) of a specified phase divided by the total alloy mass (or weight). The mass of each phase is computed from the product of each phase fraction and the total alloy mass.

In the use of the lever rule, tie line segment lengths may be determined either by direct measurement from the phase diagram using a ruler, or by subtracting compositions as taken from the composition axis.

The lever rule is therefore

$$W_L = \frac{S}{R+S} = \frac{C_\alpha - C_0}{C_\alpha - C_L}.$$

For multiphase alloys, it is often more convenient to specify relative phase amount in terms of volume fractions rather than mass fractions. Phase volume fractions are preferred because they may be determined from examination of the microstructure; furthermore, the properties of a multiphase alloy is better described by volume fractions than mass fractions. For an alloy consisting of  $\alpha$  and  $\beta$  phases, the volume fraction of the  $\alpha$  phase,  $V_\alpha$  is defined as:

$$V_\alpha = \frac{v_\alpha}{v_\alpha + v_\beta}$$

where  $v_\alpha$  and  $v_\beta$  denote the volumes of the respective phases in the alloy. An analogous expression exists for  $V_\beta$ , and, for an alloy consisting of just two phases, it is the case that  $V_\alpha + V_\beta = 1$ .

To convert between volume and mass fractions one can simply scale by the density of the relevant phase as:

$$V_\alpha = \frac{\frac{W_\alpha}{\rho_\alpha}}{\frac{W_\alpha}{\rho_\alpha} + \frac{W_\beta}{\rho_\beta}}$$

$$W_\alpha = \frac{V_\alpha \rho_\alpha}{V_\alpha \rho_\alpha + V_\beta \rho_\beta}.$$

## 22.9 Development of microstructure in isomophous alloys

### 22.9.1 Equilibrium Cooling

At this point it is instructive to examine the development of microstructures that occurs for isomorphous alloys during solidification. We first treat the situation in which the cooling occurs very slowly and where phase equilibrium is continuously maintained. As cooling begins, no microstructural or compositional changes will be realized until we reach the liquidus line. At this point, the first solid state begins to form (for copper-nickel the  $\alpha$  phase will start forming), with a composition dictated by the tie line drawn at this temperature. With continued cooling, both compositions of the liquid and  $\alpha$  phases will follow the liquidus and solidus lines, respectively.

### 22.9.2 Nonequilibrium cooling

Conditions of equilibrium solidification and the development of microstructures as described in the previous section, are realized only for extremely slow cooling rates. The reason for this is that with changes in temperature, there must be readjustments in the compositions of the liquid and solid phases in accordance with the phase diagram (i.e., the liquidus and solidus lines). These readjustments are accomplished by diffusional processes – that is, diffusion in both solid and liquid phases and also across the solid-liquid interface. Because diffusion is a time-dependent phenomenon, to maintain equilibrium during cooling, sufficient time must be allowed at each temperature to allow for the appropriate compositional readjustments. Diffusion rates are especially low for the solid phase, and for both phases, decrease with temperature. In virtually all practical solidification situations, cooling rates are much too rapid to allow these compositional readjustments and maintenance of equilibrium. Therefore other microstructures often develop.

There are some important consequences for isomorphous alloys that have solidified under nonequilibrium conditions. The distribution of the two elements within the grains will e.g. be nonuniform. A phenomenon called *segregation* – that is, concentration gradients are established across the grains. The center of each grain, which is the first part to freeze is rich in the high-melting element, whereas the concentration of the low-melting element increases with position from this region to the grain boundary. This is termed a *cored* structure, which gives rise to less than the optimal properties. As a casting having a cored structure is reheated, grain boundary regions melt first because they are rich in the low-melting component. This produces a sudden loss in mechanical integrity due to the thin liquid film that separates the grains. Furthermore, this melting may begin at a temperature below the equilibrium solidus temperature of the alloy. Coring may be eliminated by a homogenization heat treatment carried out at a temperature below the solidus point for the particular alloy composition. During this process, atomic diffusion occurs, which produces compositionally homogeneous grains.

## 22.10 Mechanical properties of isomorphous alloys

For all temperature and compositions below the melting temperature of the lowest-melting component, only a single solid phase exists. Therefore, each component experiences solid-solution strengthening.

## 22.11 Binary eutectic systems

Another type of common and relatively simple phase diagram found for binary alloys is shown on **Figure 22.4** – this is a *binary eutectic phase diagram*. A number of features of this phase diagram are important and worth noting. First, three single-phase regions are found on the diagram:  $\alpha$ ,  $\beta$  and liquid. The  $\alpha$  phase is a solid solution rich in copper; it has silver as the solute component and an FCC crystal structure. The  $\beta$  phase solid solution also has an FCC structure, but copper is the solute. Pure copper and pure silver are also considered to be  $\alpha$  and  $\beta$  phases, respectively.

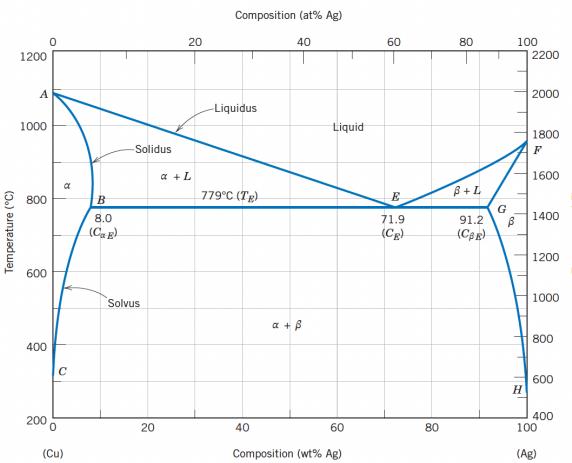
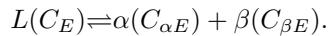


Figure 22.4: Copper-silver phase diagram

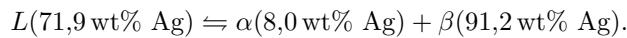
The solubility in each of these solid phases is limited, in that at any temperature below line  $BEG$  on **Figure 22.4** only a limited concentration of silver dissolves in copper (for the  $\alpha$  phase), and similarly for copper in silver (the  $\beta$  phase). The solubility limit for the  $\alpha$  phase corresponds to the boundary line, labeled  $CBA$ , between the  $\frac{\alpha}{\alpha+\beta}$  and  $\frac{\alpha}{\alpha+L}$  phase regions. At temperatures below 779 °C, the solid solubility limit line separating the  $\alpha$  and  $\alpha + \beta$  phase regions is termed a *solvus line*; the boundary  $AB$  is the *solidus line*.

As silver is added to copper, the temperature at which the alloys become totally liquid decreases along the *liquidus line*,  $AE$ ; thus, the melting temperature of copper is lowered by silver additions. The same may be said for silver: The introduction of copper reduces the temperature of complete melting along the other liquidus line,  $FE$ . These liquidus lines meet at point  $E$  on the phase diagram, with composition  $C_E$  and temperature  $T_E$ . It should be noted that there is a horizontal isotherm at 779 °C and represented by the line labelled  $BEG$  that also passes through point  $E$ .

An important reaction occurs for an alloy of composition  $C_E$  as it changes temperature in passing through  $T_E$ ; this reaction may be written as



Or, upon cooling, a liquid phase is transformed into the two solid  $\alpha$  and  $\beta$  phases at the temperature  $T_E$ . The opposite reaction occurs upon heating. This is called a *eutectic reaction* (*eutectic* means “easily melted”), and point  $E$  on the diagram is called the *eutectic point*; furthermore,  $C_E$  and  $T_E$  represent the eutectic composition and temperature, respectively. The eutectic reaction above for silver and copper may be written as



This eutectic reaction is termed an *invariant reaction* insomuch as it occurs under equilibrium conditions at a specific temperature ( $T_E$ ) and specific compositions ( $C_E$ ,  $C_{\alpha E}$  and  $C_{\beta E}$ ), which are constant (i.e., invariable) for a specific binary system. Furthermore, the horizontal solidus line  $BEG$  at  $T_E$  is sometimes called the *eutectic isotherm*.

The eutectic reaction, upon cooling, is similar to solidification for pure components in that the reaction proceeds to completion at a constant temperature, or *isothermally*, at  $T_E$ . However, the solid product of eutectic solidification is always two solid phases, whereas for a pure component only a single phase forms. Because of this eutectic reaction, phase diagrams similar to **Figure 22.4** are termed *eutectic phase diagrams*; components exhibiting this behaviour make up a *eutectic system*.

## Lecture 16 & 17: Phase diagrams, Pt: 2 & 3

2. – 7. April 2025

### 22.12 Development of microstructure in eutectic alloys

Depending on the composition, several different types of microstructure are possible for the slow cooling of alloys belonging to binary eutectic systems.

The first case is for compositions ranging between a pure component and the maximum solid solubility for that component at room temperature. For e.g. a lead-tin system, this includes lead-rich alloys containing between 0 and about 2 wt% Sn (for the  $\alpha$ -phase solid solution) and also between approximately 99 wt% Sn and pure tin (for the  $\beta$ -phase).

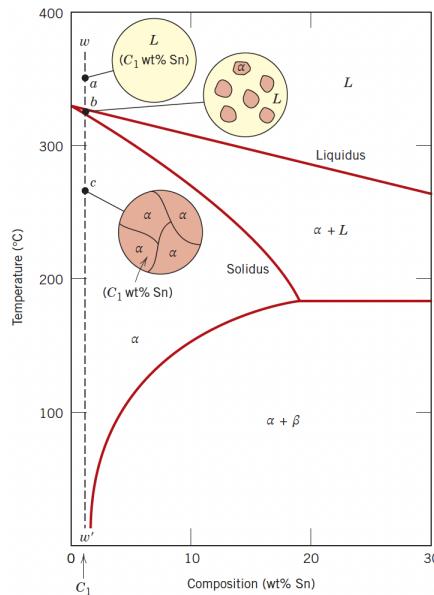


Figure 22.5: Phase diagram for lead-tin

For example, consider an alloy of composition  $C_1$  (**Figure 22.5**) as it is slowly cooled from a temperature within the liquid-phase region, say  $350^\circ\text{C}$ ; this corresponds to moving down the dashed vertical line  $ww'$  in the figure. The alloy will remain totally liquid and of composition  $C_1$  until we cross the liquidus line at approximately  $330^\circ\text{C}$ , at which time the solid  $\alpha$ -phase begins to form. While passing through this narrow  $\alpha + L$ -phase region, solidification proceeds in the same manner as was described for the copper-nickel alloy in the previous section – i.e., with continued cooling, more of the solid  $\alpha$  forms. Furthermore, liquid- and

solid-phase compositions are different, which follow along the liquidus line and solidus phase boundaries, respectively. Solidification reaches completion with a uniform composition of  $C_1$ , and no subsequent changes occur upon cooling to room temperature. This is the point  $c$  on **Figure 22.5**.

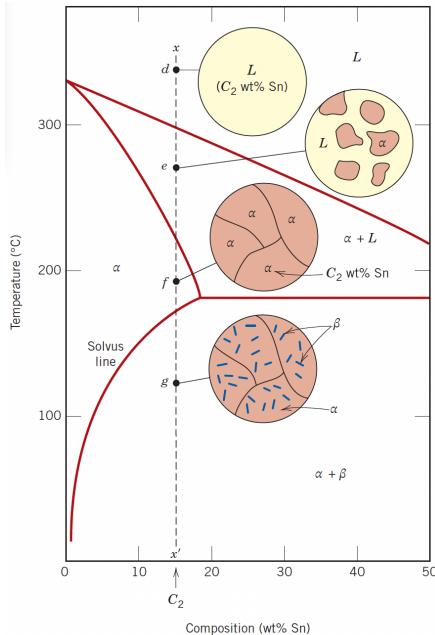
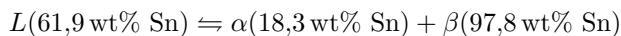


Figure 22.6: Phase diagram for lead-tin with a new composition

The second case considered is for compositions that range between the room temperature solubility limit and the maximum solid solubility at the eutectic temperature. For the lead-tin system, these compositions extend from about 2 to 18,3 wt% Sn (for lead-rich alloys) and from 97,8 to approximately 99 wt% Sn (for tin-rich alloys). We will now examine an alloy of composition  $C_2$  (**Figure 22.6**) as it is cooled along the vertical line  $xx'$ . Down to the intersection of  $xx'$  and the solvus line, changes that occur are similar to the previous case as we pass through the corresponding phase regions (as demonstrated by the points  $d$ ,  $e$ , and  $f$ ). Just above the solvus intersection, at point  $f$ , the microstructure consists of  $\alpha$  grains of composition  $C_2$ . Upon crossing the solvus line, the  $\alpha$  solid solubility is exceeded, which results in the formation of small  $\beta$ -phase particles; these are indicated in the microstructure inset at point  $g$ . With continued cooling, these particles grow in size because the mass fraction of the  $\beta$  phase increases slightly with decreasing temperature.

The third case involves solidification of the eutectic composition, 61,9 wt% Sn ( $C_3$  in **Figure 22.7**). We consider an alloy having this composition that is cooled from a temperature within the liquid-phase region (e.g. 250 °C) down the vertical line  $yy'$ . As the temperature is lowered, no changes occur until we reach the eutectic temperature, 183 °C. Upon crossing the eutectic isotherm, the liquid transforms into the two  $\alpha$  and  $\beta$  phases. This transformation can be represented by the reaction:



in which the  $\alpha$ - and  $\beta$ -phase compositions are dictated by the eutectic isotherm end points. During this transformation, there must be a redistribution of the lead and tin components because the  $\alpha$  and  $\beta$  phases have different compositions, neither of which is the same as that of the liquid (as indicated in the above equation). This redistribution is accomplished by atomic diffusion. The microstructure of the solid that results from this transformation consists of alternating layers (sometimes called *lammellae*) of the  $\alpha$  and  $\beta$  phases that form simultaneously during this transformation. This microstructure, represented schematically in **Figure 22.7** at point  $i$ , is called a *eutectic structure* and is characteristic of this reaction. A subsequent

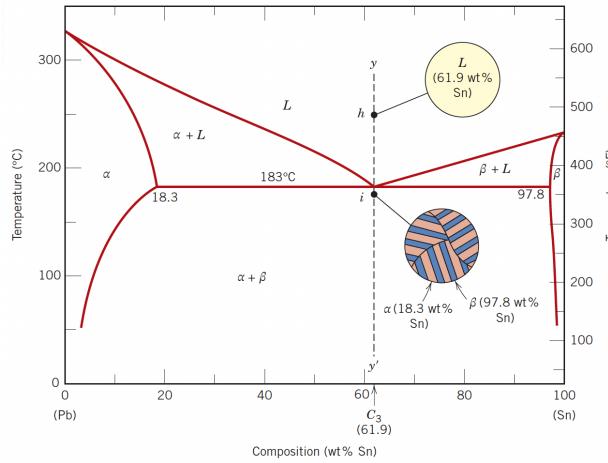


Figure 22.7: Phase diagram for lead-tin with a new composition once again

cooling of the alloy from just below the eutectic to room temperature will only result in minor microstructural alterations.

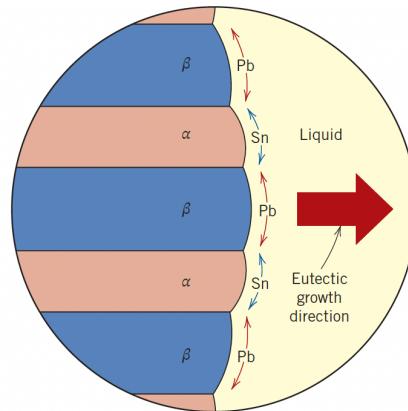


Figure 22.8: The formation of the eutectic structure for the lead-tin system

The microstructural change that accompanies this eutectic transformation is represented schematically in **Figure 22.8**, which shows the  $\alpha - \beta$  layers eutectic growing into and replacing the liquid phase. This process of the redistribution of lead and tin occurs by diffusion in the liquid just ahead of the eutectic-liquid interface. The arrow indicated the directions of diffusion of lead and tin atoms; lead atoms diffuse towards the  $\alpha$ -phase layers because this  $\alpha$  phase is lead-rich (18.3 wt% Sn and 81.7 wt% Pb); conversely, the direction of diffusion of tin will be opposite. The eutectic structure forms in these alternating layers because, for this lamellar configuration, atomic diffusion of lead and tin need only occur over relatively short distances.

The fourth and final microstructural case for this system includes all compositions other than the eutectic that, when cooled, cross the eutectic isotherm. Consider, for example the composition  $C_4$  (**Figure 22.9**), which lies to the left of the eutectic; as the temperature is lowered, we move down the line  $zz'$ , beginning at point  $j$ . The microstructural development between points  $j$  and  $l$  is similar to that for the second case, such that just prior to crossing the eutectic isotherm (point  $l$ ), the  $\alpha$  and liquid phases are present with compositions of approximately 18.3 and 61.9 wt% Sn, respectively, as determined from the appropriate tie line. As the temperature is lowered to just below the eutectic, the liquid phase, which is of the eutectic

## 22 PHASE DIAGRAMS

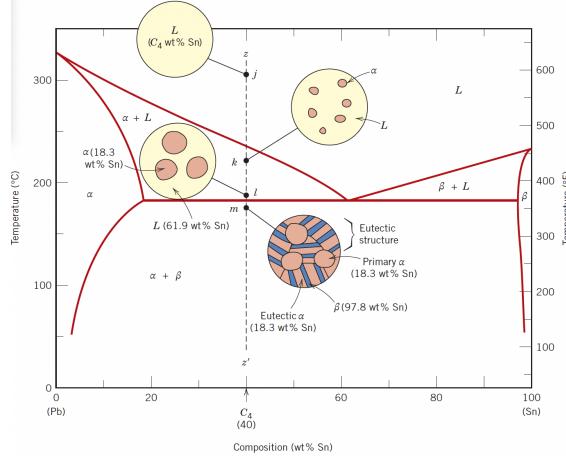


Figure 22.9: Phase diagram for the lead-tin system at yet another composition

composition, transforms into the eutectic structure (i.e. alternating  $\alpha$  and  $\beta$  lamellae); insignificant changes occur with the  $\alpha$  phase that is formed during cooling through the  $\alpha + L$  region. This microstructure is also schematically shown at the inset point  $m$  on **Figure 22.9**. This, the  $\alpha$  phase is present both in the eutectic structure and also as the phase that formed while cooling through the  $\alpha + L$  phase field. To distinguish one  $\alpha$  from the other, that which resides in the eutectic structure is called *eutectic  $\alpha$* , whereas the other that formed prior to crossing the eutectic isotherm is termed *primary  $\alpha$* .

When dealing with microstructures, it is sometimes convenient to use the term *microconstituent* – i.e., an element of the microstructure having an identifiable and characteristic structure. For example at point  $m$  on **Figure 22.9**, there are two microconstituents – primary  $\alpha$  and the eutectic structure. Thus, the eutectic structure is a microconstituent even though it is a mixture of two phases because it has a distinct lamellar structure with a fixed ratio of the two phases.

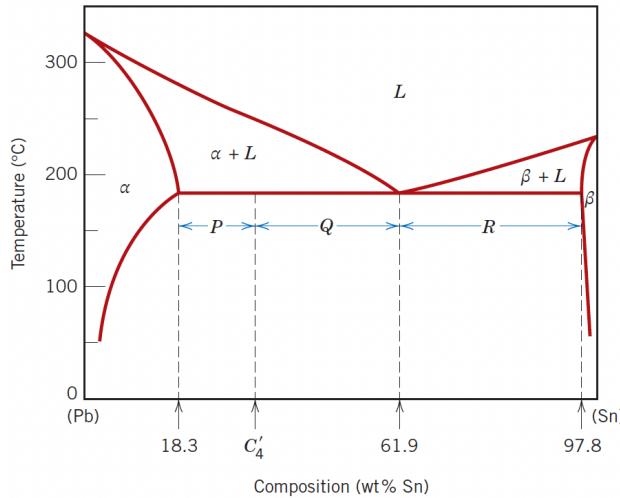


Figure 22.10: The lead-tin phase diagram in whole

It is indeed possible to compute the relative amounts of both eutectic and primary  $\alpha$  microconstituents. Because the eutectic microconstituents always forms from the liquid having the eutectic composition, this microconstituent may be assumed to have a composition of 61.9 wt% Sn. Hence, the lever rule is applied

using a tie-line between the  $\alpha - (\alpha + \beta)$  phase boundary (18,3 wt% Sn) and the eutectic composition. For example, consider the alloy of composition  $C'_4$  in **Figure 22.10**. The fraction of the eutectic microconstituent  $W_e$  is just the same as the fraction of the liquid  $W_L$  from which it transforms, or

$$W_e = W_L = \frac{P}{P+Q} = \frac{C'_4 - 18,3}{61,9 - 18,3} = \frac{C'_4 - 18,3}{43,6}.$$

Furthermore, the fraction of primary  $\alpha$ ,  $W_{\alpha'}$ , is just the fraction of the  $\alpha$  phase that existed prior to the eutectic transformation or, from **Figure 22.10**:

$$W_{\alpha'} = \frac{Q}{P+Q} = \frac{61,9 - C'_4}{61,9 - 18,3} = \frac{61,9 - C'_4}{43,6}.$$

The fractions of *total*  $\alpha$   $W_\alpha$  (both eutectic and primary), and also of total  $\beta$ ,  $W_\beta$ , are determined by use of the lever rule and a tie line that extends *entirely across the  $\alpha + \beta$  phase field*. Again, for an alloy having composition  $C'_4$ :

$$\begin{aligned} W_\alpha &= \frac{Q+R}{P+Q+R} = \frac{97,8 - C'_4}{97,8 - 18,3} = \frac{97,8 - C'_4}{79,5} \\ W_\beta &= \frac{P}{P+Q+R} = \frac{C'_4 - 18,3}{97,8 - 18,3} = \frac{C'_4 - 18,3}{79,5}. \end{aligned}$$

Analogous transformations and microstructures result for alloys having compositions to the right of the eutectic (i.e., between 61,9 and 97,8 wt% Sn). However, below the eutectic temperature, the microstructure will consist of the eutectic and primary  $\beta$  microconstituents because, upon cooling from the liquid, we pass through the  $\beta +$  liquid phase field.

When, for the fourth case represented in **Figure 22.9**, conditions of equilibrium are not maintained passing through the  $\alpha$  (or  $\beta$ ) + liquid phase region, the following consequences will be realized for the microstructure upon crossing the eutectic isotherm:

- Grains of the primary microconstituent will be cored, that is, have a nonuniform distribution of solute across the grains
- The fraction of the eutectic microconstituent formed will be greater than for the equilibrium situation

### 22.13 Equilibrium diagrams having intermediate phases or compounds

The isomorphous and eutectic phase diagrams discussed thus far are relatively simple, but for many binary systems much more complex interactions arise. The eutectic systems discussed thus far only have two solid phases,  $\alpha$  and  $\beta$ ; these are sometimes termed *terminal solid solutions* because they exist over composition ranges near the concentration extremes of the phase diagram. For other alloy systems, *intermediate solid solutions* (or *intermediate phases*) may be found at other than the two composition extremes. Such is the case for the copper-zinc system. Its phase diagram (**Figure 22.11**) may at first appear formidable because there are some invariant reactions similar to the eutectic that have not yet been discussed. In addition, there are six different solid solutions – two terminal ( $\alpha$  and  $\eta$ ) and *four* intermediate ( $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\epsilon$ ). The  $\beta'$  phase is termed an *ordered solid solution*, one in which the copper and zinc atoms are situated in a specific and ordered arrangement within each unit cell. The dashed boundaries near the bottom are dashed, as they have not been exactly determined yet. This is due to the fact that at low temperatures, diffusion rates are very slow, and inordinarily long times are required to attain equilibrium.

Commercial brass is a copper-rich copper-zinc alloy. E.g., Cartridge brass has a composition of 70 wt% Cu and 30 wt% Zn and therefore a microstructure consisting of a single  $\alpha$  phase.

## 22 PHASE DIAGRAMS

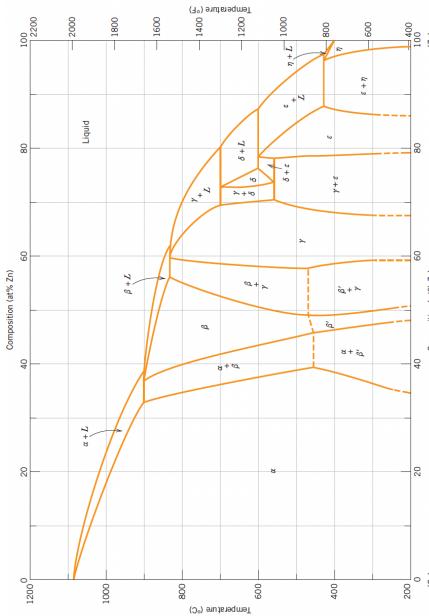


Figure 22.11: The copper-zinc phase diagram

For some systems, discrete intermediate compounds rather than solid solutions may be found on the phase diagram, and these compounds have distinct chemical formulas; for metal-metal systems, they are called *intermetallic compounds*. E.g., consider the magnesium-lead system (**Figure 22.12**). The compound  $\text{Mg}_2\text{Pb}$  has a composition of 19 wt% Mg and 81 wt% Pb and is represented as a vertical line on the diagram, rather than as a phase region of finite width; hence,  $\text{Mg}_2\text{Pb}$  can exist by itself only at this precise composition.

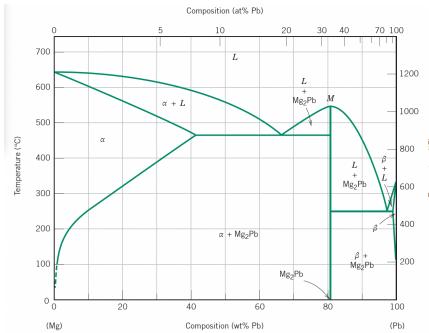
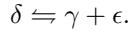


Figure 22.12: The magnesium-lead phase diagram

Several other characteristics are worth noting for this magnesium-lead system. First, the compound  $\text{Mg}_2\text{Pb}$  melts at approximately  $550^\circ\text{C}$ , as indicated by point *M* on **Figure 22.12**. Also, the solubility of lead in magnesium is rather extensive. However, the solubility of magnesium in lead is extremely limited. Finally, this phase diagram may be thought of as two simple eutectic diagrams joined back to back, one for the Mg-Mg<sub>2</sub>Pb system and the other for Mg<sub>2</sub>Pb-Pb; as such, the compound Mg<sub>2</sub>Pb is really considered to be a component.

### 22.14 Eutectoid and peritectic reactions

In addition to the eutectic, other invariant reactions involving three different phases are found for some alloy systems. One of these occurs for the copper-zinc system (**Figure 22.11**) at 560 °C and 74 wt% Zn and 26 wt% Cu. A portion of the phase diagram in this vicinity is enlarged in **Figure 22.13**. Upon cooling, a single solid  $\delta$  phase transforms into two other solid phases  $\gamma$  and  $\epsilon$  and v.v. for heating according to the reaction:



This is called a *eutectoid reaction*; the eutectoid point is labelled *E* on **Figure 22.13**. The feature distinguishing eutectoid from eutectic is that one solid phase instead of a liquid transforms into two other solid phases at a single temperature.

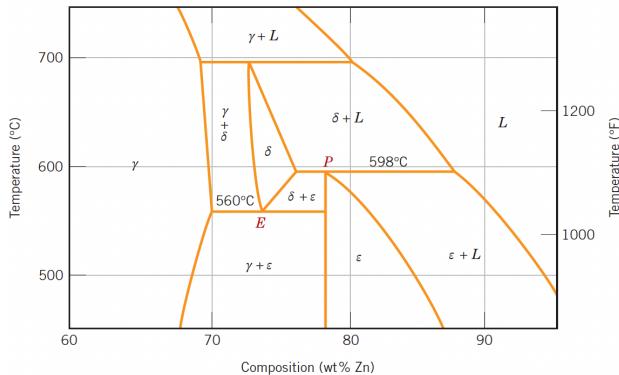
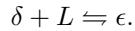


Figure 22.13: The copper-zinc diagram zoomed in near the peritectic and eutectoid region

A *peritectic reaction* is another invariant reaction involving three phases at equilibrium. With this reaction, upon heating, one solid phase transforms into a liquid phase and another solid phase. A peritectic exists for the copper-zinc system at point *P* on **Figure 22.13**. This reaction is as follows:



The low-temperature solid phase may be an intermediate solid solution (e.g.,  $\epsilon$  in the preceding reaction), or it may be a terminal solid solution. One of the latter peritectics exists at about 97 wt% Zn at 435 °C (see **Figure 22.11**), where the  $\eta$  phase, when heated, transforms into  $\epsilon$  and liquid phases. Three other peritectics are found for the Cu-Zn system, the reactions of which involve  $\beta$ ,  $\delta$ , and  $\gamma$  intermediate solid solutions as the low-temperature phases that transform upon heating.

### 22.15 Congruent phase transformations

Phase transformations may be classified according to whether there is any change in composition for the phases involved. Those for which there are no compositional changes are said to be *congruent transformations*, e.g. melting of pure metals. Conversely, for *incongruent transformations*, at least one of the phases experiences a change in composition, e.g. melting of an alloy or eutectic/eutectoid reactions.

Intermediate phases are sometimes classified on the basis of whether they melt congruently or incongruently. The intermetallic compound Mg<sub>2</sub>Pb melts congruently at the point designated *M* on **Figure 22.12**. For the nickel-titanium system on **Figure 22.14**, there is a congruent melting point for the  $\gamma$  solid solution that corresponds to the point of tangency for the pairs of liquidus and solidus lines at 1310 °C and 44.9 wt% Ti. The peritectic reaction is an example of incongruent melting for an intermediate phase.

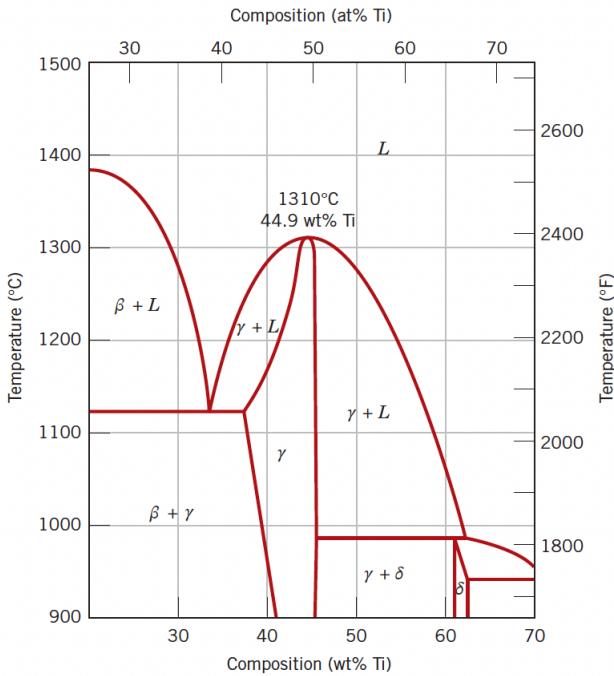


Figure 22.14: Portion of the phase diagram for nickel-titanium

## 22.16 The Gibbs phase rule

One of the most important laws of thermodynamics when talking about phase diagrams is the *Gibbs phase rule*. This rule represents a criterion for the number of phases that coexist within a system at equilibrium and is expressed by the simple equation:

$$P + F = C + N$$

Where  $P$  is the number of phases present.  $F$  is the number of *degrees of freedom* or the number of externally controlled variables (e.g., temperature, pressure, composition) that must be specified to define the state of the system completely. I.e.,  $F$  is the number of these variables that can be changed independently without altering the number of phases that coexist at equilibrium. The parameter  $C$  represents the number of components in the system. Components are normally elements or stable compounds and, in the case of phase diagrams, are the materials at the two extremes of the composition axis. Finally  $N$  is the number of noncompositional variables (e.g., temperature and pressure)

This rule will now be demonstrated by applying it to binary temperature-composition phase diagrams. More specifically the copper-silver system previously discussed. Because pressure is constant (1 atm), the parameter  $N$  is 1, as temperature is the only noncompositional variable. Therefore we have:

$$P + F = C + 1.$$

The number of components  $C$  is 2 (Cu and Ag):

$$P + F = 2 + 1 = 3$$

or:

$$F = 3 - P.$$

Let us consider the case of single-phase fields on the phase diagram (e.g.,  $\alpha$ ,  $\beta$ , and liquid regions). Because only one phase is present  $P = 1$  and

$$F = 3 - P = 3 - 1 = 2.$$

Therefore we must specify two parameters to completely describe the characteristics of any alloys that exists within one of these phase fields. These two parameters are composition and temperature, which locate, respectively, the horizontal and vertical positions of the alloy respectively.

For the situation in which two phases coexist – e.g.,  $\alpha + L$ ,  $\beta + L$ , and  $\alpha + \beta$  phase regions – the phase rule stipulates that we have one degree of freedom because:

$$F = 3 - P = 3 - 2 = 1.$$

Thus, it is necessary to specify either temperature or the composition of one of the phases to completely define the system.

For binary systems, when three phases are present, there are no degrees of freedom because:

$$F = 3 - P = 3 - 3 = 0.$$

This means that the composition of all three phases – as well as the temperature – are fixed. This condition is met for a eutectic isotherm.

## 22.17 The iron-iron carbide phase diagram

A portion of the iron-iron carbide phase diagram is shown on **Figure 22.15**. Pure iron, upon heating, experiences two changes in crystal structure before it melts. At room temperature, the stable form, called *ferrite*, or  $\alpha$ -iron, has a BCC crystal structure. Ferrite experiences a polymorphic transformation to FCC *austenite*, or  $\gamma$ -iron at  $912^\circ\text{C}$ . This austenite persists to  $1394^\circ\text{C}$  at which temperature the FCC austenite reverts back to a BCC phase known as  $\delta$ -ferrite, which finally melts at  $1538^\circ\text{C}$ . All these changes are apparent along the left vertical axis of **Figure 22.15**

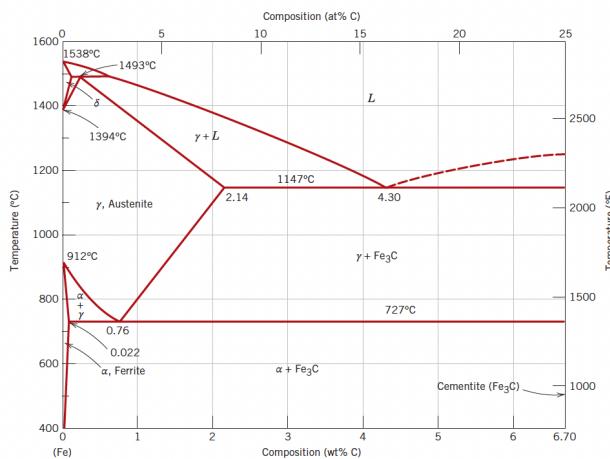


Figure 22.15: Portion of the iron-iron carbide phase diagram

The composition axis on **Figure 22.15** extends only to 6,70 wt% C; at this concentration the intermediate compound iron carbide, or *cementite* ( $\text{Fe}_3\text{C}$ ) is formed, which is represented by a vertical line on the phase diagram. Thus, the iron-carbon system may be divided into two parts: an iron rich portion (**Figure 22.15**) and the other for composition from 6,70 wt% C and up (not shown).

Carbon is an interstitial impurity in iron and forms a solid solution with each of  $\alpha$ -,  $\gamma$ - and  $\delta$ -ferrites. In the BCC  $\alpha$ -ferrite, only small concentrations of carbon are soluble (max is around 0,022 wt% C at  $727^\circ\text{C}$ ). The

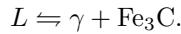
limited solubility is explained by the shape and size of the BCC interstitial positions, which make it difficult to accommodate carbon atoms. Even though present in relatively low concentrations, carbon significantly influences the mechanical properties of ferrite.

The austenite or  $\gamma$ -phase of iron when alloyed with carbon alone, is not stable below 727 °C. The maximum solubility of carbon in austenite is 2,14 wt% at 1147 °C. This is because the FCC octahedral sites are larger than the BCC tetrahedral sites.

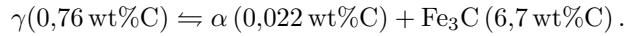
$\delta$ -ferrite is virtually the same as  $\alpha$ -ferrite except for the temperature range it exists over.  $\delta$ -ferrite is only stable at high temperatures and is therefore of no technological importance.

Cementite ( $\text{Fe}_3\text{C}$ ) forms when the solubility limit of carbon in  $\alpha$ -ferrite is exceeded below 727 °C. Cementite can also coexist with the  $\gamma$  phase between 727 °C and 1147 °C. Cementite is very hard and brittle and some very heavy duty steels utilize it to increase their strength. Also it is the case that most steel has a microstructure consisting of  $\alpha$  and  $\text{Fe}_3\text{C}$ . Strictly speaking, cementite is only metastable, meaning that it technically will transform slowly to other types of iron at low temperatures, however, this process is so slow that even heated to 700 °C it would take many years to run its course.

For the iron-iron carbide system on **Figure 22.15** there is a eutectic at 4,30 wt% at 1147 °C where the eutectic reaction is:



Also a eutectoid invariant exists at 0,76 wt% C and a temperature of 727 °C which may be represented as:



## 22.18 Development of microstructure in iron-carbon alloys

For cooling iron-iron carbon around its eutectic point a eutectic reaction will take place which produces the aforementioned eutectic phase with lamellae of the two constituents. This eutectic phase is called *pearlite* as it somewhat resembles mother of pearl in appearance.

**Hypo- and hypereutectoid alloys** Iron-iron carbon at non eutectoid-composition (fourth case from before) will now be explored. Consider a composition  $C_0$  to the left of the eutectoid; this is termed a *hypoeutectoid* alloy. Cooling this alloy along the line  $yy'$  on **Figure 22.16**. At 875 °C (point  $c$ ) the microstructure consists entirely of grains of the  $\gamma$  phase. When cooled to point  $d$  at 775 °C both the  $\alpha$  and  $\gamma$  phases will coexist. Most of the small  $\alpha$  particles form along the original  $\gamma$  grain boundaries.

While cooling an alloy through the  $\alpha + \gamma$  phase region, the composition of the ferrite phase changes with temperature along the  $\alpha - (\alpha + \gamma)$  phase boundary, line  $MN$ , becoming slightly richer in carbon. However the change in composition of the austenite is more dramatic, proceeding along the  $(\alpha + \gamma) - \gamma$  boundary, line  $MO$ . Cooling from point  $d$  to  $e$ , just above the eutectoid but still in the  $\alpha + \gamma$  region, produces an increased fraction of the  $\alpha$  phase and a microstructure similar to that also shown: the  $\alpha$  particles will have grown larger.

As the temperature is lowered just below the eutectoid, to point  $f$ , all of the  $\gamma$  phase that was present at temperature  $T_e$  transforms into pearlite. There is virtually no change in the  $\alpha$  phase that existed at point  $e$  in crossing the eutectoid temperature. The ferrite present in the pearlite is called *eutectic ferrite*, whereas the other, which formed above  $T_e$  is termed *proeutectoid ferrite*.

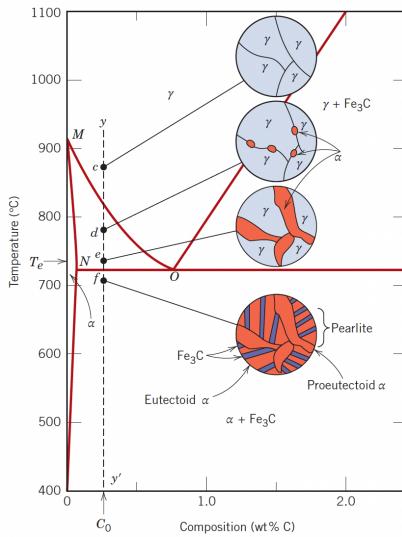


Figure 22.16: iron-iron carbon at hypoeutectoid composition

Something analogous is true for *hypereutectic alloys* – i.e. composition to the right of the eutectoid). Here pearlite is however not formed – instead cementite is formed.

## Lecture 18: Development of Microstructure and Alteration of Mechanical Properties 9. Ap

### 22.19 The kinetics of phase transformations

Under a phase transformation, normally at least one new phase is formed that has different physical or chemical characteristics and/or a different structure than the parent phase. Also, most phase transformations are not instantaneous. Rather they begin by the formation of numerous small particles of the new phase(s), which increase in size until the transformation has reached completion. On this basis, the progress of a phase transformation may be broken down into two distinct stages: nucleation and growth.

During nucleation small particles (nuclei) appear. These often consist of only a few hundred atoms and are capable of growing. During the growth stage, these nuclei increase in size, which result in the disappearance of some or all of the parent phase.

#### 22.19.1 Nucleation

One typically distinguishes between two main types of nucleation: *homogeneous* and *heterogeneous*. The distinction between them is made according to the site at which nucleation occurs. For the homogeneous type, nuclei of the new phase form uniformly throughout the parent phase, whereas for the heterogeneous type, nuclei form preferentially at structural inhomogeneities, such as container surfaces, insoluble impurities, grain boundaries, and dislocations.

**Homogeneous nucleation** To understand nucleation one also needs to know about the *Gibbs free energy*,  $G$ . In brief, free energy is a function of other thermodynamic parameters, of which one is the internal energy of the system (i.e. Enthalpy  $H$ ) and another is the entropy of the system. Relative to phase transformations, an important thermodynamic parameter is especially the change in free value  $\Delta G$ ; a transformation occurs only spontaneously when  $\Delta G$  has a negative value.

If we consider the solidification of a pure material, assuming that nuclei of the solid phase form in the interior of the liquid as atoms cluster together so as to form a packing arrangement similar to that found in the solid phase.

It is assumed that each nucleus is spherical and has a radius  $r$ . There are two contributions to the total free energy change that accompany a solidification transformation. The first is the free energy difference between the solid and liquid phases, or the volume free energy,  $\Delta G_v$ . Its value is negative if the temperature is below the equilibrium solidification temperature, and the magnitude of its contribution is the product of  $\Delta G_v$  and the volume of the spherical nucleus. The second energy contribution results from the transformation of the solid-liquid phase boundary during the solidification transformation. Associated with this boundary is a surface free energy,  $\gamma$ , which is positive; furthermore, the magnitude of this contribution is the magnitude of this and the surface area of the nucleus. Finally the total free energy change is equal to the sum of these two contributions:

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma.$$

From this it can be seen that this sum (the free energy) actually first increases, before passing through a maximum and decreasing. In a physical sense this means that as a solid particle begins to form its free energy first increases. If the cluster reaches a size corresponding to the critical radius  $r^*$  then growth will continue with an accompagniement of a decrease in free energy. However, a cluster of radius less than the critical value will shrink and redissolve. A subcritical particle is called an *embryo* and a particle of radius greater than critical is termed a *nucleus*.

A critical free energy,  $\Delta G^*$ , occurs at the critical radius. This corresponds to the *activation free energy*, which is the free energy required for the formation of a stable nucleus. We can find the critical radius and activation free energy as:

$$r^* = -\frac{2\gamma}{\Delta G_v}$$
$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}.$$

This volume free energy change  $\Delta G_v$  is the driving force for the solidification transformation, and its magnitude is a function of temperature. At the equilibrium solidification temperature  $T_m$ , the value of  $\Delta G_v$  is zero, and with decreasing temperature its value becomes increasingly negative. It can be shown that  $\Delta G_v$  is a function of temperature as:

$$\Delta G_v = \frac{\Delta H_f (T_m - T)}{T_m}$$

where  $\Delta H_f$  is the latent heat of fusion, and  $T_m$  and the temperature  $T$  are in Kelvin. One can also express the critical radius and activation free energy in terms of this as:

$$r^* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right) \left(\frac{1}{T_m - T}\right)$$
$$\Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right) \frac{1}{(T_m - T)^2}.$$

From these two equations it can be seen that both the critical radius and the activation free energy decrease as the temperature decreases.

Furthermore, the number of stable nuclei  $n^*$  (having radii greater than  $r^*$ ) is a function of temperature as

$$n^* = K_1 e^{-\frac{\Delta G^*}{kT}}$$

where the constant  $K_1$  is related to the total number of nuclei of the solid phase.

Another important temperature-dependent step is involved in and also influences nucleation: the clustering of atoms by short-range diffusion during the formation of nuclei. This diffusion effect is related to the frequency at which atoms from the liquid attach themselves to the solid nucleus  $v_d$ . The dependence of  $v_d$  on temperature is the same as for the diffusion coefficient, namely:

$$v_d = K_2 e^{-\frac{Q_d}{kT}}$$

where  $Q_d$  is a temperature-independent parameter – the activation energy for diffusion – and  $K_2$  is a temperature-independent constant. Therefore a decrease in temperature results in a reduction in  $v_d$ .

Another important parameter is the nucleation rate  $\dot{N}$  (which has units of nuclei per unit volume per second). This rate is simply proportional to the product of  $n^*$  and  $v_d$  as

$$\dot{N} = K_3 n^* v_d = K_1 K_2 K_3 e^{-\frac{\Delta G^*}{kT}} e^{-\frac{Q_d}{kT}}.$$

Here  $K_3$  is the number of atoms on a nucleus surface.

**Heterogeneous nucleation** It is often easier for nucleation to occur at surfaces and interfaces than at other sites. In order to understand this, we consider the nucleation, on a flat surface, of a solid particle from a liquid phase. It is assumed that both the liquid and solid phases “wet” this flat surface – that is, they both spread out and cover the surface. Taking a surface tension force balance in the plane of the flat surface leads to the following expression:

$$\gamma_{IL} = \gamma_{SI} + \gamma_{SL} \cos \theta.$$

One can derive the equations for  $r^*$  and  $\Delta G^*$  to be:

$$r^* = -\frac{2\gamma_{SL}}{\Delta G_v}$$

$$\Delta G^* = \left( \frac{16\pi\gamma_{SL}^3}{3\Delta G_v^2} \right) S(\theta).$$

The  $S(\theta)$  term is a function only of  $\theta$  (i.e. the shape of the nucleus), which has a numerical value between 0 and 1.

### 22.19.2 Growth

The growth step in a phase transformation begins once an embryo has exceeded the critical size  $r^*$  and becomes a stable nucleus. Particle growth occurs by long-range atomic diffusion, which normally involves several steps – for example, diffusion through the parent phase, across a phase boundary and then into the nucleus. Consequently, the growth rate  $\dot{G}$  is determined by the rate of diffusion:

$$\dot{G} = C e^{-\frac{Q}{kT}}.$$

Where  $Q$  (activation energy) and  $C$  (constant) are independent of temperature.

### 22.19.3 Kinetic considerations of Solid-State Transformations

Within many kinetic investigations, the fraction of reaction that has occurred is measured as a function of time while the temperature is maintained constant. Data are plotted as the fraction of transformed material versus the logarithm of time. For most solid-state transformations the fraction of transformation  $y$  is a function of time  $t$  as:

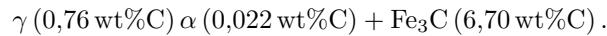
$$y = 1 - e^{-kt^n}.$$

where  $k$  and  $n$  are time independent constants for the particular reaction. This is sometimes called the *Avrami equation*. By convention the rate of transformation if taken as the reciprocal of time required for the transformation to proceed halfway to completion,  $t_{0.5}$  or:

$$\text{rate} = \frac{1}{t_{0.5}}.$$

## 22.20 Isothermal transformation diagrams

**Pearlite** Consider the iron-iron carbide eutectoid reaction:



Upon cooling, austenite, having an intermediate carbon concentration, transforms into a ferrite phase, which has a much lower carbon content, and also cementite, which has a much higher carbon concentration. The temperature dependence of this is shown in **Figure 22.17**.

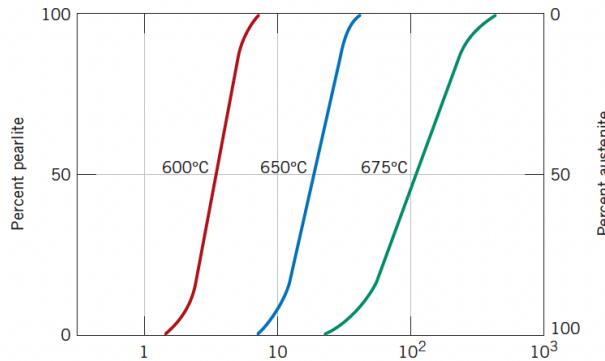


Figure 22.17: Temperature dependence of the austenite to pearlite transformation

A more convenient way of representing both the time and temperature dependence of this transformation is shown in **Figure 22.18**. Here, the vertical and horizontal axes, are respectively, temperature and the logarithm of time. Two solid curves are plotted; one represents the time required at each temperature for the initiation or start of the transformation and the other is for the transformation conclusion. The dashed curve corresponds to 50% of transformation completion. One must note that this is only valid for the mixture at eutectoid composition.

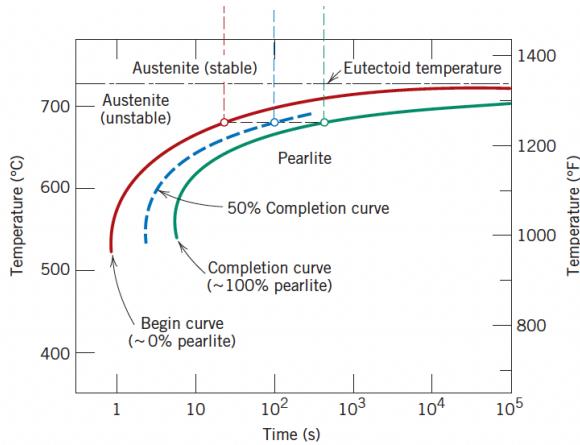


Figure 22.18: Temperature dependence of the transformation

**Lecture 19: Processing of Metals: Heat Treatment**

23. April 2025

## 23 Thermal processing of metals

### 23.1 Annealing processes

*Annealing* is the name for a form of heat treatment where a material is exposed to an elevated temperature for an extended time period and then slowly cooled. Typically this is carried out to:

- Relieve stresses
- Increase softness, ductility and toughness
- Produce a specific microstructure

Any annealing process consists of three stages:

1. Heating to the desired temperature
2. Holding or “soaking” at that temperature
3. Cooling, usually to room temperature

Time is an important parameter in these processes. During heating and cooling, temperature gradients exist between the outside and interior portions of the piece; their magnitude depend on the size and geometry of the piece. If the rate of temperature change is too great, temperature gradients and internal stresses may be induced that may lead to warping or cracking.

### 23.1.1 Process annealing

*Process annealing* is a heat treatment that is used to negate the effects of cold work (i.e., to soften and increase the ductility of a strain-hardened metal). Typically a fine grained microstructure is desired, and therefore the heat treatment is terminated before appreciable grain growth has occurred.

### 23.1.2 Stress relief

Internal stresses may develop in pieces in response to things such as plastic deformation, nonuniform cooling or other things like that. Distortion and warpage may result if the internal stresses are not removed. They may be eliminated by a *stress relief annealing* heat treatment. The annealing temperature is typically relatively low such that the effects resulting from cold working and other heat treatments are not affected.

### 23.1.3 Annealing of ferrous alloys

Many different annealing procedures are employed to enhance the properties of steel alloys.

**Normalizing** Steels that have been plastically deformed by, e.g., a roller consists of grains of pearlite (and most likely a proeutectoid phase), which are irregularly shaped and relatively large and vary substantially in size. An annealing heat treatment called *normalizing* is used to refine the grains (i.e., decrease average grain size) and produce a tougher more uniform steel. Normalizing is accomplished by heating at least 55 °C above the upper critical temperature (i.e. above the hypo-/hyper-eutectoid temperature). After sufficient time has been allowed for the alloy to completely transform to austenite – a procedure called *austenizing* – the treatment is terminated by cooling in air.

**Full anneal** A heat treatment known as *full annealing* is often used in low- and medium-carbon steels that will be machined or will experience extensive plastic deformation during a forming operation. In general, the alloy is treated by heating to a temperature of about 50 °C above the upper critical line to form austenite or austenite and Fe<sub>3</sub>C-phases. The alloy is then furnace cooled – that is, the heat-treating furnace is turned off, and both furnace and steel cool to room temperature at the same rate, which takes several hours. This gives a relatively soft and ductile material with large pearlite grains.

**Spheroidizing** Medium- and high-carbon steels having a microstructure containing even coarse pearlite may still be too hard to machine or plastically deform conveniently. Spheroidized steels have a maximum softness and ductility and are easily machined or deformed. The *spheroidizing* heat treatment, during which there is a coalescence of the Fe<sub>3</sub>C to form the spheroid particles, can take place by several methods, as follows:

- Heating the alloy at a temperature just below the eutectoid in the  $\alpha + \text{Fe}_3\text{C}$  region of the phase diagram. If the precursor microstructure contains pearlite, spheroidizing times will typically range between 15 and 25 h.
- Heating to a temperature just above the eutectoid temperature and then either cooling very slowly in the furnace or holding at a temperature just below the eutectoid temperature.
- Heating and cooling alternately within about  $\pm 50$  °C of the hypo-/hyper-eutectoid temperature.

To some degree, the rate at which spheroidite forms depends on prior microstructure. For example, it is slowest for pearlite, and the finer the pearlite, the more rapid the rate. Also, prior cold work increases the spheroidizing reaction rate.

## 23.2 Heat treatment of steels

Conventional heat treatment procedures for producing martensitic steels typically involve continuous and rapid cooling of an austenitized specimen in some type of quenching medium, such as water, oil, or air. The optimum properties of a steel that has been quenched and then tempered can be realized only if, during the quenching heat treatment, the specimen has been converted to a high content of martensite; the formation of any pearlite and/or bainite will result in other than the best combination of mechanical characteristics.

### 23.2.1 Hardenability

The influence of alloy composition on the ability of a steel alloy to transform to martensite for a particular quenching treatment is related to a parameter called *hardenability*. For every steel alloy, there is a specific relationship between the mechanical properties and the cooling rate. Hardenability is a term used to describe the ability of an alloy to be hardened by the formation of martensite as a result of a given heat treatment. Hardenability is not “hardness”.

**Jominy end-quench test** One standard procedure used to determine hardenability is the *Jominy end-quench test*. Except for alloy composition, all factors that may influence the depth to which a piece hardens (i.e., specimen size and shape and quenching treatment) are maintained constant. A cylindrical specimen 25,4 mm in diameter and 100 mm long is austenized at a prescribed temperature for a prescribed time. After removal from the furnace, it is quickly mounted in the test fixture. The lower end is quenched by a jet of water of specified flow rate and temperature. Thus, the cooling rate is at a maximum here and diminishes from this end and through the test-specimen. After the specimen has cooled to room-temperature shallow flats 0,4 mm deep are cut into the specimen where a Rockwell hardness test is made. From this a hardenability curve depicting hardness versus distance from quenched end can be made.

Possibly write more here idk :)

## 23.3 Precipitation hardening

One can also elect to introduce particles of a separate phase within the original phase matrix. This is called *precipitation hardening*.

**Heat treatments** Two requisite features must be displayed by a phase diagram of an alloy system for precipitation hardening: an appreciable maximum solubility of one component in the other, on the order of several percent; and a solubility limit that rapidly decreases in concentration of the major component with temperature reduction.

**Solution heat treating** Precipitation hardening is accomplished by two different heat treatments. The first is a *solution heat treatment* in which all solute atoms are dissolved to form a single phase solid solu-

tion. This procedure is followed by rapid cooling to quenching to a temperature which for many alloys is room temperature, to the extent that any diffusion and accompanying formation of any of the  $\beta$  phase are prevented. This a nonequilibrium situation exists.

**Precipitation heat treating** For the second or *precipitation heat treatment* the supersaturated  $\alpha$  solid solution is ordinarily heated to an intermediate temperature within the  $\alpha + \beta$  phase region. The  $\beta$  precipitate begins to form as finely dispersed particles of composition  $C_\beta$  which is sometimes called *aging*. After the appropriate aging time the alloy is cooled to room temperature: normally, the cooling rate here is not important. For some alloys, aging occurs spontaneously at room temperature over extended time periods.

### 23.4 Mechanism of hardening

Precipitation hardening is commonly employed with high-strength aluminum alloys. Perhaps the most commonly studied aluminum alloy is with copper as shown on **Figure 23.1**.

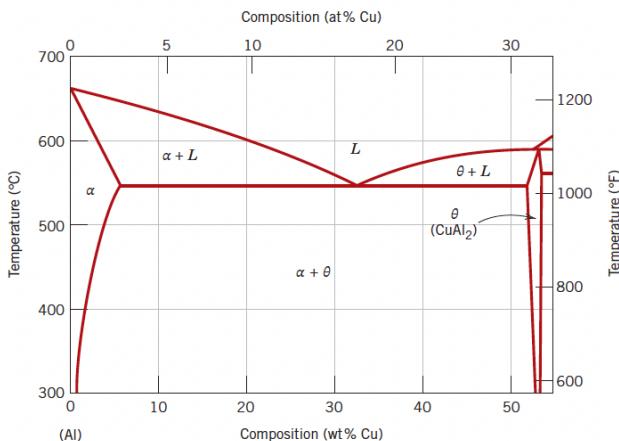


Figure 23.1: Aluminum-rich side of aluminum-copper phase diagram

The  $\alpha$ -phase is a substitutional solid solution of copper in aluminum, whereas the intermetallic compound  $\text{CuAl}_2$  is designated the  $\theta$  phase. For an aluminum-copper alloy of, say, composition 96 wt% Al–4 wt% Cu, in the development of this equilibrium  $\theta$  phase during the precipitation heat treatment, several transition phases are first formed in a specific sequence. During the initial hardening stage (at short times), copper atoms cluster together in very small thin discs that are only one or two atoms thick and approximately 25 atoms in diameter; these form at countless positions within the  $\alpha$  phase. The clusters, also called *zones*, are so small that they are not really regarded as distinct precipitate particles. However, with time and the subsequent diffusion of copper atoms, zones become particles as they increase in size. These precipitate particles then pass through two transition phases (denoted  $\theta''$  and  $\theta'$ ), before the formation of the equilibrium  $\theta$  phase. Maximum strength coincides with the formation of the  $\theta''$  phase, which may be preserved upon cooling to room temperature. The strengthening process is accelerated as the temperature is increased.

**Lecture 20: Corrosion and Degradation of Materials**

28. April 2025

## 24 Corrosion and Degradation of Materials

### 24.1 Introduction

Most materials experience some type of interaction with most environments. Often, such interactions impair a material's usefulness as a result of the deterioration of its mechanical properties, physical properties, or appearance.

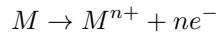
The mechanisms behind deterioration is different for the three material types. In metals, there is actual material loss either by dissolution (*corrosion*) or by the formation of a nonmetallic scale or film (*oxidation*). Ceramic materials are relatively resistant to deterioration, which usually only occurs in extreme environments – this process is also frequently called *corrosion*. For polymers, mechanisms and consequences differ from those for metals and ceramics, and the term *degradation* is most frequently used.

#### Definition 26: Corrosion

Corrosion is defined as the destructive and unintentional attack on a metal; it is electrochemical and begins at the surface.

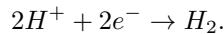
### 24.2 Electrochemical considerations

For metallic materials, the corrosion process is normally electrochemical, i.e. an oxidation reaction. A hypothetical metal M that has a valence of  $n$  (or  $n$  valence electrons) may experience oxidation according to the reaction:

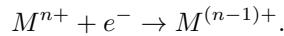


in which  $M$  becomes an  $n+$  positively charged ion and in the process loses its  $n$  valence electrons.

The electrons generated from each metal atom that is oxidized must be transferred to and become part of another chemical species in what is termed a *reduction* reaction. E.g. some metals undergo corrosion in acid solutions, which have a high concentration of  $H^+$  ions. These are reduced as follows:



Other reactions are also possible. If the acid solutions has dissolved oxygen water might be formed instead of hydrogen gas, as least to some degree and so on. Similarly, any metal ions present in the solution may also be reduced. For ions that can exist in more than one valence state (multivalent ions), reduction may occur as:



An overall electrochemical reaction must consist of at least one oxidation and one reduction reaction and will be their sums. This is called a *redox*-reaction and the individual *oxidation* and *reduction*-reactions are called *half-reactions*.

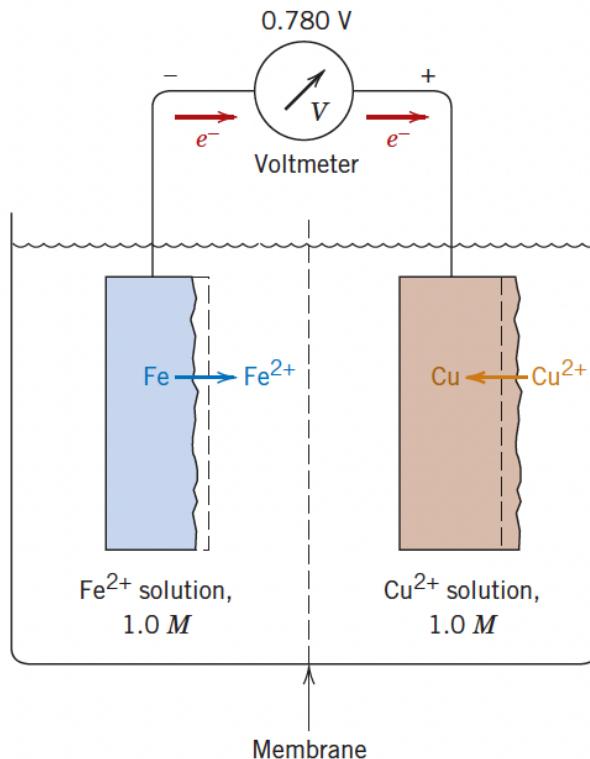
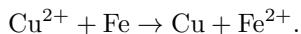


Figure 24.1: An electrochemical cell consisting of iron and copper electrodes.

#### 24.2.1 Electrode potentials

On the left hand side of **Figure 24.1** is a piece of pure iron immersed in a solution of  $\text{Fe}^{2+}$  ions of 1 M concentration. The other side similarly contains a pure copper piece immersed in a solution of copper ions. If the iron and copper electrodes are connected electrically, reduction will occur for the copper and the iron will be oxidized as follows:



Here  $\text{Cu}^{2+}$  ions deposit as metallic copper on the copper electrode, whereas iron dissolves (corrodes) on the other side and go into solution as  $\text{Fe}^{2+}$  ions.

When a net current passes through the external circuit, electrons generated from the oxidation of iron flow to the copper cell in order to reduce the  $\text{Cu}^{2+}$ . In addition, there will be some net ion motion from each cell to the other across the membrane. This is called a *galvanic couple*.

An electric potential or voltage exists between the two cell halves, and its magnitude can be determined by connecting a voltmeter. A potential of 0,78 V results for a copper-iron galvanic cell when the temperature is 25 °C.

Various electrode pairs have different voltages (e.g. a iron-zinc cell has an associated potential of 0,323 V). The magnitude of this voltage may be thought of as the driving force of the redox reaction.

### 24.2.2 The standard EMF series

These measured cell voltages represent only differences in electrical potential, and thus it is convenient to establish a reference point, or reference cell to which other cell halves may be compared. This reference point has been chosen to be hydrogen ions being reduced to hydrogen gas in the presence of a platinum catalyst.

Based on this, the *electromotive force series* shown on **Figure 24.2** can be generated. This shows the corrosion tendencies of the metals. The ones at the top are *noble* or chemically inert and as one moves down the table the metals become increasingly more active.

	<i>Electrode Reaction</i>	<i>Standard Electrode Potential, <math>V^0</math> (V)</i>
	$\text{Au}^{3+} + 3e^- \rightarrow \text{Au}$	+1.420
	$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$	+1.229
	$\text{Pt}^{2+} + 2e^- \rightarrow \text{Pt}$	~+1.2
	$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	+0.800
	$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$	+0.771
	$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4(\text{OH}^-)$	+0.401
	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	+0.340
	$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0.000
	$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$	-0.126
	$\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}$	-0.136
	$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$	-0.250
	$\text{Co}^{2+} + 2e^- \rightarrow \text{Co}$	-0.277
	$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$	-0.403
	$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	-0.440
	$\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}$	-0.744
	$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	-0.763
	$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	-1.662
	$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$	-2.363
	$\text{Na}^+ + e^- \rightarrow \text{Na}$	-2.714
	$\text{K}^+ + e^- \rightarrow \text{K}$	-2.924

Figure 24.2: EMF series

The numbers shown on **Figure 24.2** are for the reduction reactions. For the corresponding oxidation reactions the sign of the voltage must be flipped.

Let  $V_2^0$  be the cell potential for the reduction half cell and let  $V_1^0$  be the cell potential (with flipped sign) for the oxidation reaction. Then the overall cell potential  $\Delta V^0$  can be calculated as:

$$\Delta V^0 = V_2^0 - V_1^0.$$

For this reaction to occur spontaneously,  $\Delta V^0$  must be positive.

### 24.2.3 Influence of concentration and temperature on cell potential

The EMF series shown on **Figure 24.2** only applies to highly idealized electrochemical cells. Altering temperature or solution concentrations or using alloy electrodes instead of pure metals changes the cell potential, and in some cases, the spontaneous reaction direction may be reversed.

Let  $M_1$  and  $M_2$  be electrodes of pure metals, the cell potential depends on the absolute temperature  $T$  and the molar ion concentrations  $[M_1^{n+}]$  and  $[M_2^{n+}]$  according to the Nernst equation:

$$\Delta V = (V_2^0 - V_1^0) - \frac{RT}{n\mathcal{F}} \ln \left[ \frac{[M_1^{n+}]}{[M_2^{n+}]} \right]$$

where  $\mathcal{F}$  is the Faraday constant.

#### 24.2.4 The Galvanic series

Even though **Figure 24.2** is highly idealized it nonetheless indicates the relative reactivities of the metals. A more realistic and practical ranking is provided by the *Galvanic series* on **Figure 24.3**.

↑	Platinum Gold Graphite Titanium Silver Nickel alloys (Incoloy 825, Inconel 625, Hastelloy C, Chlorimet 3) Stainless steels (410, 304, 316) (passive) Monel 400 Inconel 600 (passive) Nickel 200 (passive) Copper alloys (C27000, C44300, C44400, C44500, C60800, C61400, C23000, C11000, C61500, C65500, C71500, C92300, C92200) Nickel alloys (Hastelloy B, Chlorimet 2) Inconel 600 (active) Nickel 200 (active) Copper alloys (C28000, C67500, C46400, C46500, C46600, C46700) Tin Lead Stainless steels (410, 304, 316) (active) Cast iron Wrought iron Low-carbon steel Aluminum alloys (2117, 2017, 2024) Cadmium Aluminum alloys (5052, 3004, 3003, 1100, 6053) Zinc Magnesium and magnesium alloys
↓	Increasingly inert (cathodic)  Increasingly active (anodic)

Figure 24.3: Galvanic series

### 24.3 Corrosion Rates

The half-cell potentials listed until now have assumed that the systems are at equilibrium. I.e. it has been assumed that there is no current flow through the external circuit. Real corroding systems are not at equilibrium; there is a flow of electrons from anode to cathode, which means that the previously introduced half-cell potentials cannot be applied.

Furthermore, these half-cell potentials represent the magnitude of the driving force, or the tendency for a particular reaction to take place. However, although these potentials may be used to determine spontaneous reaction directions they provide no information on corrosion rates.

The corrosion rate, or the rate of material removal as a consequence of the chemical action, is an important corrosion parameter. This may be expressed as the *corrosion penetration rate* (CPR), or the thickness loss of material per unit of time. The formula for this is:

$$\text{CPR} = \frac{KW}{\rho At}$$

where  $W$  is the weight loss after exposure time  $t$ ,  $\rho$  and  $A$  represent the density and exposed specimen area, respectively, and  $K$  is a constant. For the CPR to be expressed in millimeters per year mm/yr,  $K = 87,6$ , if one expresses weight in mg, density in g/cm<sup>3</sup>, area in cm<sup>2</sup> and time in h.

Because there is an electric current associated with electrochemical reactions, we can also express the corrosion rate in terms of this current, or more specifically the current density,  $i$ . The rate  $r$  in units of mol/m<sup>2</sup> s, is determined using the expression:

$$r = \frac{i}{nF}.$$

## 24.4 Prediction of Corrosion Rates

### 24.4.1 Polarization

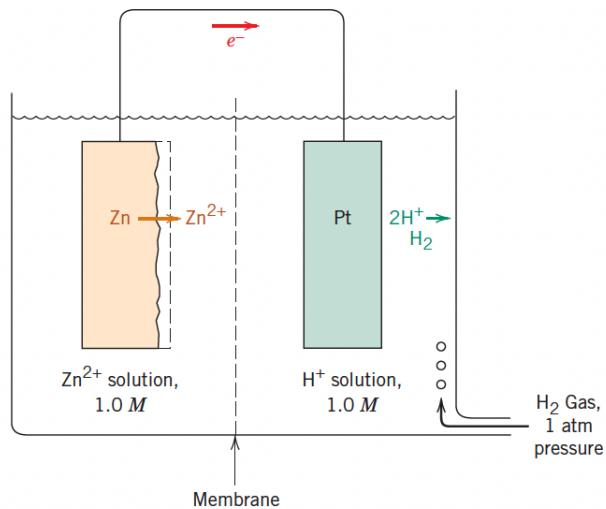


Figure 24.4: Electrochemical cell of Zinc and hydrogen that has been short-circuited

If we consider the standard Zn/H<sub>2</sub> electrochemical cell shown on **Figure 24.4** the potential of the two electrodes are not the same as shown on **Figure 24.1** because the system is not at equilibrium. The displacement of each electrode potential from its equilibrium value is termed *polarization*, and the magnitude of this displacement is the *overvoltage*, normally represented by  $\eta$ . Overvoltage is expressed in terms of plus or minus volts relative to the equilibrium potential. For example, suppose that the zinc electrode in **Figure 24.4** has a potential of -0,621 V after it has been connected to the platinum electrode. The equilibrium potential is -0,763 V and therefore:

$$\eta = -0,621 \text{ V} - (-0,763 \text{ V}) = 0,142 \text{ V}.$$

There are two types of polarization – activation and concentration.

**Activation Polarization** All electrochemical reactions consist of a sequence of steps that occur in series at the interface between the electrode and the solution. *Activation polarization* refers to the condition in which the reaction rate is controlled by the one step in the series that occurs at the slowest rate. The term *activation* is applied to this type of polarization, because an activation energy barrier is associated with this slowest, rate-limiting step.

For activation polarization, the relationship between overvoltage  $\eta_a$  and current density  $i$  is:

$$\eta_a = \pm\beta \log \frac{i}{i_0}$$

where  $\beta$  and  $i_0$  are constants for the particular half-cell. The parameter  $i_0$  is called the *exchange current density*. Equilibrium for some particular half-cell reaction is really a dynamic state on the atomic level – i.e. oxidation and reduction keep occurring but at some point they occur at the same rate so that there is no net reaction. The exchange current density is the current density at equilibrium or:

$$r_{\text{red}} = r_{\text{oxid}} = \frac{i_0}{nF}$$

Use of the term, *current density* for  $i_0$  is a little misleading inasmuch as there is no net current.  $i_0$  is determined experimentally and varies from system to system.

**Concentration Polarization** exists when the reaction rate is limited by diffusion in the solution. At high reaction rates or low solute concentrations, a depletion zone may be formed in the vicinity of the interface between the electrode and the solution, because the ions are not being replenished at an adequate pace. Thus diffusion of ions to the interface is rate controlling and the system is said to be concentration polarized.

The mathematical expression relating concentration polarization overvoltage  $\eta_c$  and current density  $i$  is:

$$\eta_c = \frac{2,3RT}{nF} \log \left( 1 - \frac{i}{i_L} \right)$$

here  $i_L$  is the limiting diffusion current density.

## 24.5 Passivity

Under particular conditions, some normally active metals and alloys lose their chemical reactivity. This phenomenon, called *passivity*, is displayed by chromium, iron, nickel, titanium and many of their alloys. It is believed that this happens as a thin oxide film on the metal surface, which serves as a protective barrier to further corrosion. Passivation is also the reason stainless steels are so resistant to oxidation. These contain at least 11% chromium, which acts as a solid-solution alloying element and minimizes the formation of rust. Aluminium also passivates.

Some metals passivate more readily than others and for some metals that are slow to form the protective oxidation layer corrosion rates may be boosted by as much as 100 000 times if the oxidation layer is broken.

## 24.6 Environmental Effects

The environmental variables which include fluid velocity, temperature and composition, can have a decided influence on the corrosion properties of the materials that are in contact with it. In most instances, increasing fluid velocity enhances the rate of corrosion due to erosive effects. The rates for most chemical reactions (including corrosion reactions) increase with temperature and the concentration of corrosive species such as  $H^+$  ions also increases corrosion rates.

Cold working a ductile metal increases its strength, but a cold-worked metal is more susceptible to corrosion than an annealed version of the same metal. Therefore one should carefully consider using cold-working in corrosive environments.

## 24.7 Forms of Corrosion

Often it is convenient, to classify corrosion according to the manner in which it manifests. Metallic corrosion is sometimes classified into eight forms: *uniform*, *galvanic*, *crevice*, *pitting*, *intergranular*, *selective leaching*, *erosion-corrosion*, and *stress corrosion*. Also the topic of Hydrogen embrittlement is presented, in a strict sense this is a type of failure rather than a form of corrosion, however, it is often a result of hydrogen produced during corrosion.

### 24.7.1 Uniform attack

Uniform attack is a form of electrochemical corrosion that occurs with equivalent intensity over the entire exposed surface and often leaves behind a scale or deposit. In a microscopic sense, the oxidation and reduction reactions occur randomly over the entire surface. Familiar examples include general rusting of steel and iron and tarnishing of silverware. This is the most common form of corrosion and it can relatively easily be predicted.

### 24.7.2 Galvanic corrosion

Galvanic corrosion occurs when two metals or alloys having different compositions are electrically coupled while exposed to an electrolyte. The less noble or more reactive of the metals experiences corrosion and the more inert metal is protected. As examples, steel screws corrode when in contact with brass in a marine environment, and if copper and steel tubing are joined in a domestic water heater, the steel corrodes in the vicinity of the junction.

The galvanic series on **Figure 24.2** indicated the relative reactivities in seawater of various metals and alloys. When two alloys are coupled in seawater, the one lower in the series experiences corrosion. It is also worth noting from this series that some alloys are listed twice (e.g. nickel and the stainless steels), in both active and passive states.

A number of measures may be taken to reduce the effects of galvanic corrosion significantly, including:

- If coupling of dissimilar metals is necessary, choose two metals that are close in the galvanic series
- Avoid an unfavourable anode-to-cathode surface area ratio; use an anode area as large as possible
- Electrically insulate dissimilar metals from each other
- Electrically connect a third, anodic metal to the other two; this is a form of cathodic protection, discussed in **subsubsection 24.9.1**

### 24.7.3 Crevice corrosion

Electrochemical corrosion may also occur as a consequence of concentration differences of ions or dissolved gases in the electrolyte solution and between two regions of the same metal piece. For such a *concentration cell*, corrosion occurs in the locale that has the lower concentration. A good example of this type of corrosion occurs in the crevices and recesses or under deposits of dirt or corrosion products where the solution becomes stagnant and there is localized depletion of dissolved oxygen. Corrosion preferentially occurring at these positions is called *crevice corrosion* and is shown on **Figure 24.5**. The crevice must be wide enough for

the solution to penetrate yet narrow enough for stagnancy: usually the width is several thousands of a millimeter.

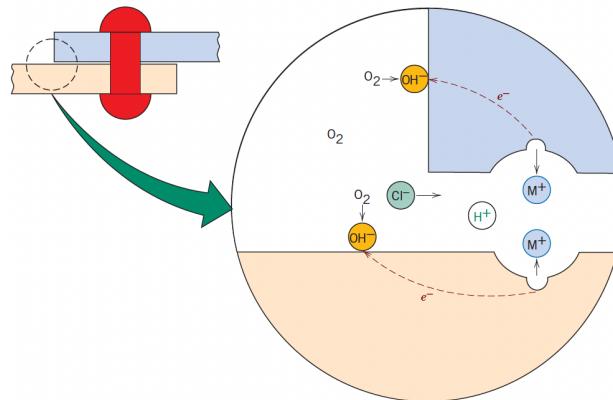


Figure 24.5: Crevice corrosion between two riveted sheets.

The proposed mechanism for crevice corrosion is illustrated in **Figure 24.5**. After oxygen has been depleted within the crevice, oxidation of the metal occurs at this position. Electrons from this electrochemical reaction are conducted through the metal to adjacent external regions, where they are consumed by reduction.

In many aqueous environments, the solution within the crevice has been found to develop high concentrations of  $\text{H}^+$  and  $\text{Cl}^-$  ions.

Crevice corrosion may be prevented by welding instead of riveting or bolting joints, and generally trying to avoid stagnant areas as much as possible.

#### 24.7.4 Pitting

Pitting is another form of very localized corrosion attack in which small pits or holes form. They ordinarily penetrate from the top of a horizontal surface downward in a nearly vertical direction. Often pitting has very little material loss and goes undetected until failure.

The mechanism in pitting is probably the same as for crevice corrosion, in that oxidation occurs within the pit itself, with complementary reduction at the surface. It is supposed that gravity causes the pits to grow downward, the solution at the pit tip becoming more concentrated and dense as the pit grows. A pit may be initiated by a localized surface defect. In fact, it has been observed that polished specimens undergo less pitting than non-polished specimens.

#### 24.7.5 Intergranular corrosion

As the name suggests, intergranular corrosion occurs preferentially along grain boundaries for some alloys and in specific environments. The net result is that a macroscopic specimen disintegrates along its grain boundaries. This type of corrosion is prevalent in some stainless steels. When heated to temperatures between 500 °C and 800 °C for sufficiently long time periods, these alloys become sensitized to intergranular attack. It is believed that this heat treatment permits the formation of small precipitate particles of chromium carbide  $\text{Cr}_2\text{C}_6$ . These particles form along the grain boundaries. Both the chromium and carbon must diffuse to

the grain boundaries to form the precipitates, which leaves achromium-depleted zone adjacent to the grain boundary. Consequentially, this grain boundary region is now highly susceptible to corrosion.

Intergranular corrosion is an especially severe problem in the welding of stainless steels when it is called *weld decay*.

#### 24.7.6 Selective leaching

Selective leaching is found in solid solution alloys and occurs when one element or constituent is preferentially removed as a consequence of corrosion processes. The most common example is the dezincification of brass, in which zinc is selectively leached from a copper-zinc brass alloy. The mechanical properties of the alloy are significantly impaired because only a porous mass of copper remains in the region that has been dezincified.

#### 24.7.7 Erosion-corrosion

Erosion-corrosion arises from the combined action of chemical attack and mechanical abrasion or wear as a consequence of fluid motion. Virtually all metal alloys are susceptible to erosion-corrosion to some degree. It is especially harmful to alloys that passivate: the abrasive action may erode away the passivation film exposing the bare metal surface. If a new protective layer is not formed quickly enough the erosion may be severe.

Erosion-corrosion is commonly found in piping, especially at bends, elbows and abrupt changes in pipe diameter.

#### 24.7.8 Stress corrosion

Stress corrosion results from the combined action of an applied tensile stress and a corrosive environment. Some materials are virtually inert in a particular corrosive medium, but become susceptible to attack once a stress is applied. Small cracks form and then propagate in a direction perpendicular to the stress. Failure behaviour is characteristic of that for a brittle material, even though the metal alloy is intrinsically ductile.

#### 24.7.9 Hydrogen embrittlement

Various metal alloys, specifically some steels, experience a significant reduction in ductility and tensile strength when atomic hydrogen penetrates into the material.

This phenomenon is called *hydrogen embrittlement*. Hydrogen in its molecular form diffuses interstitially through the crystal lattice and concentrations as low as several ppm can lead to cracking. Hydrogen embrittlement is similar to stress corrosion in that a normally ductile metal experiences brittle fracture.

### 24.8 Corrosion Environments

Corrosive environments include the atmosphere, aqueous solutions, soils, acids, bases, inorganic solvents, molten salts, liquid metals and the human body. On a tonnage basis, atmospheric corrosion accounts for

the greatest losses.

Water environments can have a variety of compositions and corrosion characteristics. Freshwater normally contains dissolved oxygen as well as minerals. Seawater contains approximately 3,5 % salt. Seawater is generally more corrosive than freshwater, frequently producing pitting and crevice corrosion.

Soils have a wide range of compositions and susceptibilities to corrosion. Compositional variables include moisture, oxygen, salt content, alkalinity and acidity as well as the presence of various forms of bacteria.

## 24.9 Corrosion prevention

Perhaps the most common and easiest way of preventing corrosion is through the judicious selection of materials once the corrosion environment has been defined.

Changing the character of the environment, if possible, may also significantly influence corrosion. Lowering the fluid temperature and/or velocity usually produces a reduction in the rate at which corrosion occurs. Often, increasing or decreasing the concentration of some species in the solution will have a positive effect.

Inhibitors are substances that, when added in relatively low concentration to the environment, decrease its corrosiveness. The specific inhibitors one can use depends on the alloys and environments one is working with.

Physical barriers to corrosion can also be applied to surfaces in the form of films or coatings. Here a large array of products are available.

### 24.9.1 Cathodic protection

One of the most effective means of corrosion prevention is *cathodic protection*. It simply involves supplying, from an external source, electrons to the metal to be protected, making it a cathode.

One cathodic protection technique employs a galvanic couple. By coupling the metal to be protected with a more reactive metal the more reactive metal “sacrifices” itself and corrodes whilst protecting the lesser reactive metal.

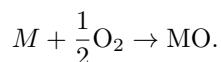
The process of *galvanizing* is simply one in which a layer of zinc is applied to the surface of steel by hot dipping. Zinc is anodic and will thus cathodically protect the steel.

The electrons can also be supplied with an external DC power source.

## 24.10 Oxidation

### 24.10.1 Mechanisms

The process of oxide layer formation is an electrochemical one, which may be expressed as:



For the oxide layer to increase in thickness it is necessary that electrons be conducted to the scale-gas interface, at which point the reduction reaction occurs. Thus, the oxide scale serves both as an electrolyte through which ions diffuse and as an electrical circuit for the passage of electrons.

#### 24.10.2 Scale types

The Pilling-Bedworth ratio is a name for the ratio of the relative volumes of oxide and metal. It can be determined as:

$$\text{P-B ratio} = \frac{A_O \rho_M}{A_M \rho_O}$$

where  $A_O$  is the molecular weight of the oxide,  $A_M$  is the molecular weight of the metal, and  $\rho_O$  and  $\rho_M$  are the oxide and metal densities, respectively.

For metals with a P-B ratio less than unity, the oxide film tends to be porous and unprotective because it is insufficient to cover the entire surface. If the ratio is greater than unity, compressive stresses result in the film as it forms. For a ratio greater than 2 to 3, the oxide coating may crack and flake off, continually exposing a fresh and unprotected metal surface. The ideal P-B ratio for the formation of a protective oxide coating is unity. Whereas unprotective ones form for P-B ratios less than unity or greater than about 2.

#### 24.10.3 Kinetics

One of the primary concerns relative to metal oxidation is the rate at which the reaction progresses. Because the oxide scales usually remains on the surface, the rate of reaction may be determined by measuring the weight gain per unit area as a function of time.

When the oxide that forms is nonporous and adheres to the metal surface, the rate of layer growth is controlled by ionic diffusion. A parabolic relationship exists between weight gain per unit area  $W$  and the time  $t$  as follows:

$$W^2 = K_1 t + K_2$$

where  $K_1$  and  $K_2$  are time-independent constants at a given temperature.

In the oxidation of metals for which the scale is porous or flakes off (i.e. for P-B ratios less than about 1 or greater than about 2), the oxidation rate expression is linear, as:

$$W = K_3 t$$

where  $K_3$  is a constant.

A third reaction rate law has been observed for very thin oxide layers (generally less than 100 nm) that form at relatively low temperatures. The dependence of weight gain on time is logarithmic and takes the form:

$$W = K_4 \log (K_5 t + K_6).$$

#### 24.10.4 Corrosion of ceramic materials

Ceramic materials, being compounds between metallic and nonmetallic elements, may be thought of as being corrosion products. Thus, they are exceedingly immune to corrosion by almost all environments, especially at room temperature.

#### 24.10.5 Degradation of polymers

Polymeric materials also experience deterioration by means of environmental interactions. However, an undesirable interaction is here called degradation rather than corrosion because the processes are dissimilar at the basic level. Polymeric degradation is not electrochemical but instead physiochemical in nature.

### 24.11 Swelling and Dissolution

When polymers are exposed to liquids, the main forms of degradation are swelling and dissolution. With swelling, the liquid or solute diffuses into and is absorbed within the polymer, the small solute molecules fit into and occupy positions among the polymer molecules. This forces apart the macromolecules such that the specimen expands or swells. The increase in chain separation leads to a reduction in the secondary intermolecular bonding forces, which in turns softens the polymer and makes it more ductile.

Swelling may be considered a partial dissolution process in which there is only limited solubility of the polymer in the solvent. Dissolution, which occurs when the polymer is completely soluble, may be thought of as a continuation of swelling. As a rule of thumb, the greater the similarity of chemical structure between the solvent and polymer, the greater the likelihood of swelling and/or dissolution. For example, many hydrocarbon rubbers readily absorb hydrocarbon liquids such as gasoline, but absorb virtually no water.

Swelling and dissolution traits also are affected by temperature, as well as by the characteristics of the molecular structure. In general, increasing molecular weight, increasing degree of crosslinking and crystallinity, and decreasing temperature result in a reduction of these deteriorative processes.

### 24.12 Bond Rupture

Polymers may also experience degradation by a process termed *scission* – the severance or rupture of molecular chain bonds. This changes the chain lengths and in turn the properties of the polymer.

#### 24.12.1 Radiation effects

Certain types of radiation possess sufficient energy to penetrate a polymer specimen and interact with the constituent atoms or their electrons. One such reaction is *ionization*, in which the radiation removes an orbital electron from a specific atom converting it into an ion. As a consequence one of the covalent bonds associated with the atom is broken and there is a rearrangement of atoms at that point.

#### 24.12.2 Chemical reaction effects

Oxygen, ozone and other substances can cause or accelerate chain scission as a result of chemical reaction. This is especially prevalent in vulcanized rubbers that have doubly bonded carbon atoms along the backbone molecular chains and are exposed to ozone.

This is why the side walls on rubber tires develop cracks as they age. These cracks result from a large number of ozone-induced scissions.

### 24.12.3 Thermal effects

Thermal degradation is the scission of molecular chains at elevated temperatures. Thermal stability is related primarily to the magnitude of the bonding energies between the various atomic constituents of the polymer: Higher bonding energies result in more thermally stable materials.

## 24.13 Weathering

Many polymeric materials serve in applications that require exposure to outdoor conditions. Any resultant degradation is termed weathering, which may be a combination of several different processes. Under these conditions, deterioration is primarily a result of oxidation, which is initiated by ultraviolet radiation from the sun. Some polymers, such as nylon and cellulose, are also susceptible to water absorption, which produces a reduction in their hardness and stiffness. Resistance to weathering among the various polymers is quite diverse. The fluorocarbons are virtually inert under these conditions; some materials, however, including poly(vinyl chloride) and polystyrene, are susceptible to weathering.