STRUCTURE OF MATERIALS
The Key to its Properties
A Multiscale Perspective

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Properties of Materials
The Scale of “Microstructures”
Crystal Structures
+ Defects
→ Microstructure
With Examples from the Materials World
PROPERTIES

Structure sensitive
E.g. Yield stress, Fracture toughness

Structure Insensitive
E.g. Density, Elastic Modulus

Structure ⇒ Microstructure
What determines the properties?

- Cannot just be the composition!
  - Few 10s of ppm of Oxygen in Cu can degrade its conductivity
- Cannot just be the amount of phases present!
  - A small amount of cementite along grain boundaries can cause the material to have poor impact toughness
- Cannot just be the distribution of phases!
  - Dislocations can severely weaken a crystal
- Cannot just be the defect structure in the phases present!
  - The presence of surface compressive stress toughens glass

Length Scales Involved

Nucleus → Atom → Crystal → Microstructure → Component

Defects

Length Scales:
- Angstroms: $10^{-10}$ to $10^{-9}$
- Nanometers
- Microns
- Centimeters

Dislocation Stress fields → Nanometers

Microstructure

Grain Size

*Simple Unit Cells
Processing determines shape and microstructure of a component.
Processing determines shape and microstructure of a component

Atom → Structure → Crystal → Microstructure → Component

Thermo-mechanical Treatments:
- Casting
- Metal Forming
- Welding
- Powder Processing
- Machining

Phases + Defects:
- Crystalline
- Quasicrystalline
- Amorphous
- Ferromagnetic
- Ferroelectric
- Superconducting
- Vacancies
- Dislocations
- Twins
- Stacking Faults
- Grain Boundaries
- Voids
- Cracks

Structure based:
- Avoid Stress Concentrators
- Good Surface Finish

Property based:

Residual Stress
Why is BCC Iron the stable form of Iron at room temperature and not the FCC form of Iron?

G vs T showing regions of stability of FCC and BCC Iron

(Computed using thermo-calc software and database developed at the Royal Institute of Technology, Stockholm)

This *functional* definition of “microstructure” includes all length scales.
Microstructure

- Phases
- Defects
- Residual Stress

Defects:
- Vacancies
- Dislocations
- Twins
- Stacking Faults
- Grain Boundaries
- Voids
- Cracks
Microstructure

Phases + Defects +

- Vacancies
- Dislocations
- Twins
- Stacking Faults
- Grain Boundaries
- Voids
- Cracks

Residual Stress

Defects (Crystalline)
- Vacancies
- Dislocations

Microstructural
- Phase Transformation
- Voids
- Cracks

Component
- Stress corrosion cracking
- Residual Surface Compressive Stress
CRYSTAL STRUCTURES
Crystal =

Lattice *(Where to repeat)*

+ 

Motif *(What to repeat)*

Crystal =

Space group *(how to repeat)*

+ 

Asymmetric unit *(Motif': what to repeat)*

*Unit cell of BCC lattice*
Progressive lowering of symmetry amongst the 7 crystal systems

- Cubic
  - Tetragonal
  - Orthorhombic
- Monoclinic
- Triclinic

Arrow marks lead from supergroups to subgroups
1. Cubic Crystals

\[ a = b = c \]

\[ \alpha = \beta = \gamma = 90^\circ \]

- Simple Cubic (P)
- Body Centred Cubic (I) – BCC
- Face Centred Cubic (F) - FCC

Point groups \( \Rightarrow 23, \bar{4}3m, m\bar{3}, \bar{4}32, \frac{4}{m}, \frac{3}{m}, \frac{2}{m} \)

Fluorite Octahedron

Garnet Dodecahedron

Pyrite Cube

[Vapor grown NiO crystal
Tetrakaidecahedron
(Truncated Octahedron)]

Crystals and Properties

- (The symmetry of) Any physical property of a crystal has at least the symmetry of the crystal
- Crystals are anisotropic with respect to most properties
- The growth shape of a (well grown) crystal has the internal symmetry of the crystal
- Polycrystalline materials or aggregates of crystals may have isotropic properties (due to averaging of many randomly oriented grains)
- The properties of a crystal can be drastically altered in the presence of defects (starting with crystal defects)
CLASSIFICATION OF DEFECTS BASED ON DIMENSIONALITY

0D (Point defects)
- Vacancy
- Impurity
- Frenkel defect
- Schottky defect

1D (Line defects)
- Dislocation
- Disclination
- Dispiration

2D (Surface / Interface)
- Surface
- Interphase boundary
- Grain boundary
- Twin boundary
- Stacking faults
- Anti-phase boundaries

3D (Volume defects)
- Twins
- Precipitate
- Faulted region
- Voids / Cracks
- Thermal vibration
Imperfect point-like regions in the crystal about the size of 1-2 atomic diameters
Vacancy

- Missing atom from an atomic site
- Atoms around the vacancy displaced
- Tensile stress field produced in the vicinity

Tensile Stress Fields
**SUBSTITUTIONAL IMPURITY**
- Foreign atom replacing the parent atom in the crystal
- E.g. Cu sitting in the lattice site of FCC-Ni

**INTERSTITIAL IMPURITY**
- Foreign atom sitting in the void of a crystal
- E.g. C sitting in the octahedral void in HT FCC-Fe
Interstitial C sitting in the octahedral void in HT FCC-Fe

- $r_{\text{Octahedral void}} / r_{\text{FCC atom}} = 0.414$
- $r_{\text{Fe-FCC}} = 1.29 \text{ Å}$ $\Rightarrow$ $r_{\text{Octahedral void}} = 0.414 \times 1.29 = 0.53 \text{ Å}$
- $r_C = 0.71 \text{ Å}$
- $\Rightarrow$ Compressive strains around the C atom
- Solubility limited to 2 wt% (9.3 at%)

Interstitial C sitting in the octahedral void in LT BCC-Fe

- $r_{\text{Tetrahedral void}} / r_{\text{BCC atom}} = 0.29 \cdot r_C = 0.71 \text{ Å}$
- $r_{\text{Fe-BCC}} = 1.258 \text{ Å}$ $\Rightarrow$ $r_{\text{Tetrahedral void}} = 0.29 \times 1.258 = 0.364 \text{ Å}$
- $\Rightarrow$ But C sits in smaller octahedral void- displaces fewer atoms
- $\Rightarrow$ Severe compressive strains around the C atom
- Solubility limited to 0.008 wt% (0.037 at%)
Equilibrium Concentration of Vacancies

- Formation of a vacancy leads to missing bonds and distortion of the lattice
- The potential energy (Enthalpy) of the system increases
- Work required for the formation of a point defect → Enthalpy of formation ($\Delta H_f$) [kJ/mol or eV/defect]
- Though it costs energy to form a vacancy its formation leads to increase in configurational entropy
- $\Rightarrow$ above zero Kelvin there is an equilibrium number of vacancies

$$\Delta G = \Delta H - T \Delta S$$

$$S_{Config} = k \ln(\omega)$$

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Kr</th>
<th>Cd</th>
<th>Pb</th>
<th>Zn</th>
<th>Mg</th>
<th>Al</th>
<th>Ag</th>
<th>Cu</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>kJ / mol</td>
<td>7.7</td>
<td>38</td>
<td>48</td>
<td>49</td>
<td>56</td>
<td>68</td>
<td>106</td>
<td>120</td>
<td>168</td>
</tr>
<tr>
<td>eV / vacancy</td>
<td>0.08</td>
<td>0.39</td>
<td>0.5</td>
<td>0.51</td>
<td>0.58</td>
<td>0.70</td>
<td>1.1</td>
<td>1.24</td>
<td>1.74</td>
</tr>
</tbody>
</table>
- Certain equilibrium number of vacancies are preferred at $T > 0K$

- Vacancies play a role in:
  - Diffusion
  - Climb
  - Electrical conductivity
  - Creep etc.
1D
(Line defects)
The shear modulus of metals is in the range 20 – 150 GPa

\[ \tau_m = \frac{G}{2\pi} \]

The theoretical shear stress will be in the range 3 – 30 GPa

Actual shear stress is 0.5 – 10 MPa

I.e. (Shear stress)_{theoretical} > 100 * (Shear stress)_{experimental} !!!!

Dislocations weaken the crystal
Usually dislocations have a mixed character and *Edge* and *Screw* dislocations are the ideal extremes.
Motion of dislocations

Conservative
(Glide)

Non-conservative
(Climb)

Motion of Edge dislocation

Motion of dislocation \perp to the slip plane

- For edge dislocation: as \( \mathbf{b} \perp \mathbf{t} \rightarrow \) they define a plane \( \rightarrow \) the slip plane
- Climb involves addition or subtraction of a row of atoms below the half plane
  - +ve climb = climb up \( \rightarrow \) removal of a plane of atoms
  - -ve climb = climb down \( \rightarrow \) addition of a plane of atoms
Mixed dislocations

Pure Edge

Pure screw
Role of Dislocations

- Slip
- Fracture
- Fatigue
- Creep
- Diffusion (Pipe)

Structural

- Incoherent Twin
- Grain boundary (low angle)
- Semicohherent Interfaces
- Disc of vacancies ~ edge dislocation

Creep mechanisms in crystalline materials

- Cross-slip
- Dislocation climb
- Vacancy diffusion
- Grain boundary sliding
2D
(Surface / Interface)
<p>| The grain boundary region may be distorted with atoms belonging to neither crystal |
| The thickness may be of the order of few atomic diameters |
| The crystal orientation changes abruptly at the grain boundary |
| In an low angle boundary the orientation difference is $&lt; 10^\circ$ |
| In the low angle boundary the distortion is not so drastic as the high-angle boundary → can be described as an array of dislocations |
| <strong>Grain boundary energy is responsible for grain growth on heating</strong> |
| $\sim (&gt;0.5T_m)$ |
| Large grains grow at the expense of smaller ones |
| The average no. of nearest neighbours for an atom in the grain boundary of a close packed crystal is 11 |</p>
<table>
<thead>
<tr>
<th>Type of boundary</th>
<th>Energy (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain boundary between BCC crystals</td>
<td>0.89</td>
</tr>
<tr>
<td>Grain boundary between FCC crystals</td>
<td>0.85</td>
</tr>
<tr>
<td>Interface between BCC and FCC crystals</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Grain boundaries in SrTiO$_3$
Twin Boundary

- The atomic arrangement on one side of the twin boundary is related to the other side by a symmetry operation (usually a mirror).
- Mirror twin boundaries usually occur in pairs such that the orientation difference introduced by one is restored by the other.
- The region between the regions is called the twinned region.

Annealing twins (formed during recrystallization)

Deformation twins (formed during plastic deformation)

Twin boundary in Fe doped SrTiO₃ bicrystals (*artificially prepared*)

High-resolution micrograph

Grain size and strength

\[ \sigma_y = \sigma_i + \frac{k}{\sqrt{d}} \]

- \( \sigma_y \rightarrow \) Yield stress
- \( \sigma_i \rightarrow \) Stress to move a dislocation in single crystal
- \( k \rightarrow \) Locking parameter (measure of the relative hardening contribution of grain boundaries)
- \( d \rightarrow \) Grain diameter

Hall-Petch Relation
Defects:

Further Enquiry
The role played by a random defect is very different from the role played by a structural defect in various phenomena.
Low Angle Grain Boundaries
No visible Grain Boundary

~8º TILT BOUNDARY IN SrTiO₃ POLYCRYSTAL

Dislocation structures at the Grain boundary

Fourier filtered image
Ordered defects become part of the structure and hence affect the basic symmetry of the structure.

- Vacancies
- Stacking Faults
Crystal with vacancies

E.g. $V_6C_5$, $V_8C_7$
Effect of Atomic Level Residual Stress

Yield Point Phenomenon

Interaction of the stress fields of dislocations’ with Interstitial atoms’
3D
(Volume defects)

&

MICROSTRUCTURES
HAADF micrographs of the GP zones:
(a) Intercalated monatomic Cu layers several nm in width are clearly resolved,
(b) a GP-zone two Cu layers thick can ‘chemically’ be identified.

Bright field TEM micrograph of an Al-3.3% Cu alloy, aged at room temperature for 100 days, showing the GP-I zones.
Precipitate particle

Hardening effect

Increase in surface area due to particle shearing

Part of the dislocation line segment (*inside the precipitate*) could face a higher PN stress
Pinning effect of the precipitate

Can act like a Frank-Reed source

\[ \tau \sim \frac{Gb}{2r} \]
Controlling microstructures:

*Examples*
Fe-Cementite diagram

Peritectic

L + δ → γ

1493°C

ε

Eutectic

L → γ + Fe₃C

1147°C

γ

γ + Fe₃C

723°C

Eutectoid

γ → α + Fe₃C

2.06

- Austenite (γ) → FCC
- Ferrite (α) → BCC
- Cementite (Fe₃C) → Orthorhombic

Fe → Fe₃C

0.16 0.8 4.3 6.7

%C →

[1] rruff.geo.arizona.edu/doclib/zk/vol74/ZK74_534.pdf
Time-Temperature-Transformation (TTT) Curves – Isothermal Transformation

Eutectoid steel (0.8%C)

- Austenite
- Pearlite
- Pearlite + Bainite
- Bainite
- Martensite

Eutectoid temperature

Ms → Mf


Time-Temperature-Transformation (TTT) Curves – Isothermal Transformation

Austenite

Pearlite

Pearlite + Bainite

Bainite

Martensite

Eutectoid steel (0.8% C)

\( Eutectoid temperature \)

\( T \)

\( t \) (s)

\( M_s \)

\( M_f \)
Different cooling treatments

Eutectoid steel (0.8%C)

M = Martensite

P = Pearlite

Water quench

Oil quench

Normalizing

Full anneal

Coarse P

Fine P
Harness of Martensite as a function of Carbon content

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Hardness (Rc)</th>
<th>Tensile strength (MN / m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse pearlite</td>
<td>16</td>
<td>710</td>
</tr>
<tr>
<td>Fine pearlite</td>
<td>30</td>
<td>990</td>
</tr>
<tr>
<td>Bainite</td>
<td>45</td>
<td>1470</td>
</tr>
<tr>
<td>Martensite</td>
<td>65</td>
<td>-</td>
</tr>
<tr>
<td>Martensite tempered at 250 °C</td>
<td>55</td>
<td>1990</td>
</tr>
</tbody>
</table>
Cooling

[C1, C2, C3] → T → 0.80.02

Eutectoid

\[ \gamma \rightarrow \alpha + \text{Fe}_3\text{C} \]

Pro-eutectoid

Cementite

Pearlite

White CI:
3.4% C, 0.7% Si, 0.6% Mn

Grey CI:
3.4% C, 1.8% Si, 0.5% Mn

Nodular CI:
3.4% C, 0.1% P, 0.4% Mn, 1.0% Ni, 0.06% Mg

Malleable CI:
2.5% C, 1.0% Si, 0.55% Mn

Heat Treatment

\[
\text{Fe}_3\text{C} \rightarrow \text{Graphite Nodules}
\]

Change Composition

L → γ + (Fe₃C) → α + Fe₃C + (Fe₃C)

Graphite nodules

Ferrite

Ferritic Matrix

10 μm

Fully Malleabilized

10 μm
Texture can reintroduce anisotropy in material properties

Cubic Crystal (3 Elastic Moduli)

Anisotropic

Polycrystal

Isotropic

[100]

Schematic

Texture

Rolling/Extrusion

Anisotropic

Cold Worked

Elongated

Equiaxed

Annealed

Textured samples

Moly Permalloy: 4% Mo, 79% Ni, 17% Fe

To understand the properties of materials the structure at many different lengthscales must be viewed.
Ionic Crystals

- Overall electrical neutrality has to be maintained

Frenkel defect

- Cation (being smaller get displaced to interstitial voids)
- E.g. AgI, CaF$_2$
Schottky defect

- Pair of anion and cation vacancies
- E.g. Alkali halides
Other defects due to charge balance

- If \( \text{Cd}^{2+} \) replaces \( \text{Na}^{+} \) → one cation vacancy is created

Defects due to off stoichiometry

- \( \text{ZnO} \) heated in \( \text{Zn} \) vapour → \( \text{Zn}_y\text{O} \) \((y > 1)\)
- The excess cations occupy interstitial voids
- The electrons (2\(e^-\)) released stay associated to the interstitial cation
- FeO heated in oxygen atmosphere → Fe$_x$O  ($x < 1$)
- Vacant cation sites are present
- Charge is compensated by conversion of ferrous to ferric ion:
  \[
  \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-
  \]
- For every vacancy (of Fe cation) two ferrous ions are converted to ferric ions → provides the 2 electrons required by excess oxygen
Progressive lowering of symmetry amongst the 7 crystal systems

Arrow marks lead from supergroups to subgroups

Superscript to the crystal system is the order of the lattice point group
A semimetal is a material with a small overlap in the energy of the conduction band and valence bands. However, the bottom of the conduction band is typically situated in a different part of momentum space (at a different k-vector) than the top of the valence band. One could say that a semimetal is a semiconductor with a negative indirect bandgap, although they are seldom described in those terms.

Schematically, the figure shows
A) a semiconductor with a direct gap (like e.g. CuInSe₂),
B) a semiconductor with an indirect gap (like Si) and
C) a semimetal (like Sn or graphite).

The figure is schematic, showing only the lowest-energy conduction band and the highest-energy valence band in one dimension of momentum space (or k-space). In typical solids, k-space is three dimensional, and there are an infinite number of bands.

Unlike a regular metal, semimetals have charge carriers of both types (holes and electrons), so that one could also argue that they should be called 'double-metals' rather than semimetals. However, the charge carriers typically occur in much smaller numbers than in a real metal. In this respect they resemble degenerate semiconductors more closely. This explains why the electrical properties of semimetals are partway between those of metals and semiconductors.

As semimetals have fewer charge carriers than metals, they typically have lower electrical and thermal conductivities. They also have small effective masses for both holes and electrons because the overlap in energy is usually the result of the fact that both energy bands are broad. In addition they typically show high diamagnetic susceptibilities and high lattice dielectric constants.

The classic semimetallic elements are arsenic, antimony, and bismuth. These are also considered metalloids but the concepts are not synonymous. Semimetals, in contrast to metalloids, can also be compounds, such as HgTe, and tin and graphite are typically not considered metalloids.

Graphite and hexagonal boronitride (BN) are an interesting comparison. The materials have essentially the same layered structure and are isoelectronic, which means that their band structure should be rather similar. However, BN is a white semiconductor and graphite a black semimetal, because the relative position of the bands in the energy direction is somewhat different. In one case the bandgap is positive (like case B in the figure), explaining why BN is a semiconductor. In the other case the conduction band lies sufficiently lower to overlap with the valence band in energy, rendering the value for the bandgap negative (see C).
