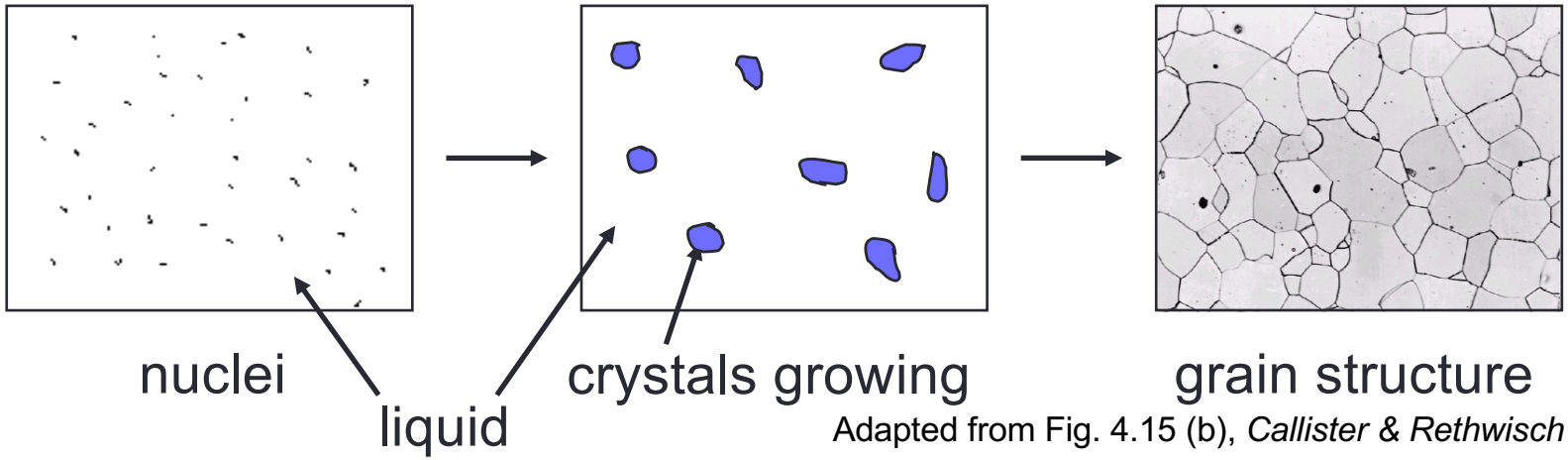
Chapter 4: Imperfections in Solids

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



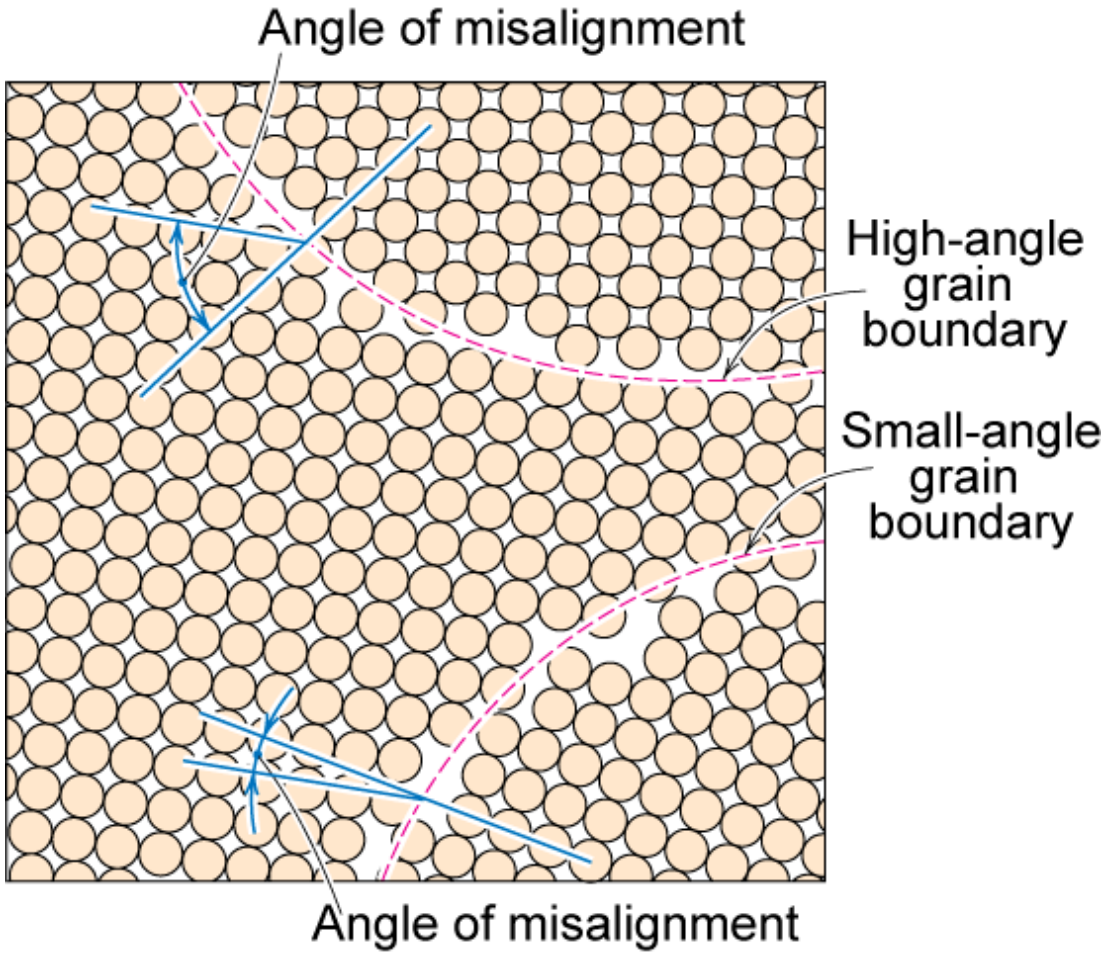
Adapted from Fig. 4.15 (b), *Callister & Rethwisch 9e.*

- Crystals grow until they meet each other

Polycrystalline Materials

Grain Boundaries

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

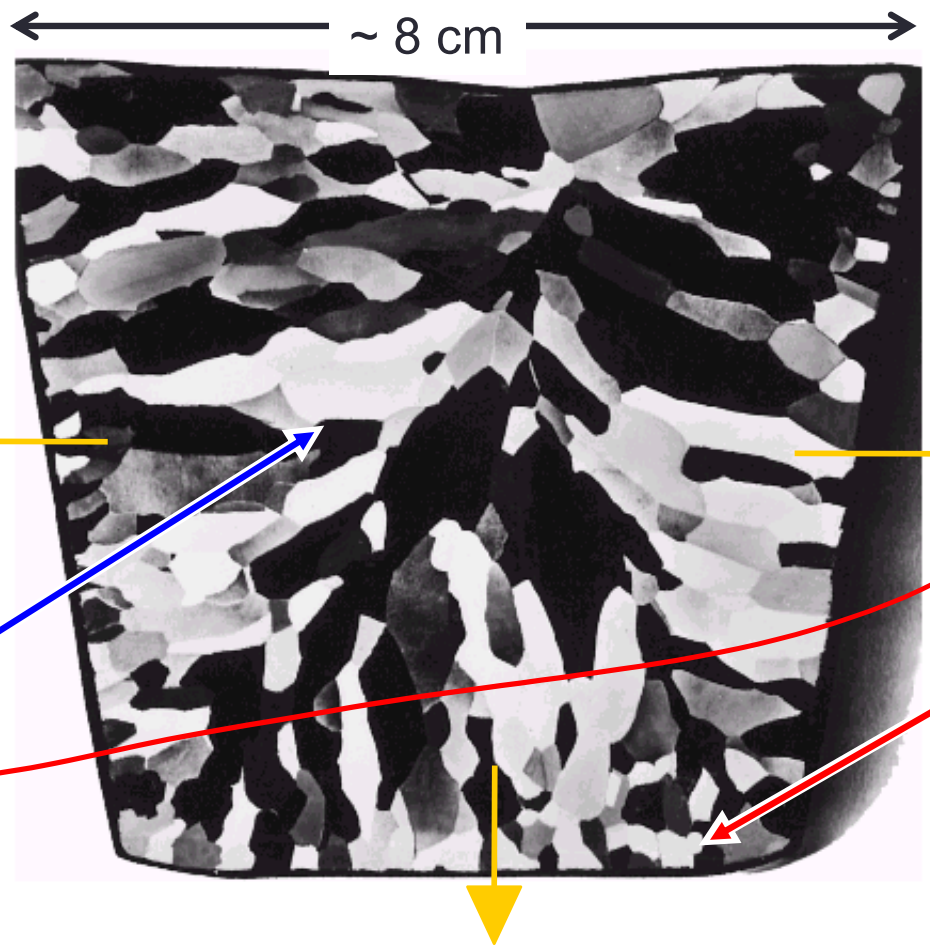


Adapted from Fig. 4.8,
Callister & Rethwisch 9e.

Solidification

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

- columnar (elongated grains)



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

Imperfections in Solids

There is no such thing as a perfect crystal.

- What are these imperfections?
- Why are they important?

Many of the important properties of materials are due to the presence of imperfections.

Types of Imperfections

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

Point defects

- Dislocations

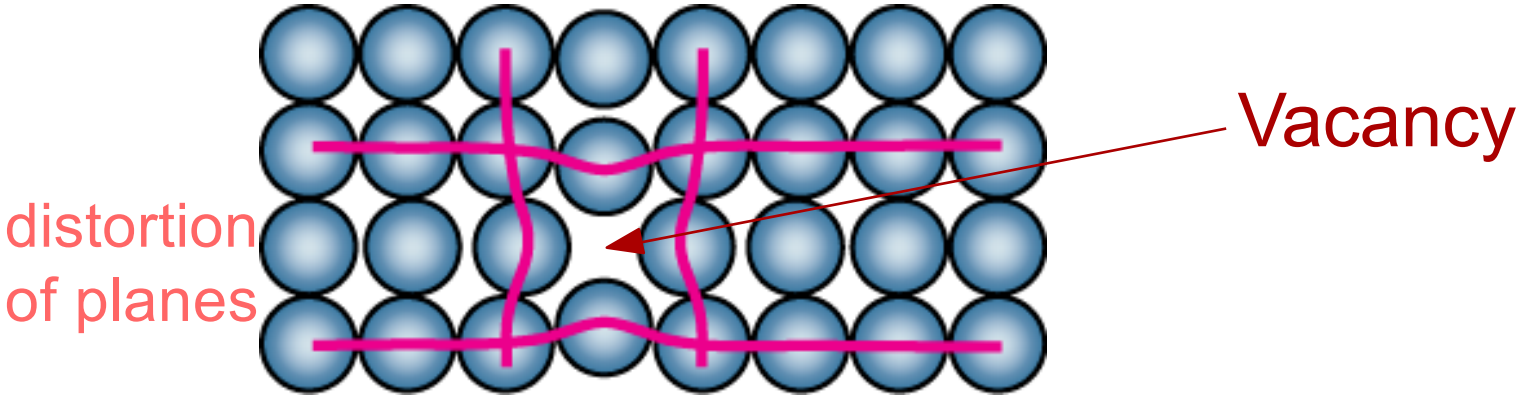
Line/linear defects

- Grain Boundaries

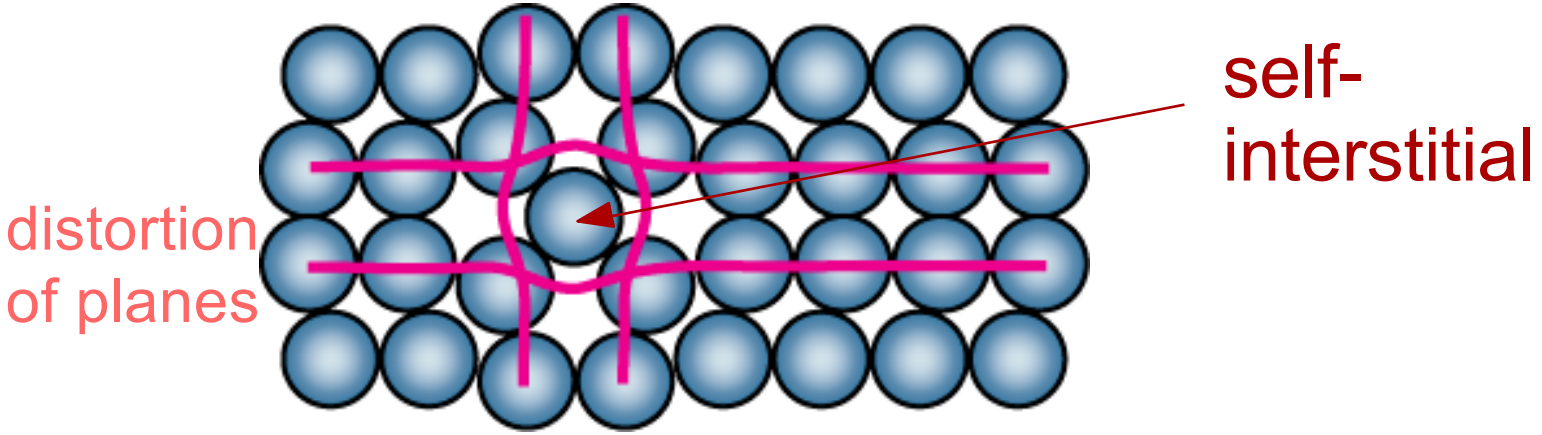
Area/planar defects

Point Defects in Metals

- Vacancies:
  -vacant atomic sites in a structure.



- Self-Interstitials:
  -"extra" atoms positioned between atomic sites.



Equilibrium Concentration: Point Defects

- Equilibrium concentration varies with temperature!

No. of defects

Activation energy

$$\frac{N_V}{N} = \exp\left(\frac{-Q_V}{kT}\right)$$

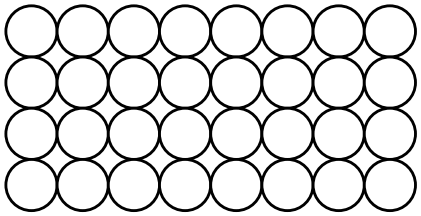
No. of potential defect sites

Temperature

Boltzmann's constant

(1.38 x 10^{-23} J/atom-K)

(8.62 x 10^{-5} eV/atom-K)



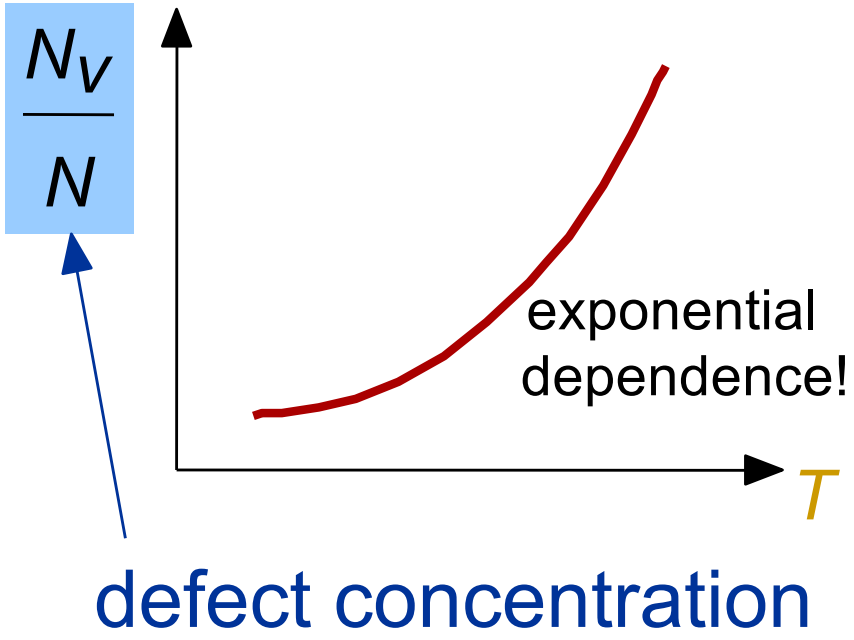
Each lattice site is a potential vacancy site

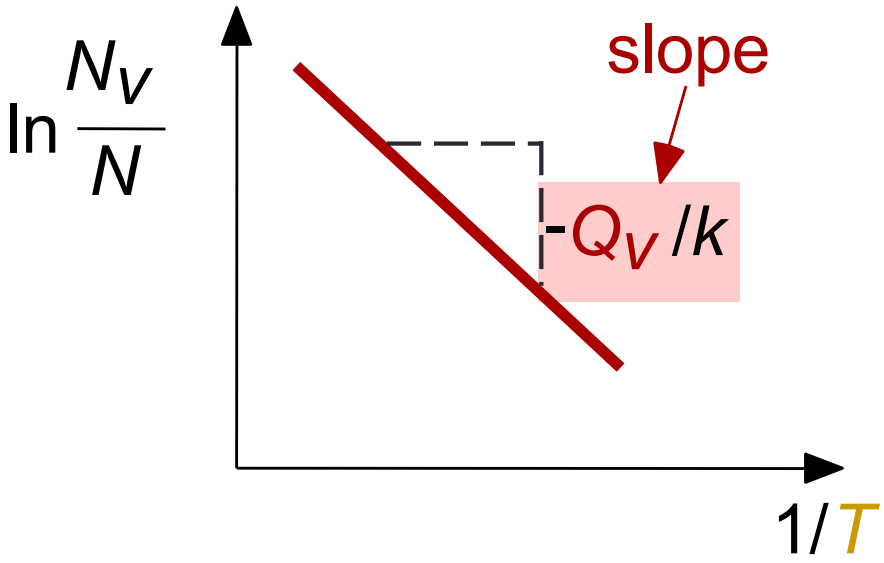
Measuring Activation Energy

- We can get Q_v from an experiment.
- Measure this...

$$\frac{N_V}{N} = \exp\left(\frac{-Q_V}{kT}\right)$$

- Replot it...

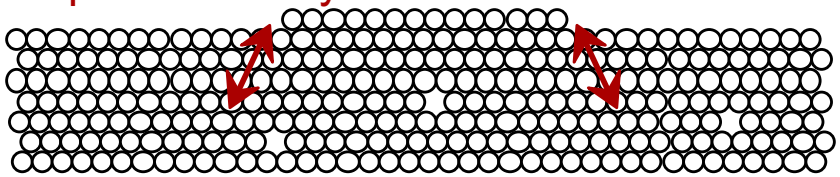


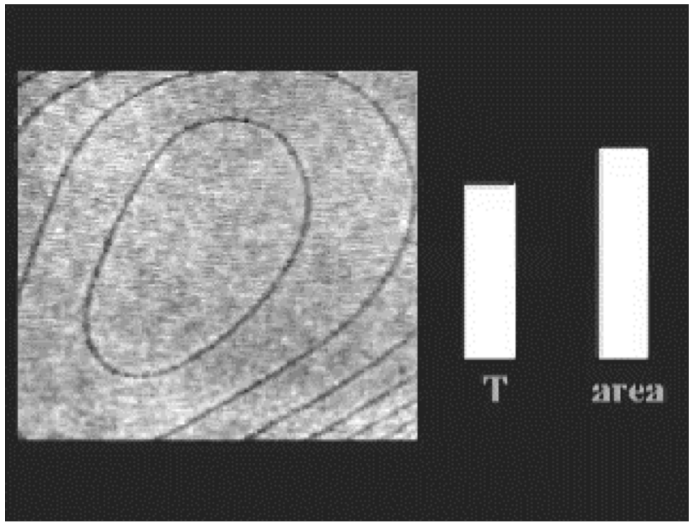


Observing Equilibrium Vacancy Conc.

- Low energy electron microscope view of a (110) surface of NiAl.
- Increasing temperature 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.

Island grows/shrinks to maintain equil. vancancy conc. in the bulk.





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Estimating Vacancy Concentration

- Find the equil. # of vacancies in 1 m^3 of Cu at 1000°C.
- Given: $10^6\ cm^3 = 1\ m^3$

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

$Q_V = 0.9$ eV/atom $\quad N_A = 6.022 \times 10^{23}$ atoms/mol

Avogadro's #

0.9 eV/atom

$$\frac{N_V}{N} = \exp\left(\frac{-Q_V}{kT}\right) = 2.7 \times 10^{-4}$$

1273 K

8.62×10^{-5} eV/atom-K

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

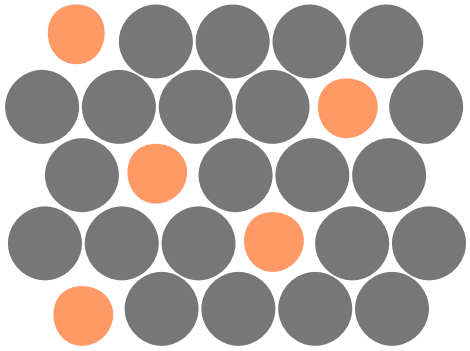
- Answer: *ρ needs to be in g/m^3*

$N_V = (2.7 \times 10^{-4})(8.0 \times 10^{28})$ sites $= 2.2 \times 10^{25}$ vacancies

Imperfections in Metals (i)

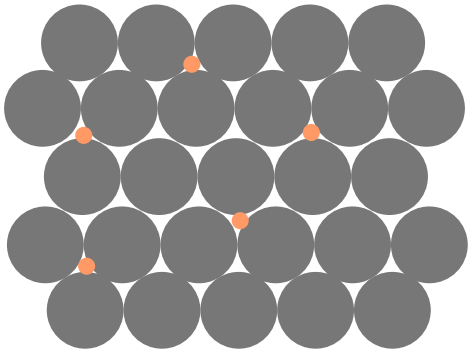
Two outcomes if impurity (B) added to host (A):

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



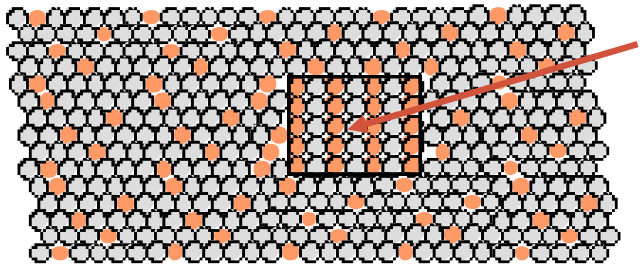
Substitutional solid soln.
(e.g., Cu in Ni)

OR



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

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



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

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Imperfections in Metals (ii)

Conditions for substitutional solid solution (S.S.)

- W. Hume – Rothery rule
  - 1. Atomic size factor: Δr (atomic radius) < 15%
  - 2. Same crystal structure for pure metals
  - 3. Proximity in periodic table
    - i.e., similar electronegativities
  - 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

Imperfections in Metals (ii)

- For complete substitutional solubility: the above criteria must be met:
  (1) the difference in atomic radius must be less than ±15%;
  (2) the crystal structures must be the same;
  (3) the valences should be the same;
  (4) the electronegativities must be similar.

Valence & Electronegativity

(3)the valences should be the same;

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

(4)the electronegativities must be similar.

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

Imperfections in Metals (ii)

- For incomplete substitutional solubility: can meet only part of the criteria (less than 4 criteria)
- For interstitial solid solution: must meet these
  1. Impurity (solute) atom must be smaller than interstitial sites in host (solvent) lattice
  2. Similar electronegativities

Imperfections in Metals (iii)

Application of Hume–Rothery rules – Solid Solutions

- Which of the following systems (i.e., pair of metals) would you expect to exhibit complete solid solubility?

(a) Cr (host) –V(impurity)

Metal	*Atomic Radius (nm)*	*Crystal Structure*	*Electronegativity*	*Valence*
Cr(24)	0.125	BCC	1.6	+3
V(23)	0.132	BCC	1.5	+5 (+3)

(b) Mg(host)-Zn(impurity)

Metal	*Atomic Radius (nm)*	*Crystal Structure*	*Electronegativity*	*Valence*
Mg	0.160	HCP	1.3	+2
Zn	0.133	HCP	1.7	+2

Imperfections in Metals (iii)

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Cr(24)	0.125	BCC	1.6	+3
V(23)	0.132	BCC	1.5	+5 (+3)

6% difference

(b) Mg(host)-Zn(impurity)

Metal	*Atomic Radius (nm)*	*Crystal Structure*	*Electronegativity*	*Valence*
Mg	0.160	HCP	1.3	+2
Zn	0.133	HCP	1.7	+2

17% difference

Imperfections in Metals (iii)

Application of Hume–Rothery rules – Solid Solutions

1. Would you predict more Al or Ag to dissolve in Zn?

More Al because size is closer and val. is higher – but not too much – FCC in HCP

2. More Zn or Al in Cu?

Surely Zn since size is closer in size thus causing lower distortion (4% vs 12%)

Element	*Atomic Radius (nm)*	*Crystal Structure*	*Electro-nega-tivity*	*Valence*
Cu	0.1278	FCC	1.8	+1(+2)
C	0.071			
H	0.046			
O	0.060			
Ag	0.1445	FCC	1.4	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.7	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.7	+2
Ni	0.1246	FCC	1.8	+2
Zn	0.1332	HCP	1.7	+2

Table on p. 135, *Callister & Rethwisch 9e.*

Interstitial Solid Solution

- Conditions: (W. Hume – Rothery rule)
  1. Impurity (solute) atom must be smaller than interstitial sites in host (solvent) lattice (MOST IMPORTANT)
  2. Similar electronegativities

Element	*Atomic Radius (nm)*	*Δr (%)*	*Crystal Structure*	*Electro-nega-tivity*	*Valence*
Cu	0.1278		FCC	1.8	+1(+2)
C	0.071	-44		2.5	
H	0.046	-64		2.1	
O	0.060	-53		3.5	
Ag	0.1445	+13	FCC	1.4	+1
Al	0.1431	+12	FCC	1.5	+3
Co	0.1253	-2	HCP	1.7	+2
Cr	0.1249	-2	BCC	1.6	+3
Fe	0.1241	-3	BCC	1.7	+2
Ni	0.1246	-3	FCC	1.8	+2
Zn	0.1332	+4	HCP	1.7	+2

Impurities in Solids

- Specification of composition
  - weight percent

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

m_1 = mass of component 1

  - atom percent

$$C_1' = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100$$

n_{m1} = number of moles of component 1