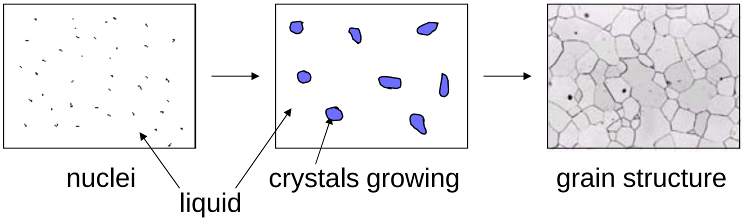
CHP 4: IMPERFECTIONS IN SOLIDS

ISSUES TO ADDRESS...

- What are the Solidification mechanisms?
- What types of defects arise in solids?
- Can the number and type of defects be varied and controlled?
- How do defects affect material properties?
- Are defects undesirable?

Imperfections in Solids

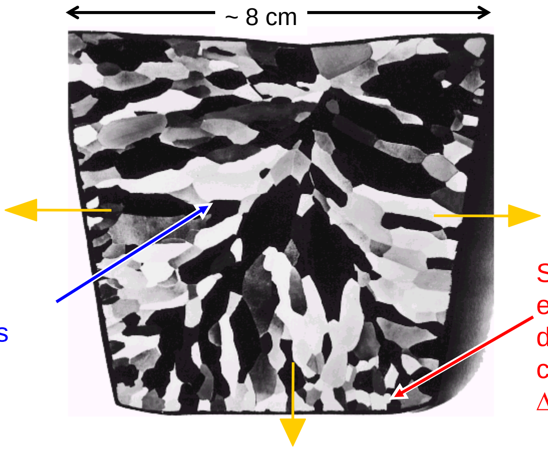
- Solidification- result of casting of molten material
  - 2 steps
    - Nuclei form
    - Nuclei grow to form crystals – grain structure
- Start with a molten material – all liquid



- Crystals grow until they meet each other

Solidification

Grains can be - equiaxed (roughly same size in all directions)
- columnar (elongated grains)



heat
flow

Columnar in area with less undercooling

Shell of equiaxed grains due to rapid cooling (greater ΔT) near wall

Grain refiner - added to make smaller, more uniform, equiaxed grains.

Types of Imperfections

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

atomic size defects

Point defects

- Dislocations

lines defects

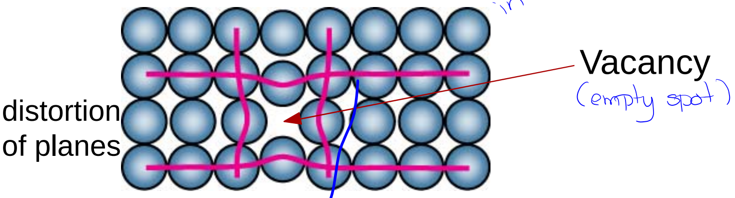
- grain Boundaries

Area defects

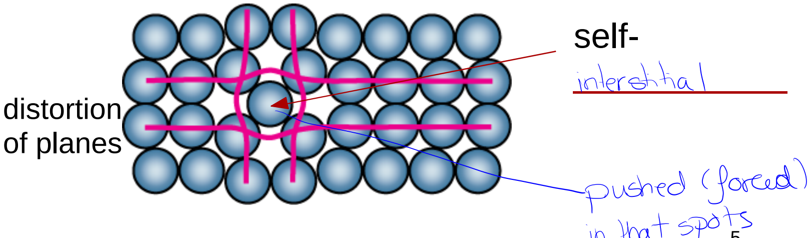
Point Defects

- Vacancies:
  -vacant atomic sites in a structure.

slight distortions in atomic structure



- Self-I interstitials:
  -"extra" atoms positioned between atomic sites.



POINT DEFECTS

VACANCY - Missing atom from lattice.

Sometimes produced during solidification, sometimes by physical factors, (heating, neutrons, working) but present in all crystals.

Usually low, but reaches 1 vacancy in 10,000 atoms as temperature rises to melting point.

Equilibrium Concentration: Point Defects

- Equilibrium concentration varies with Temperature !

No. of defects

Activation energy

No. of potential defect sites.

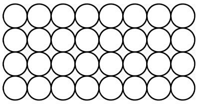
$$\frac{N_v}{N} = \exp\left(\frac{-Q_v}{kT}\right)$$

Temperature

Boltzmann's constant

$(1.38 \times 10^{-23}$ J/atom-K)

$(8.62 \times 10^{-5}$ eV/atom-K)



Each lattice site is a potential vacancy site

MEASURING Activation ENERGY

- We can get Q from an experiment.

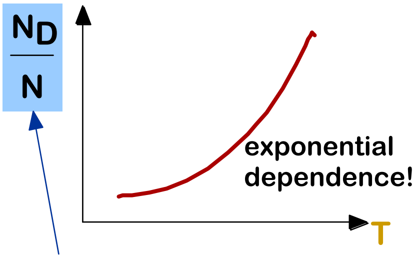
$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)$$

taking natural logs of both sides….

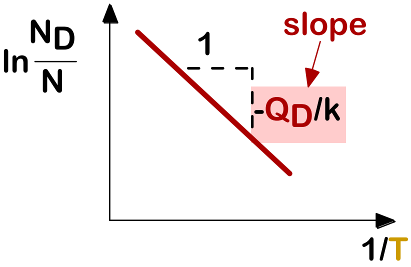
$$\ln\left[\frac{N_D}{N}\right] = -\frac{Q_D}{k}\frac{1}{T}$$

- Measure this...

Plot $\ln\left[\frac{N_D}{N}\right]$ versus $\frac{1}{T}$



defect concentration



ESTIMATING VACANCY CONC.

- **Find the equil. # of vacancies in 1m^3 of Cu at 1000C.**
- **Given:**

$\rho = 8.4$ g/cm^3 $\quad A_{Cu} = 63.5$g/mol

$Q_V = 0.9$eV/atom $\quad N_A = 6.02 \times 10^{23}$ atoms/mole

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right) = 2.7 \cdot 10^{-4}$$

0.9eV/atom

1273K

8.62×10^{-5} eV/atom-K

For 1m^3, $N = \rho \times \frac{N_A}{A_{Cu}} \times 1\text{m}^3 = 8.0 \times 10^{28}$ sites

- **Answer:**

$N_D = 2.7 \cdot 10^{-4} \cdot 8.0 \times 10^{28}$ sites $= 2.2 \times 10^{25}$ vacancies

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impurities IN SOLIDS

Pure metals are difficult to make and not often used.

Gold (usually alloyed Cu, Ni, Pt) → to increase mechanical strength

24 Carat = 99.98%-99.95% gold, thus 14 carat = 14/24th

Copper (99.99%) for electronics as impurities reduce electrical conductivity.

Platinum for thermo-electric applications.

Usually engineering metals are combined with other metals or elements to give alloys. (increased strength, corrosion resistance etc.)

mixtures ↓

e.g. STEEL → Iron (Fe) + Carbon (C)
Brass → Cu + Zn (zinc)
BRONZE → Cu + Sn (tin)
TITANIUM Alloy → Ti + 4 Al + 6 V (vanadium)
Nimonics up to10 metals

Simplest alloy is **SOLID SOLUTION.**

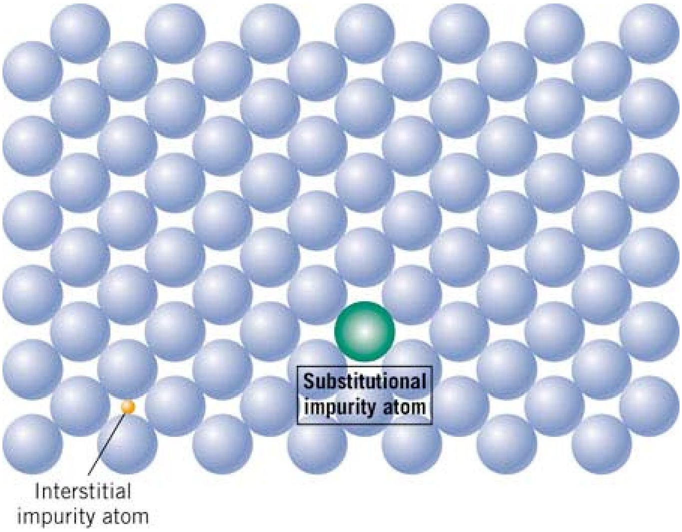
Atoms of Element B are dissolved randomly into Element A (host).
"SOLVENT" - major element (host)
“ Solute " - minor element (impurity)

One phase (all crystals/grains are the same as the next except for orientation i.e. same composition).
e.g.. Liquid solutions - water + alcohol

SUBSTITUTIONAL AND interstitial SOLID SOLUTIONS

SUBSTITUTIONAL SOLID SOLUTIONS

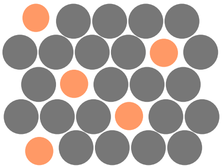
A host atom is replaced by a different type of atom. The substitutional atom can be either larger or smaller than the host atom but occupies its position. Causes a distortion to surrounding lattice.



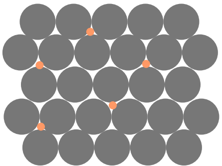
__________ Defects in Alloys

Two outcomes if impurity (B) added to host (A):

- Solid solution of B in A (i.e., random dist. of point defects)



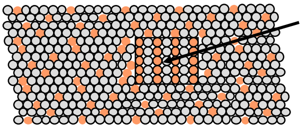
OR



Substitutional solid soln.
(e.g., Cu in Ni)

Interstitial solid soln.
(e.g., C in Fe)

- Solid solution of B in A plus particles of a new __________ (usually for a larger amount of B)



Second phase particle
--different composition
--often different structure.

Imperfections in Solids

Conditions for substitutional solid solution (S.S.)

- W. Hume – __________ rule
  - – 1. Δr (atomic radius) < 15%
  - – 2. Proximity in periodic table
    - i.e., similar electronegativities
  - – 3. Same __________ structure for pure metals
  - – 4. Valency
    - All else being equal, a metal will have a greater tendency to dissolve a metal of higher valency than one of lower valency

A slight difference in size can be tolerated (a slight distortion to lattice), but there is a limit to this, e.g.

	Copper (FCC)	-	Nickel (FCC)	Size%
r =	0.128 nm		0.125 nm	2.3%

Similar electronegativites, valence: Cu: +1, (+2), Ni: +2. **100% solubility.**

Whereas:	Copper (fcc)	-	Lead (fcc)	Size%
r =	0.128		0.175	36.7

Only 0.1% solubility

INTERSTITIAL SOLID SOLUTIONS

Impurity atoms go into spaces (____________) between host atoms. Usually spaces are __________so interstitial atoms have to be small.

E.g. Hydrogen atoms in iron (from poor welding) - bad
Carbon atoms in iron – deliberate – to produce steel.

COMPOSITIONS

In industry usually use weight % for alloys: easier to add x kgs of Mg to Y tonnes of Aluminum.

$$C_1 = \frac{m_1}{m_1 + m_2} x100$$

C1 is the wt% of element 1 where m_1 and m_2 are the weights of elements 1 and 2.

For chemical/scientific measures often need **atomic %.**

$$C'_1 = \frac{n_{m1}}{n_{m1} + n_{m2}} x100 \qquad n_{m1} = \frac{m'_1}{A_1} \qquad (\text{g/g.mol}^{-1}) \rightarrow \text{mol.}$$

n_{m1} is the number of moles of element 1, m'_1 is the mass (grams) and A_1 is the atomic weight of element 1 (g/mole) etc.

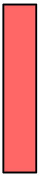
Line Defects

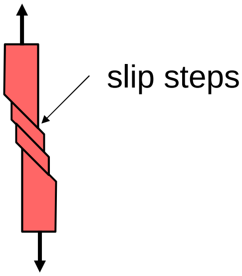
Dislocations:

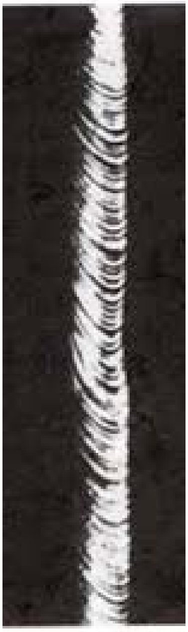
- are line defects,
- _________between crystal planes result when dislocations move,
- produce _____________ (plastic) deformation.

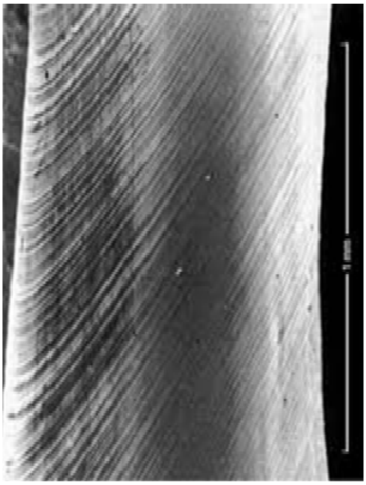
Schematic of Zinc (HCP):

- before deformation
- after tensile elongation









Imperfections in Solids

Linear Defects (Dislocations)

- Are one-dimensional defects around which atoms are misaligned

- Edge dislocation:
  - extra half-plane of atoms inserted in a crystal structure
  - **b** ⊥ to dislocation line
- Screw dislocation:
  - spiral planar ramp resulting from shear deformation
  - **b** || to dislocation line

Burger’s vector, **b**: measure of lattice distortion

Dislocations make metals weaker than they should be, BUT also allow metals to be deformed (ie. allow plastic deformation).(Chp. 6)

Imperfections in Solids

Edge Dislocation

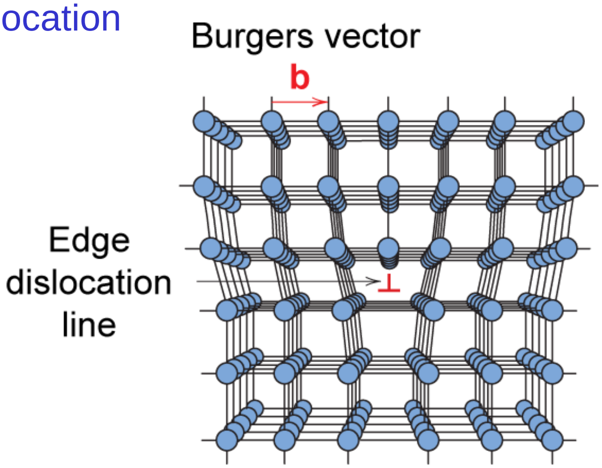
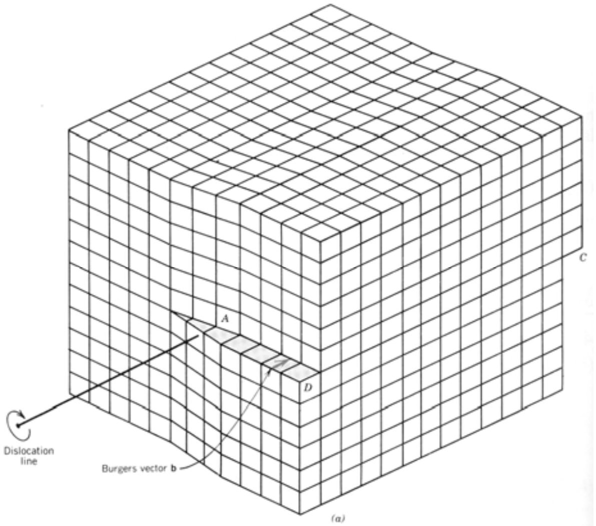


FIGURE 4.4 (*a*) A screw dislocation within a crystal. (*b*) The screw dislocation in (*a*) as viewed from above. The dislocation line extends along line *AB*. Atom positions above the slip plane are designated by open circles, those below by solid circles. (Figure (*b*) from W. T. Read, Jr., *Dislocations in Crystals,* McGraw-Hill Book Company, New York, 1953.)



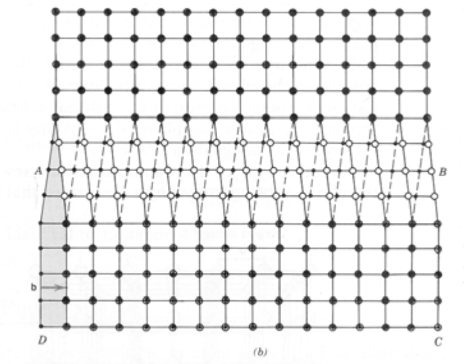


FIGURE 4.4 (*a*) A screw dislocation within a crystal. (*b*) The screw dislocation in (*a*) as viewed from above. The dislocation line extends along line *AB*. Atom positions above the slip plane are designated by open circles, those below by solid circles. (Figure

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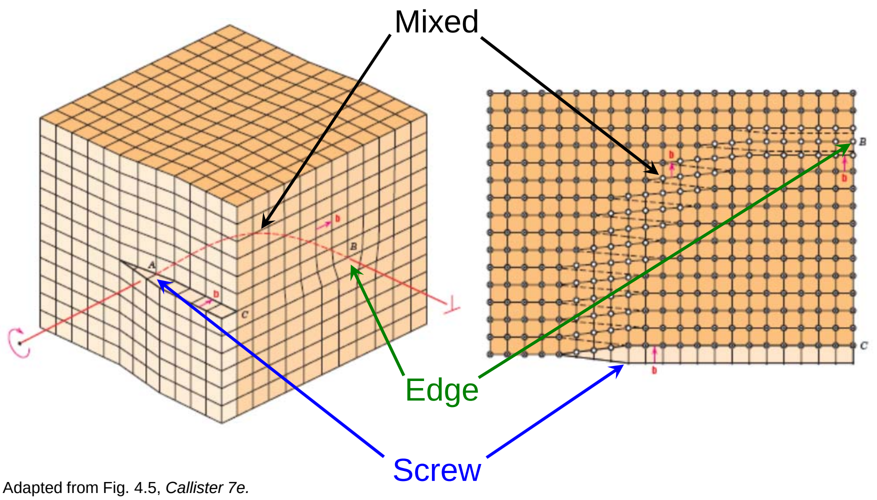
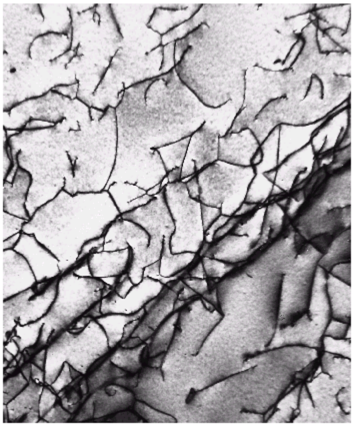
Edge, Screw, and Mixed Dislocations



Adapted from Fig. 4.5, *Callister 7e.*

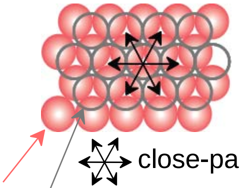
Imperfections in Solids

Dislocations are visible in __________ micrographs



Dislocations & Crystal Structures

- Structure: close-packed planes & directions are preferred.



view onto two close-packed planes.

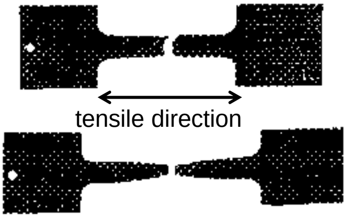
close-packed directions

close-packed plane (bottom)

close-packed plane (top)

- Comparison among crystal structures:
  FCC: __________ close-packed planes/directions;
  HCP: only one plane, 3 directions;
  BCC: __________

- Specimens that were tensile tested.



INTERFACIAL DEFECTS

Defects between crystals or materials

__________ Defects

Material surface: boundary between material and atmosphere. Atomic bonding disrupted. More reactive.

Grain Boundaries

Regions where grains (crystals) join. Because __________ grains (crystals) have different orientations then some _______ at boundaries. Atomic bonding disrupted. More reactive chemically.

If a solid is made of only one crystal called: **Single Crystal**

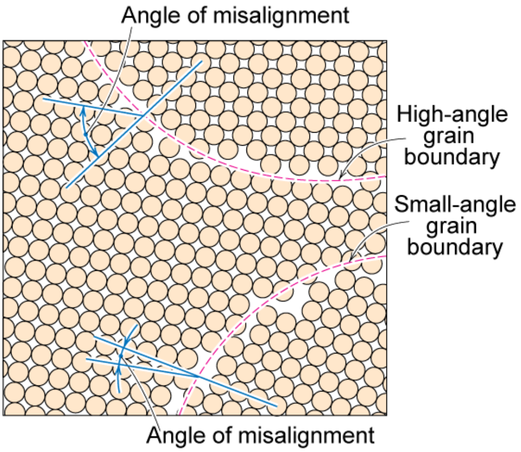
If solid has many Crystals → **Polycrystalline**.

Most materials/metals are _______________. I.e. composed of many crystals/grains joined together.

Polycrystalline Materials

Grain _______________

- regions between crystals
- transition from lattice of one region to that of the other
- slightly disordered
- low density in grain boundaries
  - high mobility
  - high _____________
  - high chemical reactivity

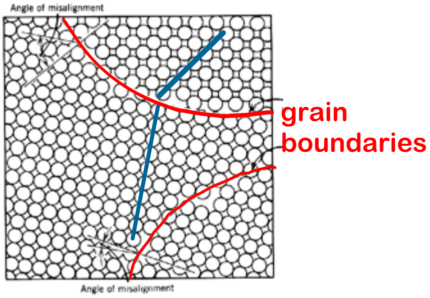


AREA DEFECTS: GRAIN BOUNDARIES

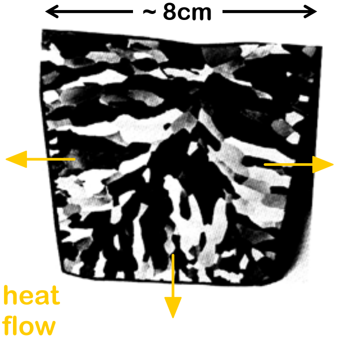
Grain boundaries:

- are boundaries between crystals.
- are produced by the solidification process, for example.
- have a change in crystal orientation across them.
- __________ dislocation motion.

Schematic



Metal Ingot



Bulk/Volume Defects

Larger defects such as cracks, pores (holes), other stuff.

Grains, grain boundaries can be observed in metals/ceramics:

- Section and Grind sample.
- ___________ (diamond paste).
- Etch (chemical attack) Occurs ______________ depending upon crystal orientation and in grain boundaries.
- View **MICROSTRUCTURE** with microscope.

Can also use other techniques eg: Scanning Electron Microscope, SEM

Can measure properties such as ________ **SIZE**. This effects strength, toughness etc.

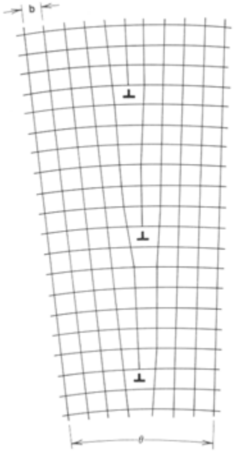
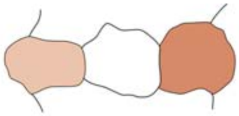


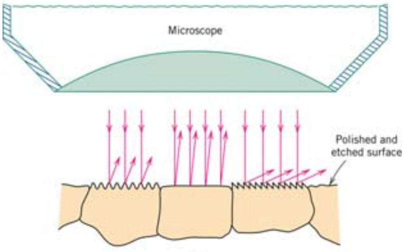
FIGURE 4.8 Demonstration of how a tilt boundary having an angle of misorientation θ results from an alignment of edge dislocations.

OPTICAL MICROSCOPY

- **Useful up to 2000X magnification.**
- **Polishing removes surface features (e.g., scratches)**
- **___________ changes reflectance, depending on crystal orientation.**



(a)



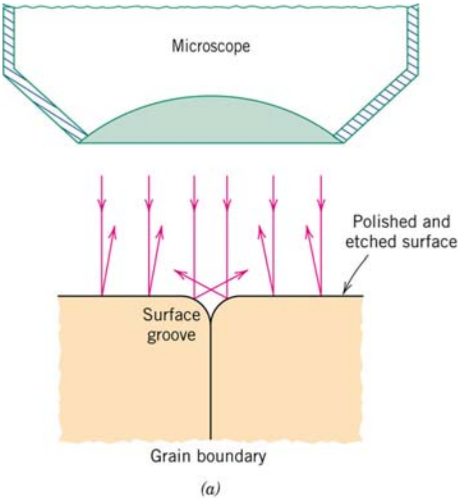
(b)

(c)

micrograph of Brass (Cu and Zn)

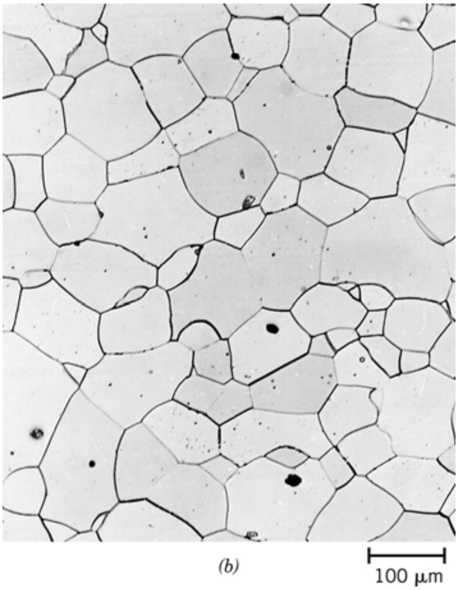
Grain boundaries...

- are imperfections,
- are more susceptible to etching,
- may be revealed as dark lines,
- change direction in a polycrystal.



Fe-Cr alloy

Fe-Cr alloy



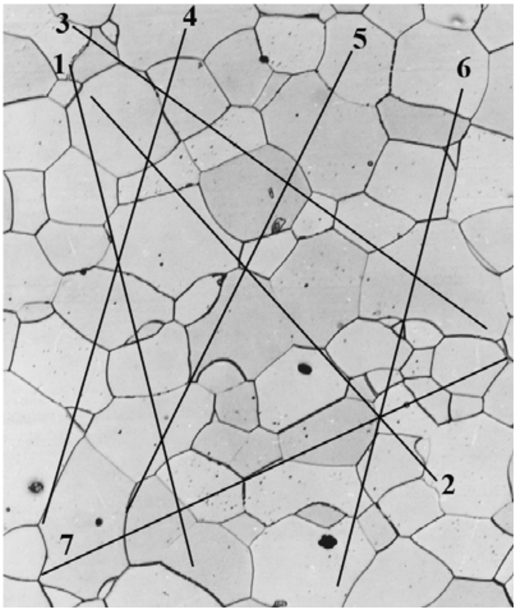
Grain Size Determination

Grain size in metals can affect several mechanical properties especially ___________. Can measure grain size by:

Intercept method:

- Draw equal length lines ___________ across photomicrograph. (l)
- No.of grains intercepted, per line is counted. (n_g)
- Line length divided by average no. of grains per line (l/n_g)
- This is then divided by magnification of photo to give average grain diameter. $(l/n_g)/M$ = Avg. g.d.

Photomicrograph Mag: 100X
7 randomly oriented straight lines labeled, (60 mm long)



Line	No. of grains intersected
1	11
2	10
3	9
4	8.5
5	7
6	10
7	8
AVG	9.1

Avg. Grain Dia. = $(l/n_g)/M$

$(60/9.1)/100 = 6.59 \times 10^{-2}$mm

Grain Size (cont)

- _____ **Grain size Number (n)**
- Take photo at 100X and compare with ASTM standard charts of grain size. Each chart shows particular grain size (n). As n increases, grain size __________. Select chart that is closest match to actual structure.

$$N = 2^{n-1}$$

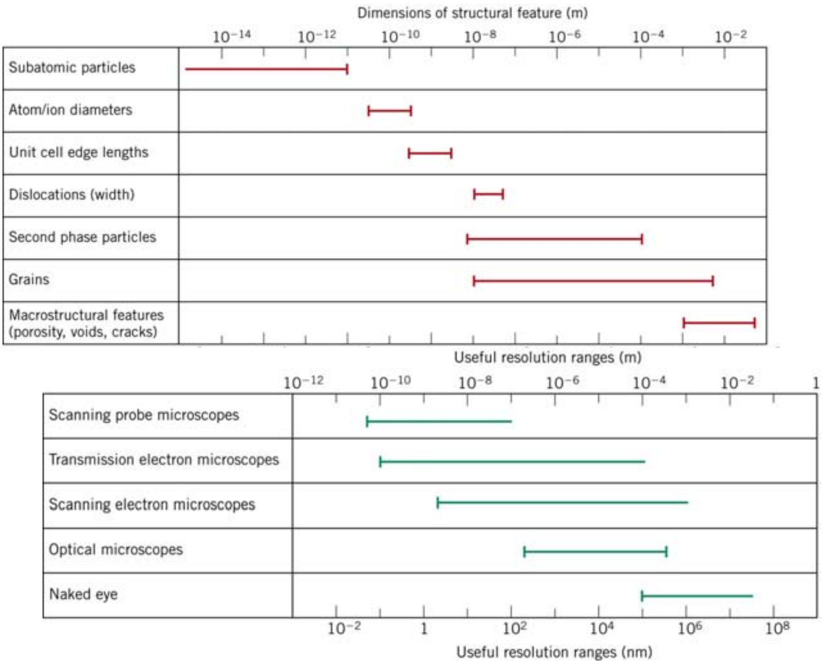
- where N is the average number of grains per square inch at Magnification X100
- n = ASTM grain size number

Microscopy

Optical resolution ca. 10^{-7} m = 0.1 μm = 100 nm

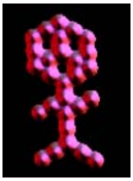
For higher resolution need higher frequency

- X-Rays? Difficult to __________.
- Electrons
  - wavelengths ca. 3 pm (0.003 nm)
    - (Magnification - 1,000,000X)
  - ___________ resolution possible
  - Electron beam focused by magnetic lenses.

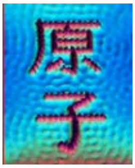


Scanning Tunneling Microscopy (STM)

- Atoms can be arranged and imaged!



Carbon monoxide molecules arranged on a platinum (111) surface.



Iron atoms arranged on a copper (111) surface. These Kanji characters represent the word “atom”.

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SUMMARY

- **Point, Line, and Area defects arise in solids.**
- **The number and type of defects can be varied and controlled (e.g., T controls vacancy conc.)**
- **Defects affect material properties (e.g., grain boundaries control crystal slip).**
- **Defects may be desirable or undesirable**
  (e.g., dislocations may be good or bad, depending on whether plastic deformation is desirable or not.)