Chapter Outline

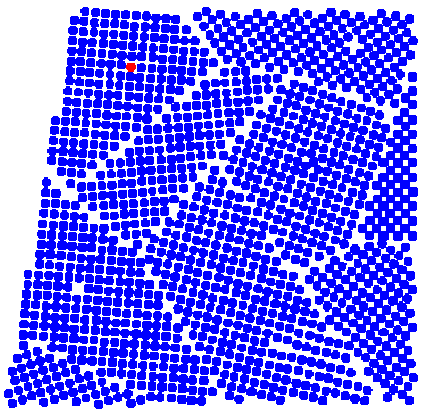
"Crystals are like people, it is the defects in them which tend to make them interesting!" - Colin Humphreys.

- **Defects in Solids**
  - **0D, Point defects**
    - ✓ vacancies
    - ✓ interstitials
    - ✓ impurities, weight and atomic composition
  - **1D, Dislocations**
    - ✓ edge
    - ✓ screw
  - **2D, Grain boundaries**
    - ✓ tilt
    - ✓ twist
  - **3D, Bulk or Volume defects**
  - **Atomic vibrations**

4.9 - 4.10 Microscopy & Grain size determination – Not Covered / Not Tested

Defects – Introduction (I)

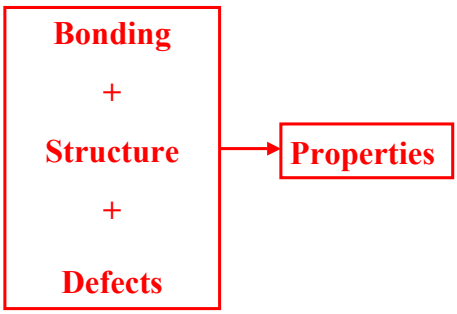
Real crystals are never perfect, there are always defects



Schematic drawing of a poly-crystal with many defects by Helmut Föll, University of Kiel, Germany.

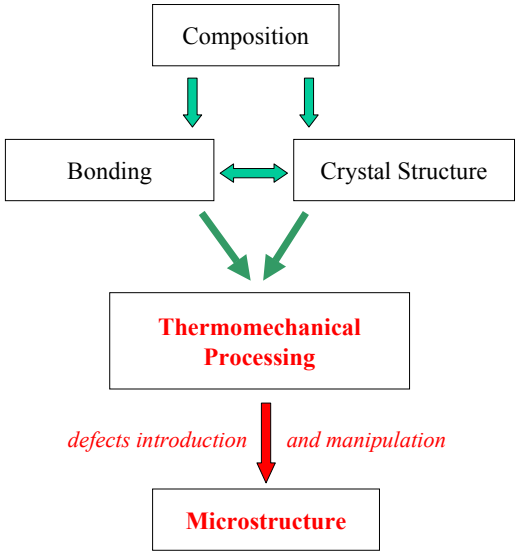
Defects – Introduction (II)

Defects have a profound impact on the macroscopic properties of materials



Defects – Introduction (III)

The processing determines the defects

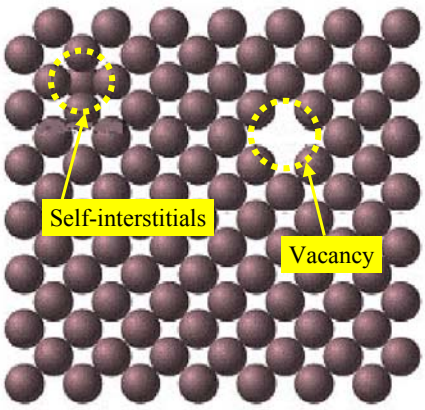


Types of Defects

Defects may be classified into four categories depending on their dimension:

- **0D, Point defects**: atoms missing or in irregular places in the lattice (vacancies, interstitials, impurities)
- **1D, Linear defects**: groups of atoms in irregular positions (e.g. screw and edge dislocations)
- **2D, Planar defects**: the interfaces between homogeneous regions of the material (grain boundaries, external surfaces)
- **3D, Volume defects**: extended defects (pores, cracks)

Point defects: vacancies & self-interstitials



Vacancy - a lattice position that is vacant because the atom is missing.

Interstitial - an atom that occupies a place outside the normal lattice position. It may be the same type of atom as the others (self interstitial) or an impurity interstitial atom.

How many vacancies are there?

The equilibrium number of vacancies formed as a result of thermal vibrations may be calculated from thermodynamics:

$$N_v = N_s \exp\left(-Q_v / k_B T\right)$$

where N_s is the number of regular lattice sites, k_B is the Boltzmann constant, Q_v is the energy needed to form a vacant lattice site in a perfect crystal, and T the temperature in Kelvin (note, not in ^oC or ^oF).

Using this equation we can estimate that at room temperature in copper there is one vacancy per 10^{15} lattice atoms, whereas at high temperature, just below the melting point there is one vacancy for every 10,000 atoms.

Note, that the above equation gives the lower end estimation of the number of vacancies, a large numbers of additional (non-equilibrium) vacancies can be introduced in a growth process or as a result of further treatment (plastic deformation, quenching from high temperature to the ambient one, etc.)

Let's estimate the number of vacancies in Cu at room T

$$N_v = N_s \exp\left(-Q_v / k_B T\right)$$

The Boltzmann's constant $k_B = 1.38 \times 10^{-23}$ J/atom-K = 8.62×10^{-5} eV/atom-K

The temperature in Kelvin T = 27^o C + 273 = 300 K.
$k_B T = 300 \text{ K} \times 8.62 \times 10^{-5}$ eV/K = 0.026 eV

The energy for vacancy formation Q_v = 0.9 eV/atom

The number of regular lattice sites $N_s = N_A \rho / A_{cu}$
$N_A = 6.023 \times 10^{23}$ atoms/mol
$\rho = 8.4$ g/cm^3
$A_{cu} = 63.5$ g/mol

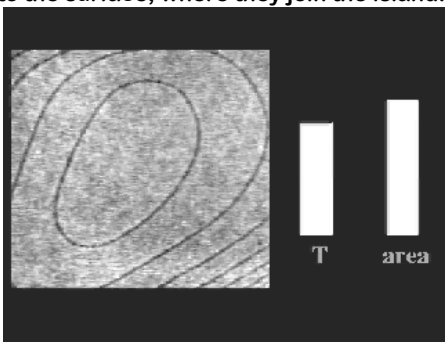
$$N_s = \frac{\left(6.023\times10^{23}\ \text{atoms}/\text{mol}\right)\times\left(8.4\ \text{g}/\text{cm}^3\right)}{63.5\ \text{g}/\text{mol}} = 8\times10^{22}\ \text{atoms}/\text{cm}^3$$

$$N_v = 8\times10^{22}\ \frac{\text{atoms}}{\text{cm}^3}\exp\left(-\frac{0.9\,\text{eV/atom}}{0.026\,\text{eV/atom}}\right) =$$

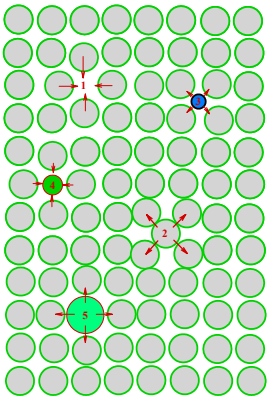
$$= 7.4\times10^{7}\ \text{vacancies}/\text{cm}^3$$

OBSERVING EQUIL. VACANCY CONC.

- **Low energy electron microscope view of a (110) surface of NiAl.**
- **Increasing T causes surface island of atoms to grow.**
- **Why? The equil. vacancy conc. increases via atom motion from the crystal to the surface, where they join the island.**



Other point defects: self-interstitials, impurities



Schematic representation of different point defects:
(1) vacancy;
(2) self-interstitial;
(3) interstitial impurity;
(4,5) substitutional impurities

The arrows show the local stresses introduced by the point defects.

Self-interstitials

Self-interstitials in metals introduce large distortions in the surrounding lattice $\Rightarrow$ the energy of self-interstitial formation is ~ 3 times larger as compared to vacancies ($Q_i \sim 3 \times Q_v$) $\Rightarrow$ equilibrium concentration of self-interstitials is very low (less than one self-interstitial per cm^3 at room T).

Impurities

Impurities - atoms which are different from the host

- All real solids are impure. Very pure metals 99.9999% - one impurity per 10^6 atoms
- May be intentional or unintentional
  Examples: carbon added in small amounts to iron makes steel, which is stronger than pure iron. Boron added to silicon change its electrical properties.
- **Alloys** - deliberate mixtures of metals
  Example: sterling silver is 92.5% silver – 7.5% copper alloy. Stronger than pure silver.

Solid Solutions

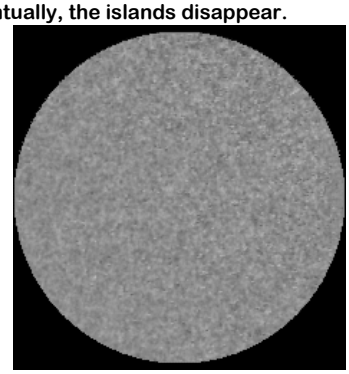
Solid solutions are made of a host (the solvent or matrix) which dissolves the minor component (solute). The ability to dissolve is called solubility.

- **Solvent**: in an alloy, the element or compound present in greater amount
- **Solute**: in an alloy, the element or compound present in lesser amount
- **Solid Solution**:
  - ✓ homogeneous
  - ✓ maintain crystal structure
  - ✓ contain randomly dispersed impurities (substitutional or interstitial)
- **Second Phase:** as solute atoms are added, new compounds / structures are formed, or solute forms local *precipitates* (discussed in Chapter 9)

Whether the addition of impurities results in formation of solid solution or second phase depends the nature of the impurities, their concentration and temperature, pressure…

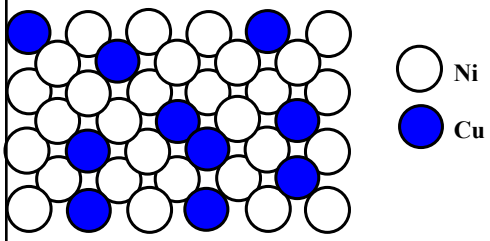
ALLOYING A SURFACE

- Low energy electron microscope view of a (111) surface of Cu.
- Sn islands move along the surface and "alloy" the Cu with Sn atoms, to make "bronze".
- The islands continually move into "unalloyed" regions and leave tiny bronze particles in their wake.
- Eventually, the islands disappear.



Reprinted with permission from: A.K. Schmid, N.C. Bartelt, and R.Q. Hwang, "Alloying at Surfaces by the Migration of Reactive Two-Dimensional Islands", Science, Vol. 290, No. 5496, pp. 1561-64 (2000). Field of view is 1.5 μm and the temperature is 290K.

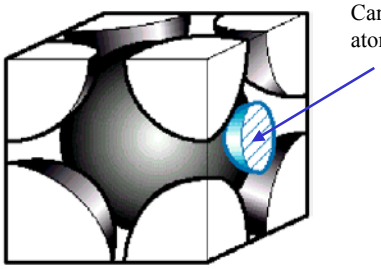
Substitutional Solid Solutions



Factors for high solubility:

- Atomic size factor - atoms need to "fit" ⇒ solute and solvent atomic radii should be within ~ 15%
- Crystal structures of solute and solvent should be the same
- Electronegativities of solute and solvent should be comparable (otherwise new inter-metallic phases are encouraged)
- Generally more solute goes into solution when it has higher valency than solvent

Interstitial Solid Solutions



Interstitial solid solution of C in α-Fe. The C atom is small enough to fit, after introducing some strain into the BCC lattice.

Factors for high solubility:

- For fcc, bcc, hcp structures the voids (or interstices) between the host atoms are relatively small ⇒ atomic radius of solute should be significantly less than solvent

Normally, max. solute concentration ≤ 10%, (2% for C-Fe)

Composition / Concentration

Composition can be expressed in

- **weight percent**, useful when making the solution
- **atom percent**, useful when trying to understand the material at the atomic level

- **Weight percent** (wt %): weight of a particular element relative to the total alloy weight. For two-component system, concentration of element 1 in wt. % is

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100$$

- **Atom percent** (at %): number of moles (atoms) of a particular element relative to the total number of moles (atoms) in alloy. For two-component system, concentration of element 1 in at. % is

$$C_1' = \frac{n_{m_1}}{n_{m_1} + n_{m_2}} \times 100$$

where $n_{m1} = m'_1/A_1$ m'_1 is weight in grams of element 1, A_1 is atomic weight of element 1)

Composition Conversions

Weight % to Atomic %:

$$C_1' = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

$$C_2' = \frac{C_2 A_1}{C_1 A_2 + C_2 A_1} \times 100$$

Atomic % to Weight %:

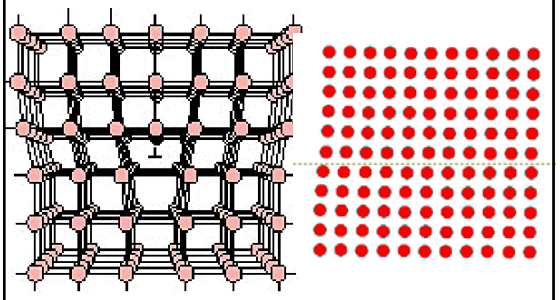
$$C_1 = \frac{C_1' A_1}{C_1' A_1 + C_2' A_2} \times 100$$

$$C_2 = \frac{C_2' A_2}{C_1' A_1 + C_2' A_2} \times 100$$

Textbook, pp. 71-74

Dislocations—Linear Defects

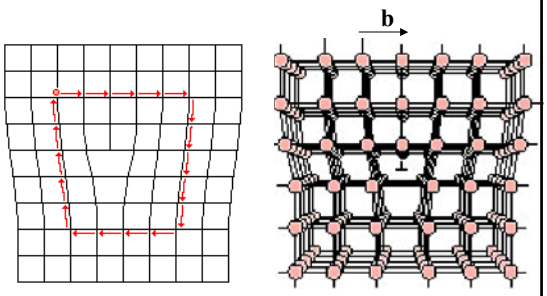
Dislocations are linear defects: the interatomic bonds are significantly distorted only in the immediate vicinity of the dislocation line. This area is called the **dislocation core**. Dislocations also create small elastic deformations of the lattice at large distances.



Dislocations are very important in mechanical properties of material (Chapters 6, 7, 8). Introduction/discovery of dislocations in 1934 by Taylor, Orowan and Polyani marked the beginning of our understanding of mechanical properties of materials.

Description of Dislocations—Burgers Vector

To describe the size and the direction of the main lattice distortion caused by a dislocation we should introduce so-called **Burgers vector b**. To find the Burgers vector, we should make a circuit from from atom to atom counting the same number of atomic distances in all directions. If the circuit encloses a dislocation it will not close. The vector that closes the loop is the Burgers vector **b**.

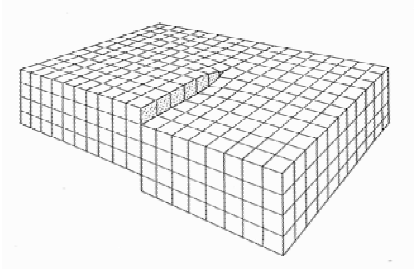


Dislocations shown above have Burgers vector directed perpendicular to the dislocation line. These dislocations are called **edge dislocations**.

Edge and screw dislocations

Dislocations shown in previous slide are **edge dislocations,** have Burgers vector directed perpendicular to the dislocation line.

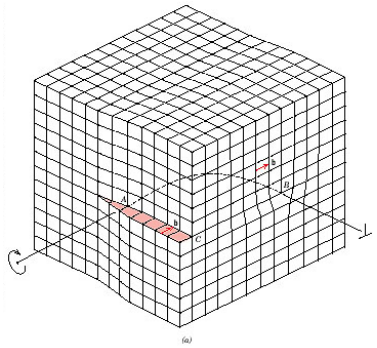
There is a second basic type of dislocation, called **screw dislocation**. The screw dislocation is parallel to the direction in which the crystal is being displaced (Burgers vector is parallel to the dislocation line).



Find the Burgers vector of a screw dislocation.
How a screw dislocation got its name?

Mixed/partial dislocations *(not tested)*

The exact structure of dislocations in real crystals is usually more complicated than the ones shown in this pages. Edge and screw dislocations are just extreme forms of the possible dislocation structures. Most dislocations have mixed edge/screw character.



To add to the complexity of real defect structures, dislocation are often split in "partial" dislocations that have their cores spread out over a larger area.

Interfacial Defects

External Surfaces

Surface atoms have have unsatisfied atomic bonds, and higher energies than the bulk atoms ⇒ Surface energy, γ (J/m^2)

- Surface areas tend to minimize (e.g. liquid drop)
- Solid surfaces can "reconstruct" to satisfy atomic bonds at surfaces.

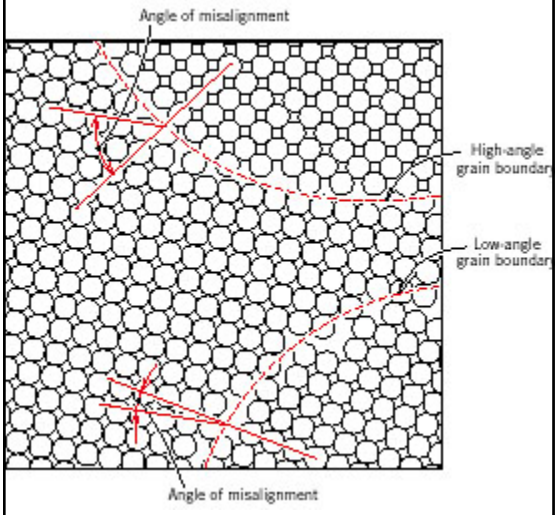
Grain Boundaries

Polycrystalline material comprised of many small crystals or grains. The grains have different crystallographic orientation. There exist atomic mismatch within the regions where grains meet. These regions are called **grain boundaries**.

Surfaces and interfaces are reactive and impurities tend to segregate there. Since energy is associated with interfaces, grains tend to grow in size at the expense of smaller grains to minimize energy. This occurs by diffusion (Chapter 5), which is accelerated at high temperatures.

High and Low Angle Grain Boundaries

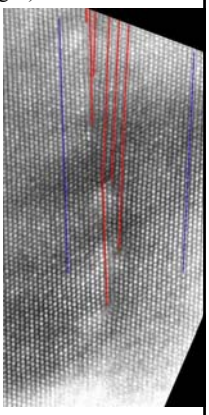
Depending on misalignments of atomic planes between adjacent grains we can distinguish between the low and high angle grain boundaries



Tilt and Twist Grain Boundaries

Low angle grain boundary is an array of aligned edge dislocations. This type of grain boundary is called **tilt boundary** (consider joint of two wedges)

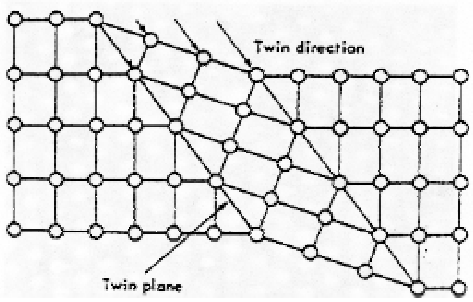
Transmission electron microscope image of a small angle tilt boundary in Si. The red lines mark the edge dislocations, the blue lines indicate the tilt angle



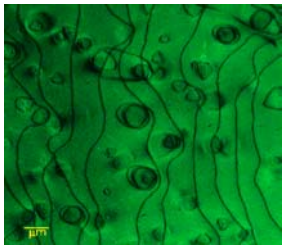
Twist boundary - the boundary region consisting of arrays of screw dislocations (consider joint of two halves of a cube and twist an angle around the cross section normal)

Twin Boundaries *(not tested)*

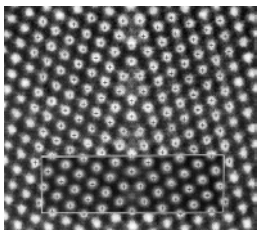
Low-energy **twin boundaries** with mirrored atomic positions across boundary may be produced by deformation of materials. This gives rise to **shape memory metals**, which can recover their original shape if heated to a high temperature. Shape-memory alloys are twinned and when deformed they untwin. At high temperature the alloy returns back to the original twin configuration and restore the original shape.



Electron Microscopy *(not tested)*



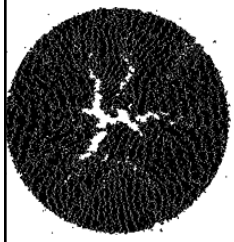
Dislocations in Nickel (the dark lines and loops), transmission electron microscopy image, Manchester Materials Science Center.



High-resolution Transmission Electron Microscope image of a tilt grain boundary in aluminum, Sandia National Lab.

Bulk or Volume Defects

- **Pores** - can greatly affect optical, thermal, mechanical properties
- **Cracks** - can greatly affect mechanical properties
- **Foreign inclusions** - can greatly affect electrical, mechanical, optical properties



A cluster of microcracks in a melanin granule irradiated by a short laser pulse. Computer simulation by L. V. Zhigilei and B. J. Garrison.

Atomic Vibrations

- Heat causes atoms to vibrate
- Vibration amplitude increases with temperature
- Melting occurs when vibrations are sufficient to rupture bonds
- Vibrational frequency ~ 10^{13} Hz
- Average atomic energy due to thermal excitation is of order kT

Summary

Make sure you understand language and concepts:

- Alloy
- Atom percent
- Atomic vibration
- Boltzmann's constant
- Burgers vector
- Composition
- Dislocation line
- Edge dislocation
- Grain size
- Imperfection
- Interstitial solid solution
- Microstructure
- Point defect
- Screw dislocation
- Self-Interstitial
- Solid solution
- Solute
- Solvent
- Substitutional solid solution
- Vacancy
- Weight percent