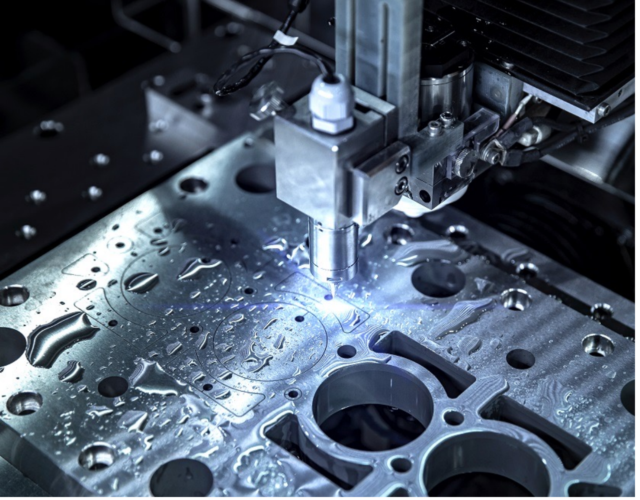

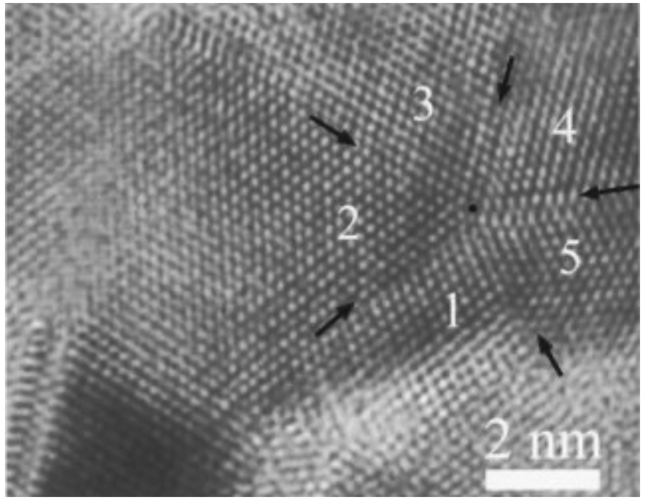

Materials Engineering I (MSE 214)

Lecture 7: Metals – Introduction

Prof. Daryl W. Yee

Email: (daryl.yee@epfl.ch)

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Week 6 Recap: Additive Manufacturing

Injection Molding

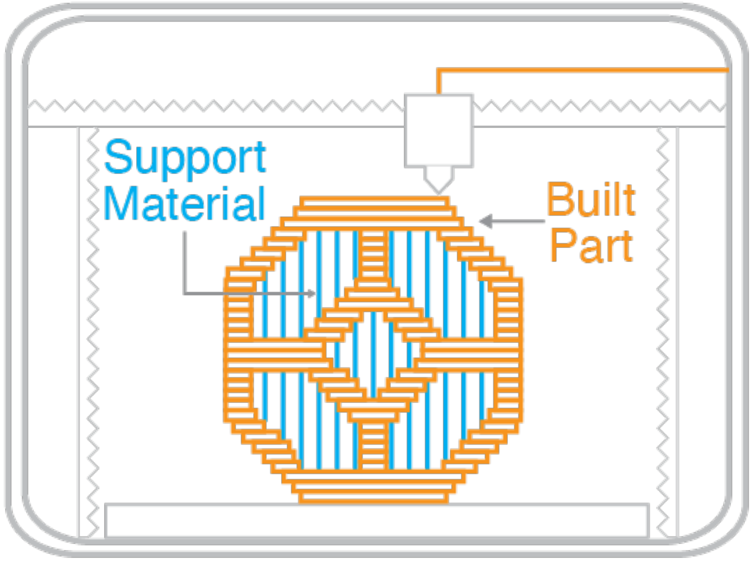
High throughput
Rapid
High startup cost
Not easy to pivot to different part
Not suited for small-medium production volume

Additive Manufacturing

Low throughput
Slow
Low startup cost
Easy to pivot to different parts
Suited for small-medium production volume

Week 6 Recap: Additive Manufacturing

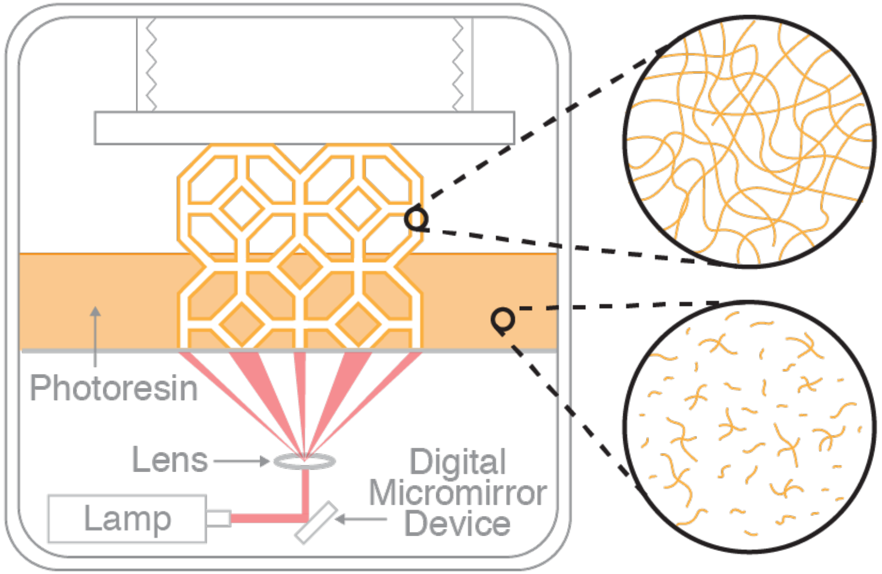
Material Extrusion



Family of AM techniques where a material is deposited through a nozzle onto a substrate

Principle: Heat polymer beyond T_g and/or T_m to soften it and allow it to flow

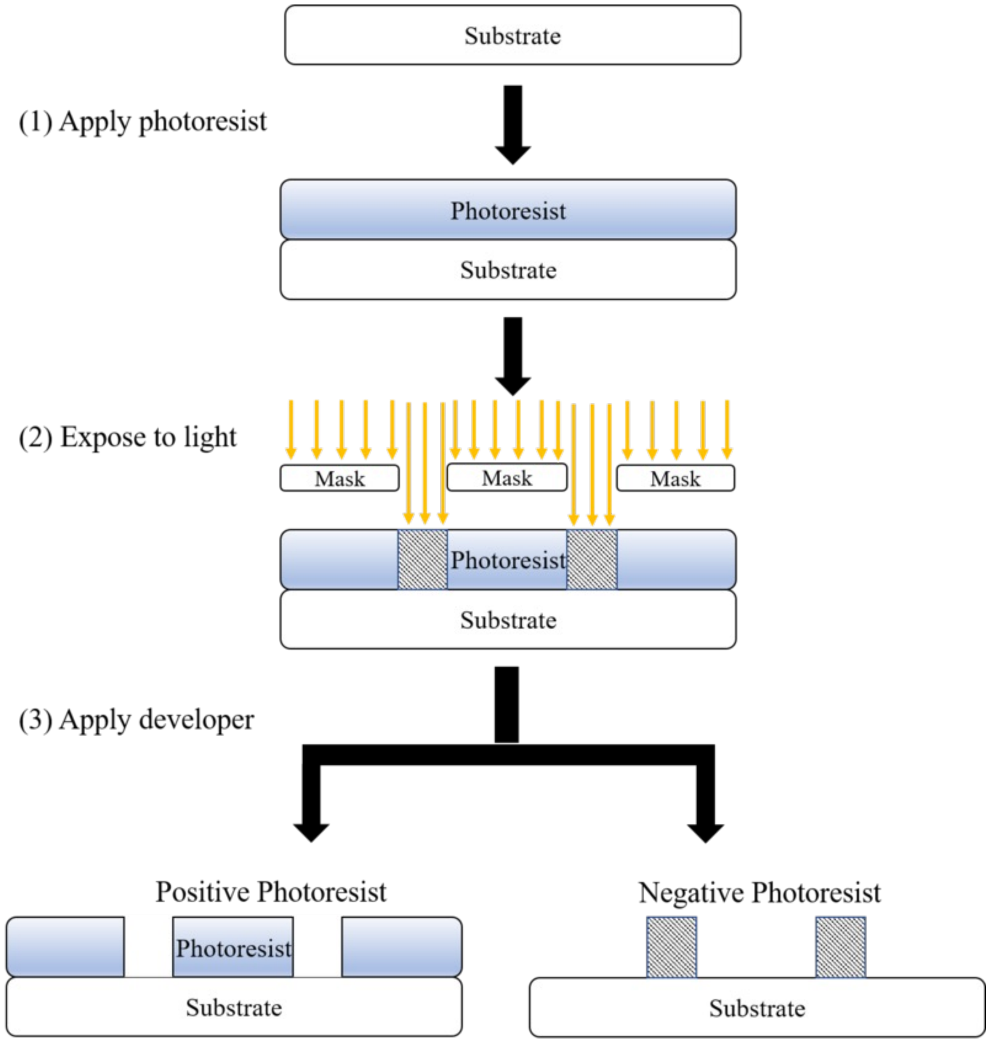
Vat Photopolymerization



Family of AM techniques where a liquid photo-polymer in a "vat" is cured via photo-polymerization

Principle: Use light to spatially initiate chain-growth polymerization

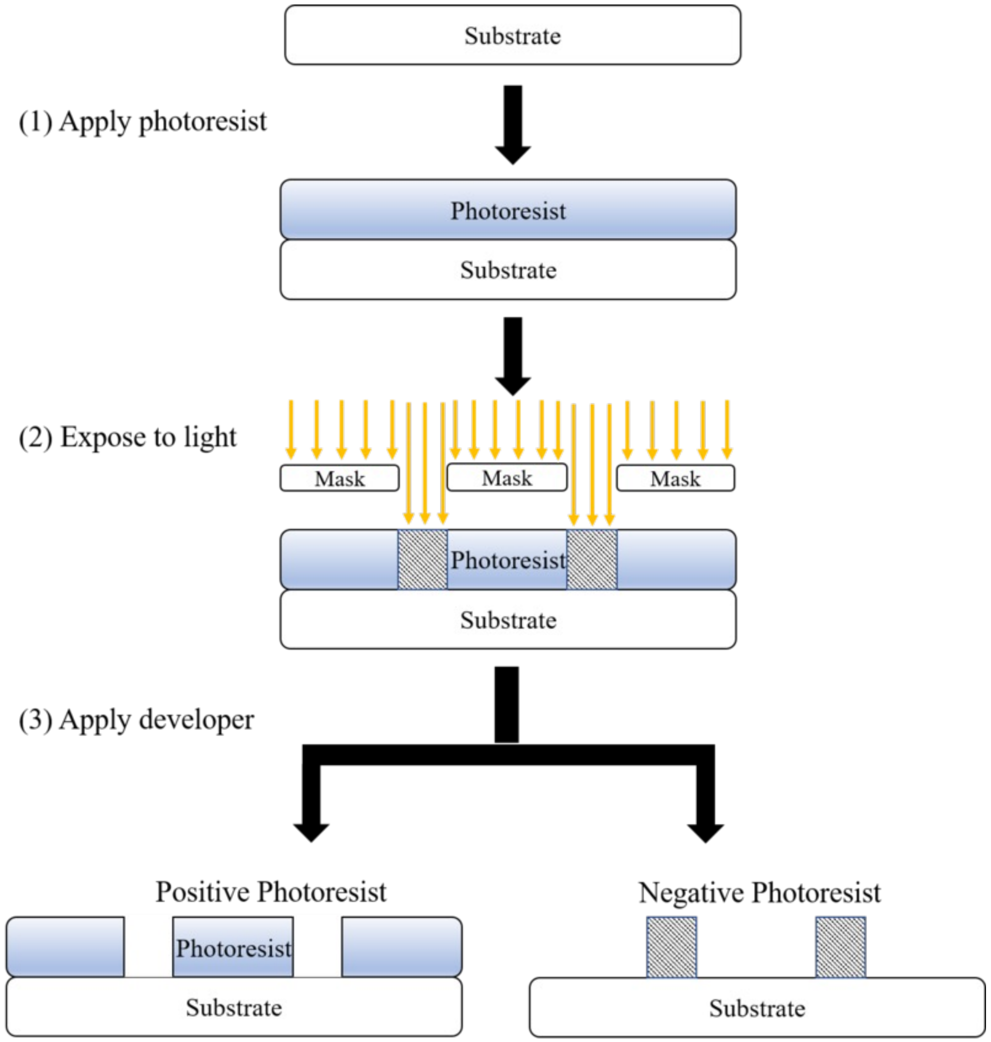
Week 6 Recap: Photolithography



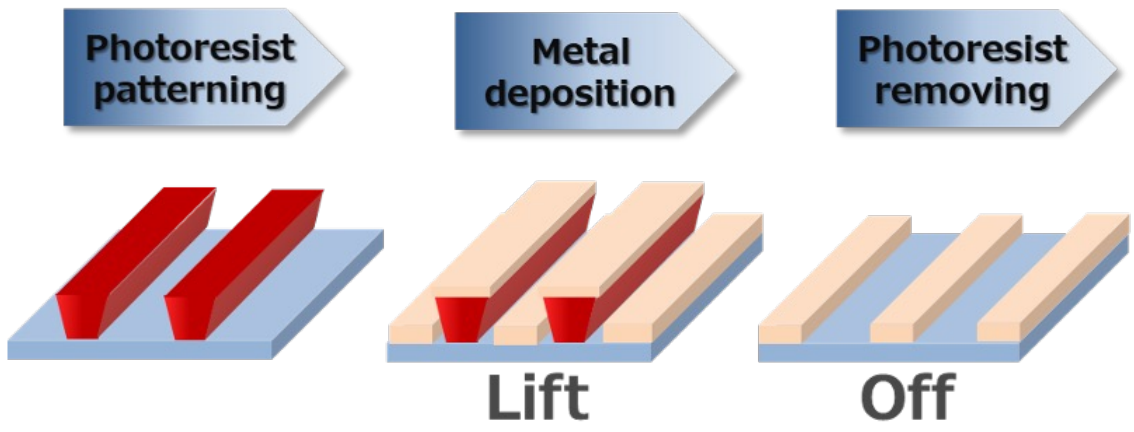
Positive resists:
Light causes the polymers to be less resistant to dissolution (by lowering molecular weight, decreasing crosslink density, etc.)

Negative resists:
Light causes the polymers to be more resistant to dissolution (by increasing crosslink density)

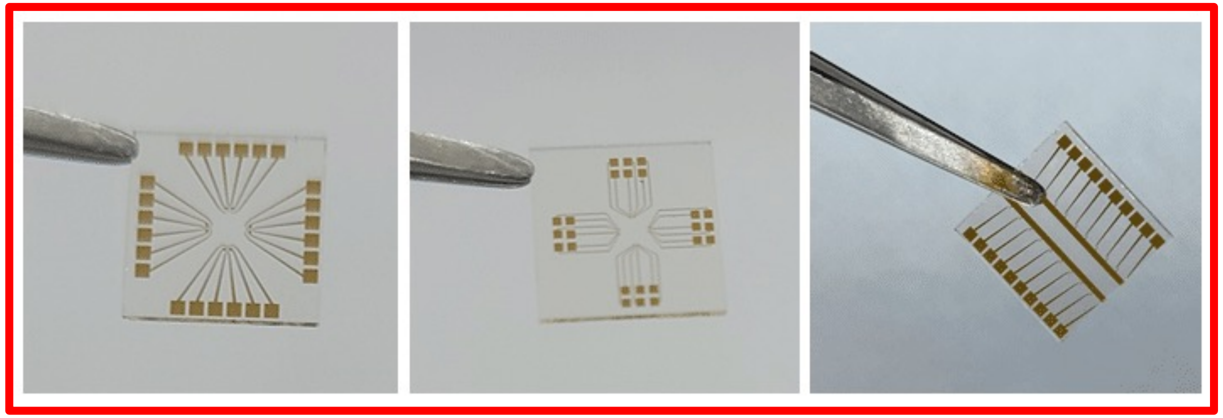
Week 6 Recap: Photolithography



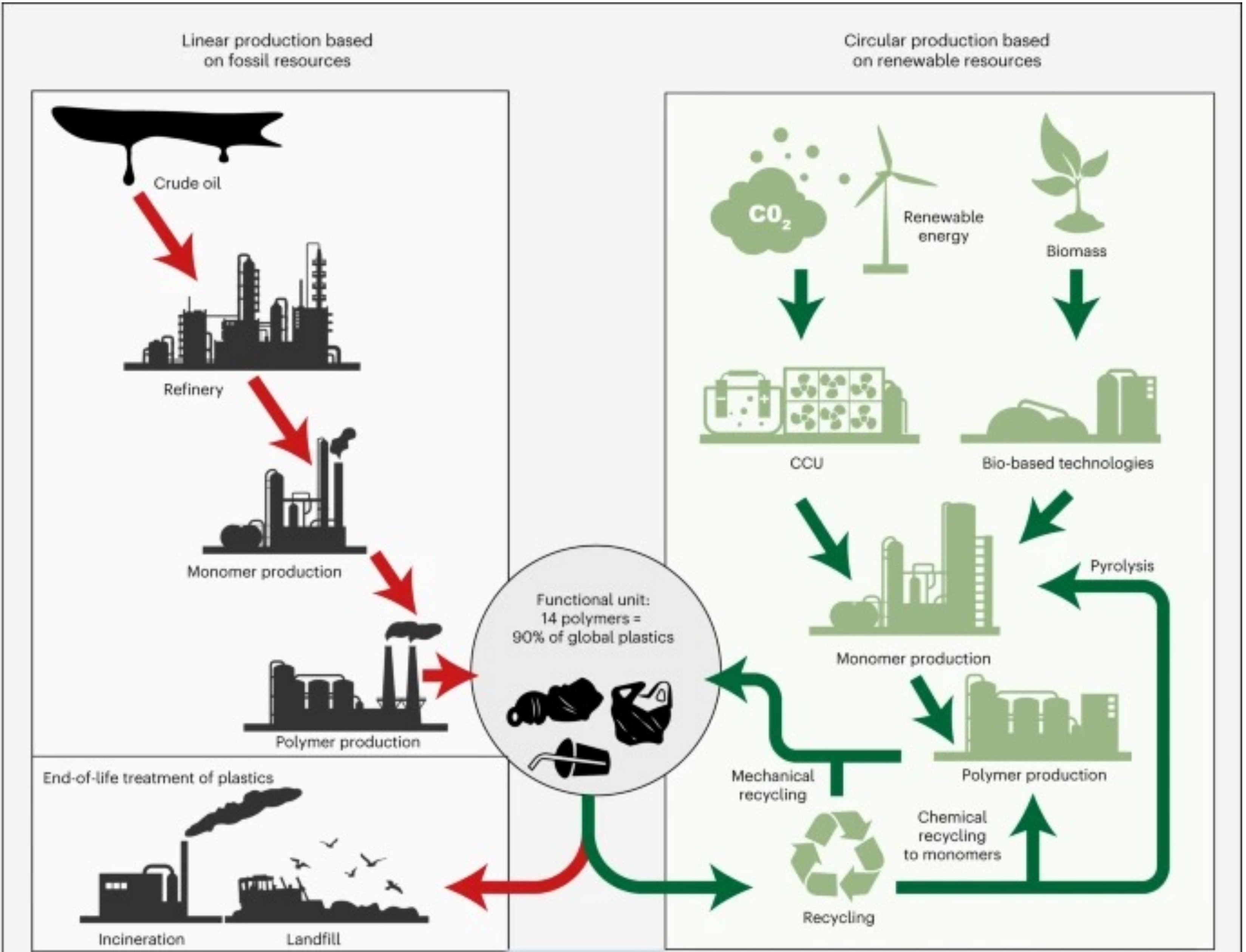
Metal patterning via lift-off (additive)



Used to make these microelectrodes



Week 6 Recap: Polymer Sustainability

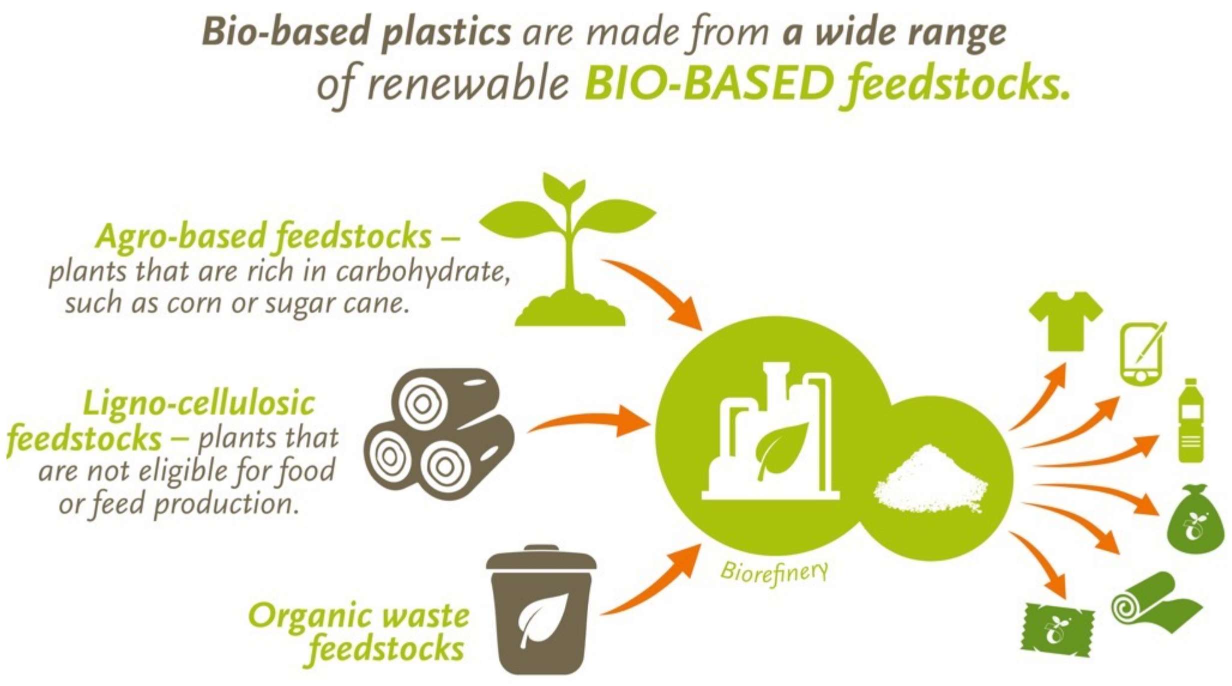


Polymers are not inherently bad, but the way we produce and use them are not sustainable!

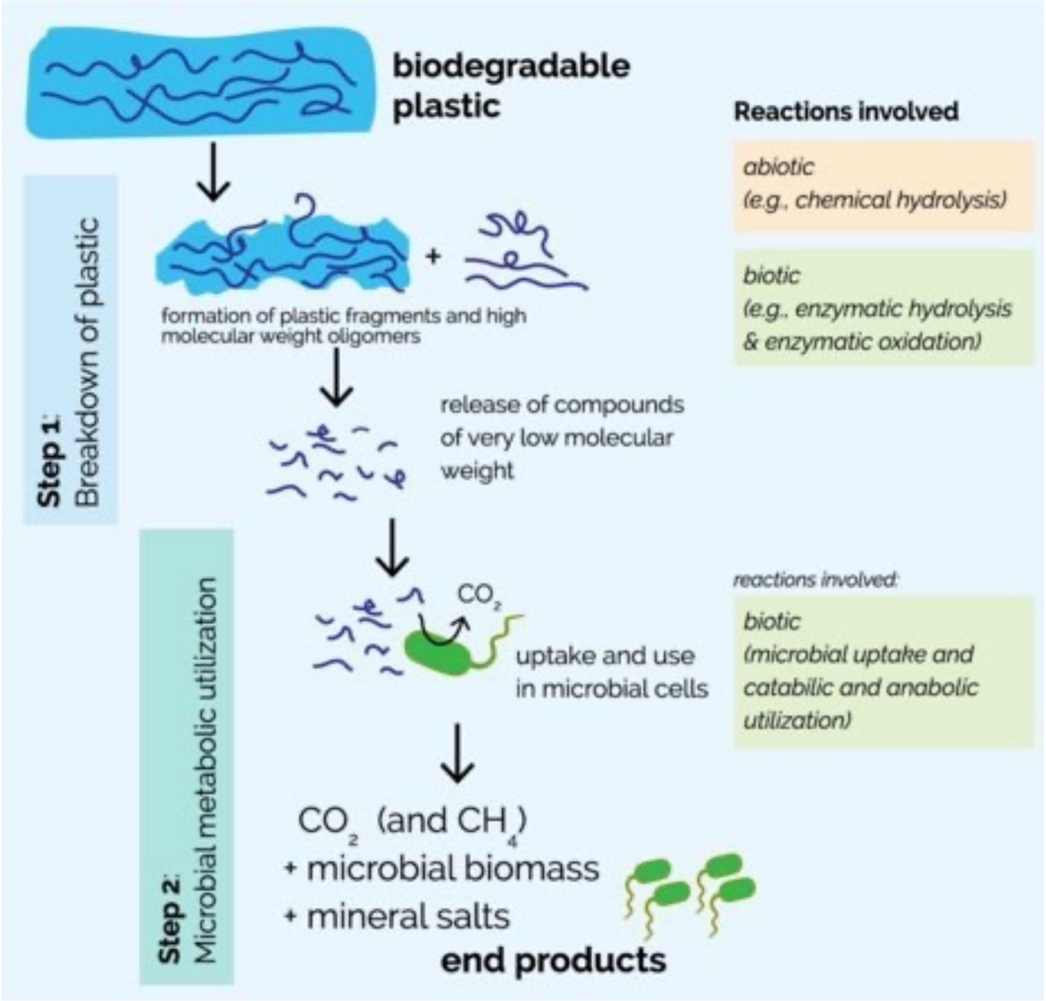
Complex challenge that encompasses science, manufacturing, policy, and politics

Week 6 Recap: Polymer Sustainability

Bio-based Feedstock



Biodegradable Polymers



Week 6 Recap: Polymer Sustainability

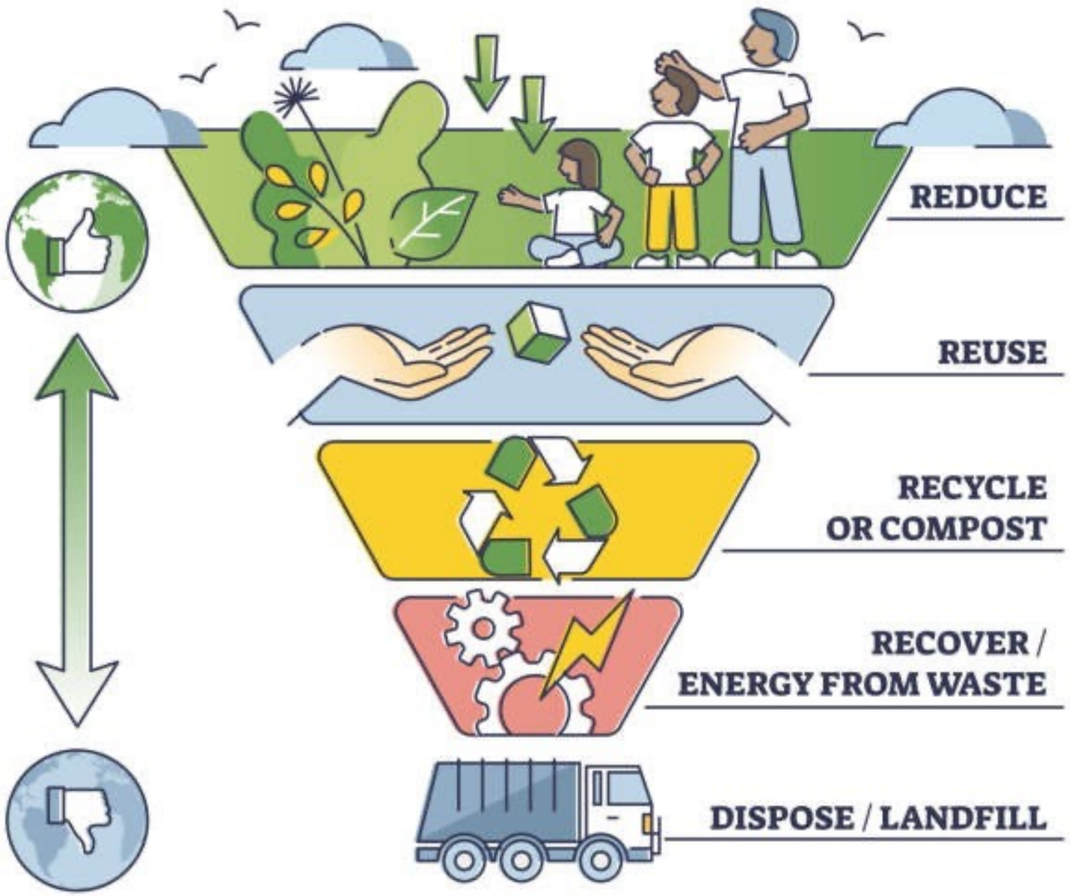
Life cycle assessment (LCA) is needed to determine and understand the environment footprint of a product

LCA is important but difficult to achieve!

Misleading if not all variables/consequences are taken into consideration.

Week 6 Recap: Polymer Sustainability

Recycling is not that effective. Reduce and reuse!



Policy can be a powerful tool to enact broad changes in society

Timeline

Key dates related to the Directive on single-use plastics

4 February 2022 — **Commission adopts Implementing Decision 2022/162**

Implementing Decision 2022/162 lays down rules for the calculation, verification and reporting on the reduction in the consumption of single-use plastic food containers and beverage cups

1 October 2021 — **Commission adopts Implementing Decision 2021/1752**

Implementing Decision 2021/1752 lays down rules for the calculation, verification and reporting of data on the separate collection of waste single-use plastic beverage bottles

3 July 2021 — **The EU no longer allows certain single-use plastic items to be placed on the Member States market; and marking requirements enter into force**

Find out more about the marking specifications and download the pictograms

31 May 2021 — **Commission adopts guidelines on single-use plastics products, and implementing decision on reporting on fishing gear**

View the guidelines in all EU languages

View the implementing decision on reporting on fishing gear

2 July 2019 — **Directive on single-use plastics enters into force**

Hide 2 items

16 January 2018 — **Publication of the EU plastics strategy - outlining the need for a legislative proposal on single-use plastics**

Exercise 5, Qn 2

Given what you have learnt about polymer solvation, suggest a possible way to separate the polymer from the solution. Explain why your proposed method will work.

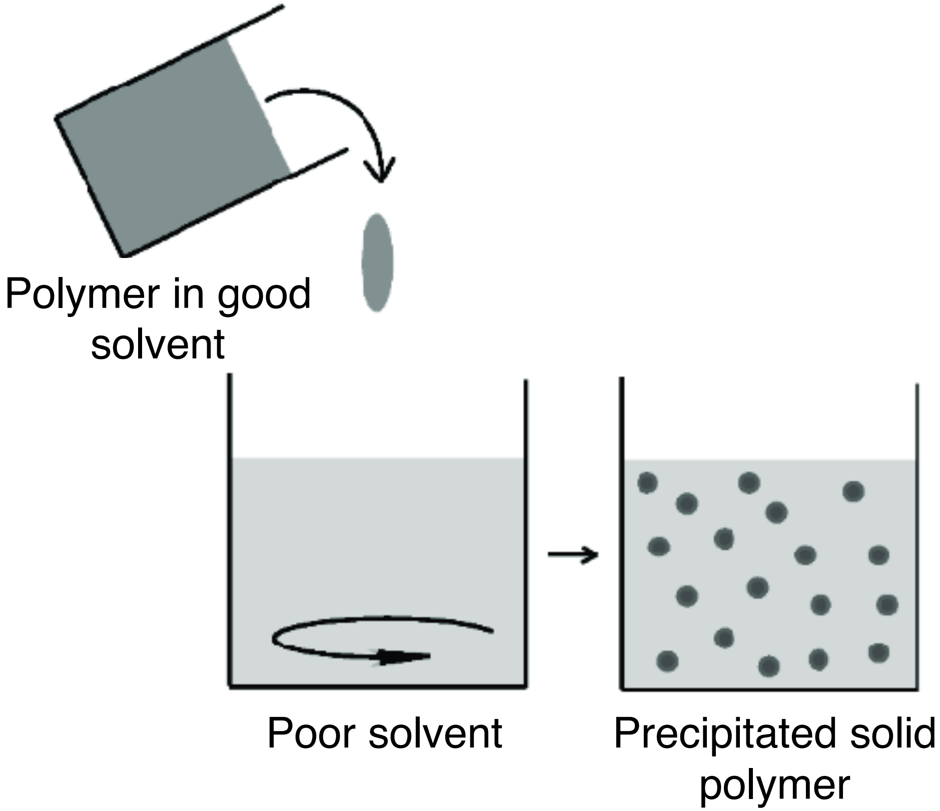
Main concept:

You want the polymer to be in a poor solvent.

Remember: Polymers are soluble in good solvents and insoluble in poor solvents.

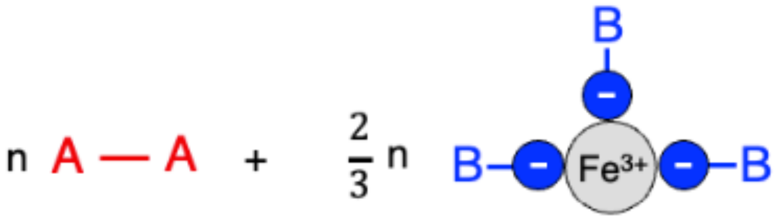
In principle you could evaporate all the solvent out, but this is really energy inefficient! (Think industry)

Best approach:



Exercise 5, Qn 3

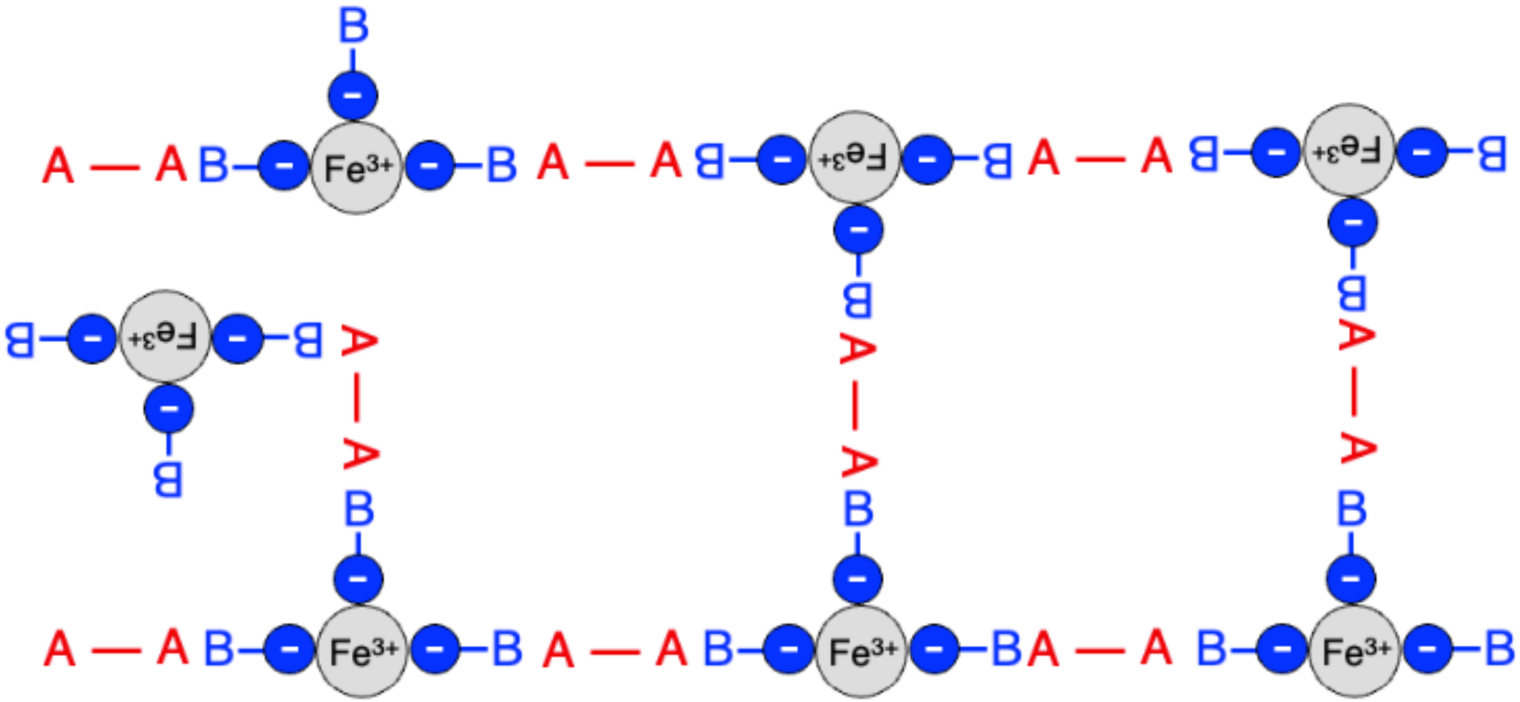
What kind of crosslinks exist in this polymer?



Note 1: If you see A—A and B—B, that is a hint that this is a step-growth polymerization

Note 2: The n and 2/3 n were there just to keep the functional groups stoichiometric

To answer this question, the simplest thing to do is to try and draw the polymer



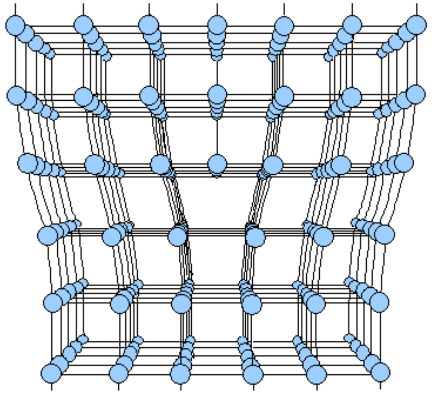
What happens if I disrupt the Fe^{3+} and  ?

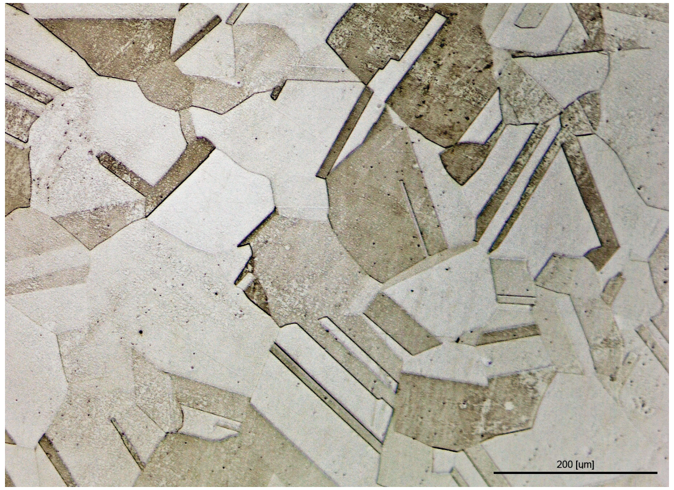
Part 2 of MSE 214: From Polymers to Metals

MSE 214 – Metals (English; ~5 Lectures)

Goal: Basic understanding of metallurgy

1) What are metals?
2) Metals and phase diagrams
3) What is the microstructure of metals?
4) How are metal parts made (manufacturing)?
5) What are the properties of metals?
6) How do I control the properties of metals?
7) How do I pick the right metal for my needs?





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Tentative Outline — Metals

Schedule subject to change.

Week	Date	Lecture (0915-1000 / 1015-1100)	Exercise (1115-1200)
8	30.10.24	Introduction to Metals	Polymer Sustainability
9	06.11.24	Phase Diagrams (I)	Introduction Metals
10	13.11.24	Phase Diagrams (II) + Properties (I)	Phase Diagrams
11	20.11.24	Properties (II)	Properties
12	27.11.24	Composites (I) – Prof. Bourban	TBD
13	04.12.24	Composites (II) – Prof. Bourban	TBD
14	11.12.24	Manufacturing + Sustainability	
15	18.12.24	Review	

Week 7 Learning Objectives

- **Understand what a metal is**
  - Terms: band theory, valence band, conduction band, band gap, crystal structure
- **Know how to classify metals**
  - Composition, crystal structure, mechanical properties, temperature stability, density, corrosion resistance, microstructure
- **Understand what an alloy is and how the Hume-Rothery rules can be used to predict its formation**
- **Understand what a dislocation is and why it enables deformation of metals**

WHY SHOULD WE CARE ABOUT ~~POLYMERS~~ METALS?

Metals are present in our daily lives!

- Iron
- Aluminium
- Copper
- Manganese
- Etc.

- Aluminium
- Nickel
- Tantalum
- Copper
- Zinc
- Etc.

- Aluminium
- Nickel
- Iron
- Copper
- Titanium
- Etc.

- Gold
- Silver
- Platinium
- Palladium
- Iridium
- Etc.

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Metals are present in our daily lives!

Why do we use metals?

Why do we use these particular metals?

Why do we manufacture metals in these ways?

Some statistics and facts about Metals

- Iron is the most abundant metal on earth
- Steel is the second most consumed raw material globally (1.9 billion tons in 2023)
- Steel is one of the most recycled materials in the world (~70%)
- Steel production accounts for 7% of greenhouse gas emissions annually
- Copper and its alloys have antimicrobial properties
- The only metal that is a liquid at room temperature and pressure is mercury (poisonous!)

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What are Metals?

<u>Previously taught:</u>
<u>Metals are materials that are</u>

a) Electrically conductive

b) Thermally conductive

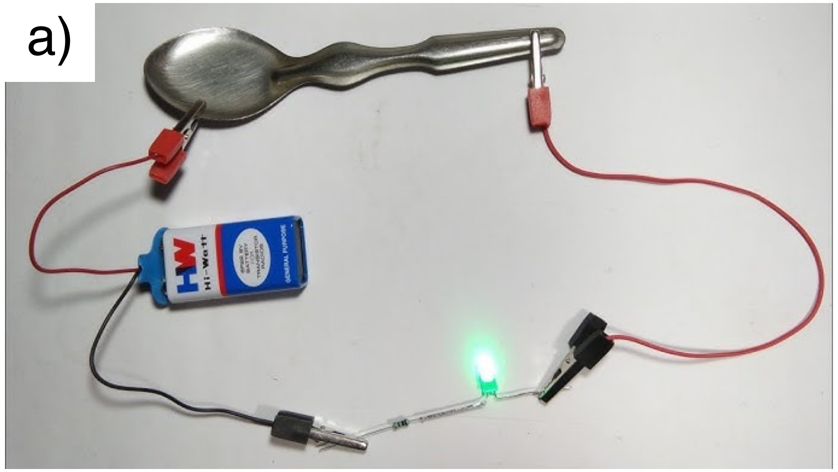
c) Lustrous (shiny)

d) Ductile

e) Malleable (can be hammered into shape)

f) Readily loses electrons to form cations

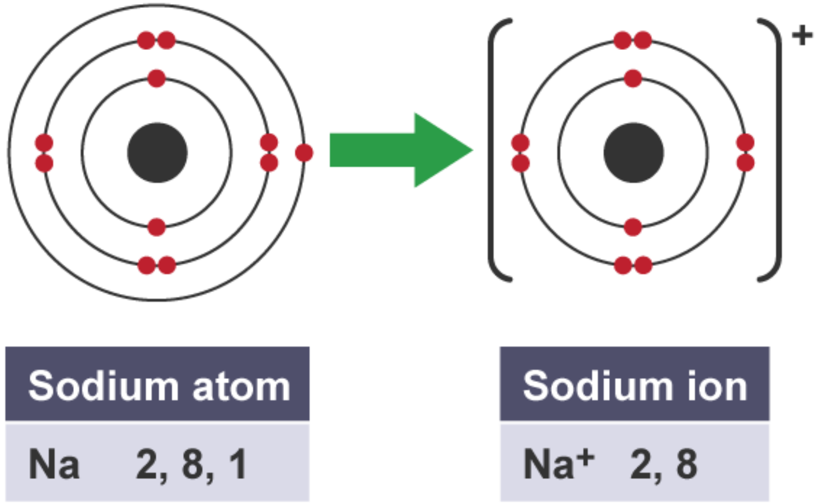
a)



c)

e)

f)



What are Metals?

<u>Previously taught:</u>
<u>Metals are materials that have</u>

Metallic bonding!

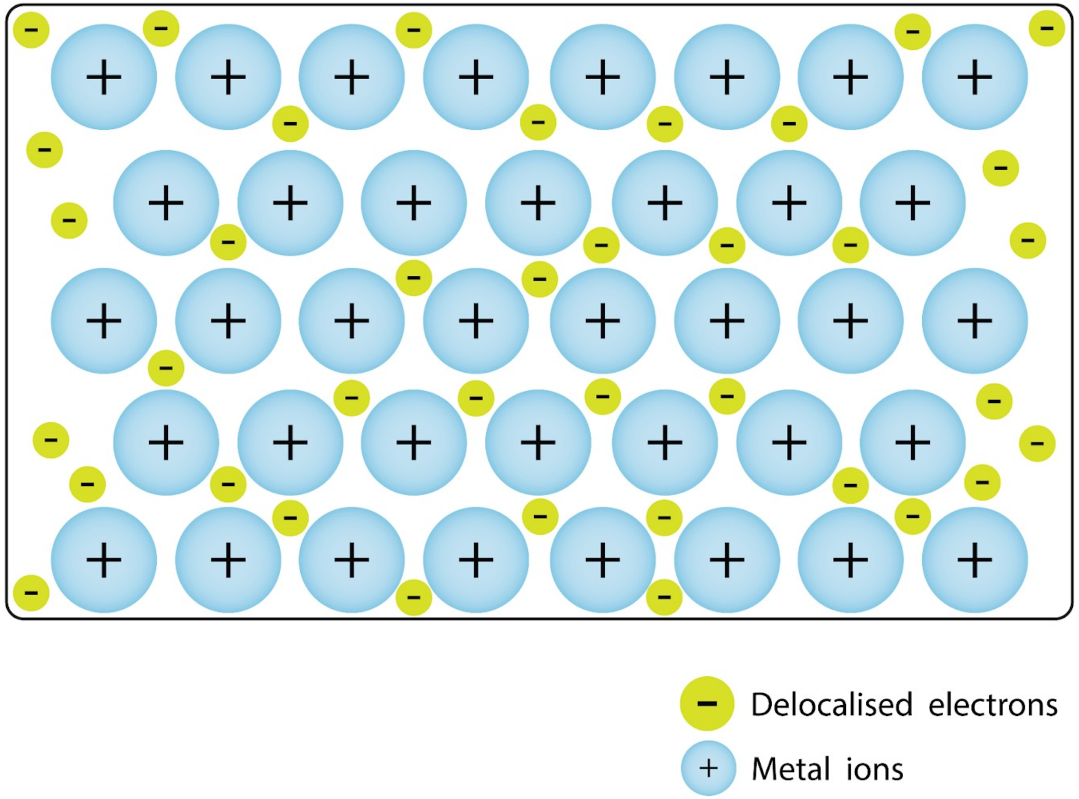
↓

Ion cores surrounded by a "sea of electrons"

Electrons act as a "glue" to hold the ions together

Metallic bond is thus nondirectional in character

Delocalized electrons enables electrical conductivity



This is a very simplified picture of metallic bonding!
Many misconceptions and inaccuracies!

See: "Misconceptions about Metals", Journal of Chemical Education, 2024

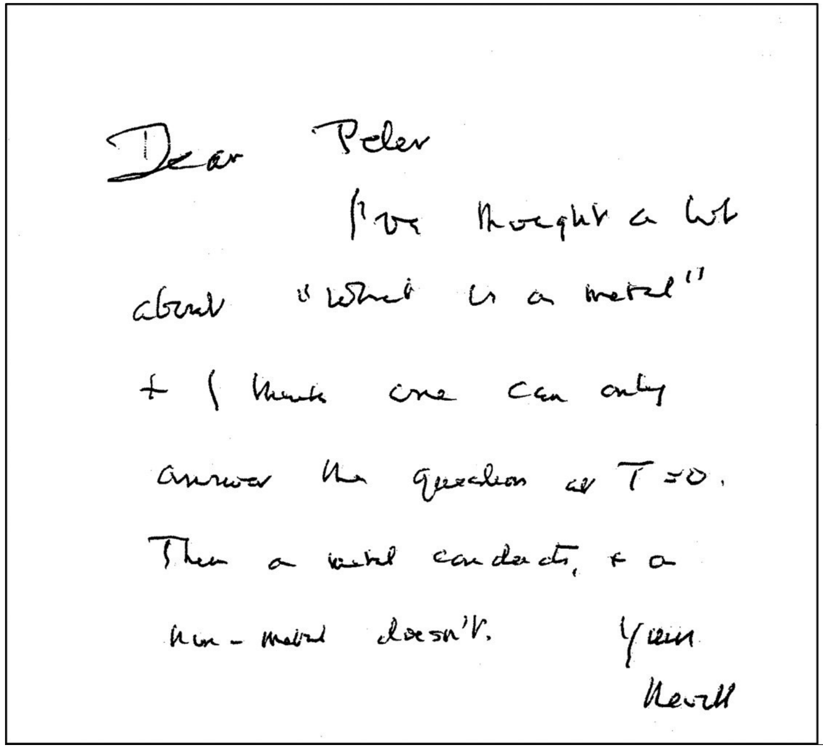
What are Metals?

More precise definition:

Metals are defined by their ability to conduct electricity at absolute zero (0 K)

"Dear Peter, I've thought a lot about "What is a metal?" and I think one can only answer this question at T=0. There a metal conducts, and a non-metal doesn't"

Letter from Sir Nevill Mott (Nobel Prize Physics, 1977) to Prof. Peter Edwards (Cambridge)

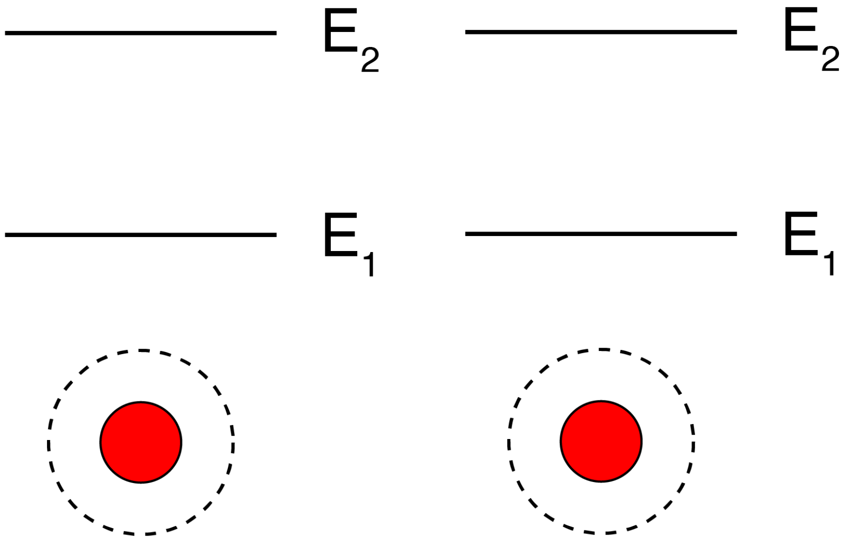


Dear Peter

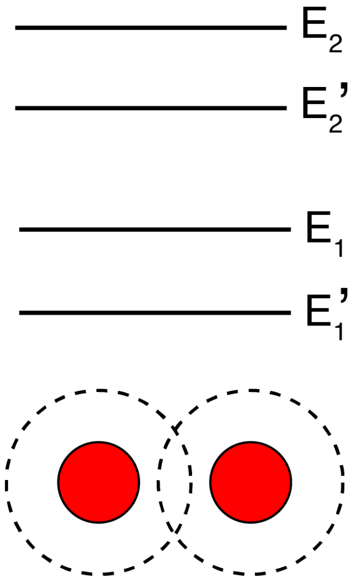
I've thought a lot about "What is a metal" & I think one can only answer the question at T=0. Then a metal conducts, & a non-metal doesn't.

Yours
Nevill

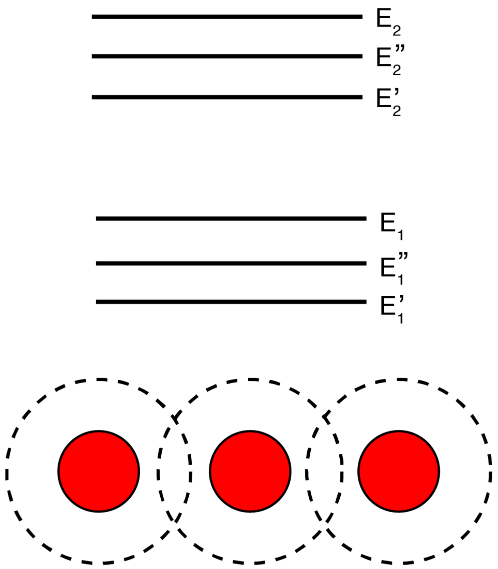
What are Metals? — A very brief look at band theory



2 non-interacting atoms
Electrons do not interact



2 interacting atoms.
Electrons interact
Energy levels split into two

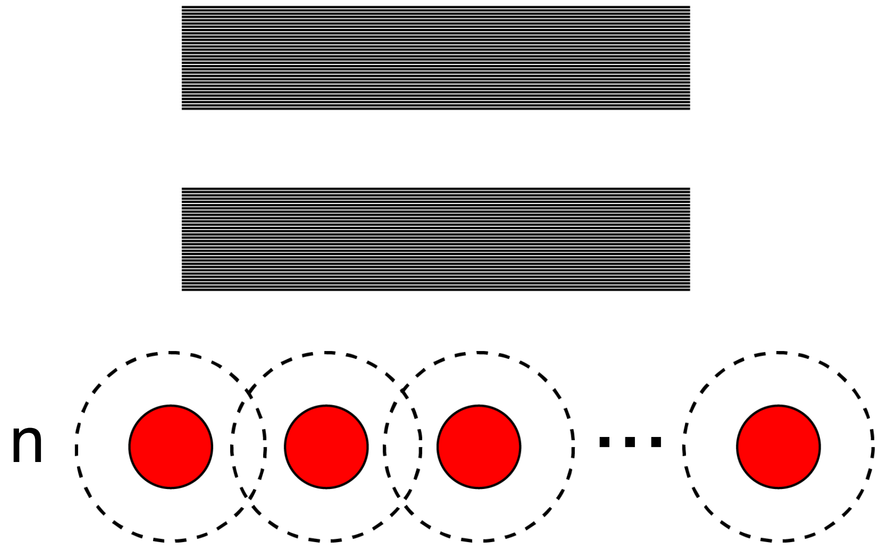


3 interacting atoms.
Electrons interact
Energy levels split into three

Electrons can only possess certain discrete energy values*

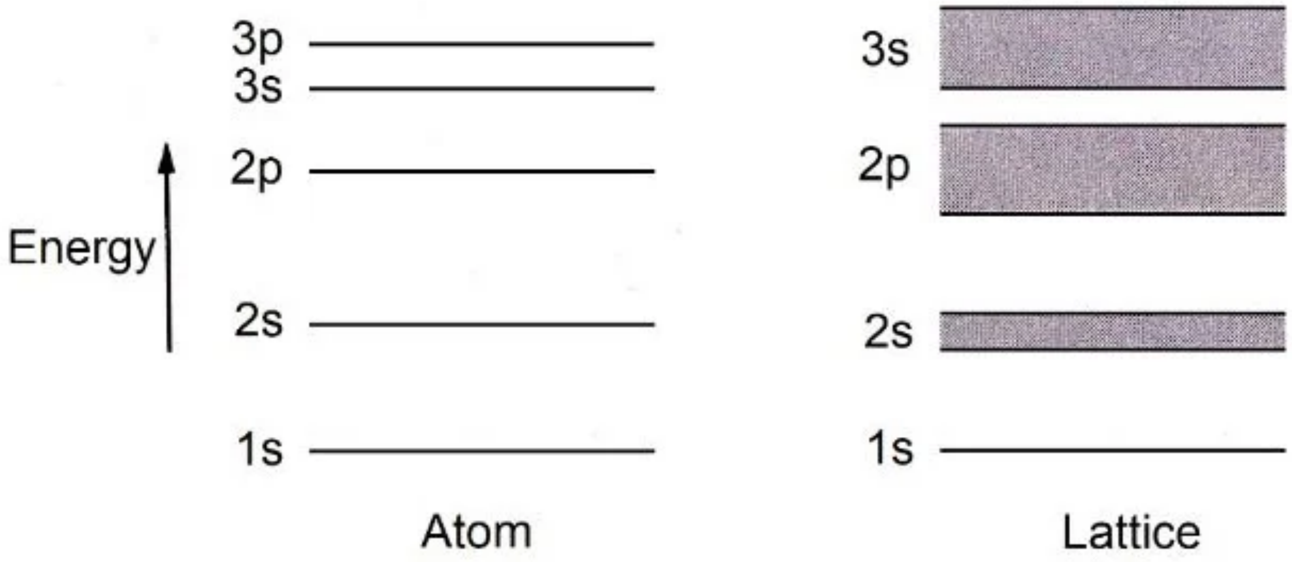
*Comes about from quantum physics. Take it as the truth for now

What are Metals? — A very brief look at band theory



n interacting atoms
Electrons interact
Energy levels split into n levels
Gaps between levels are small
Think of it as an **energy band**

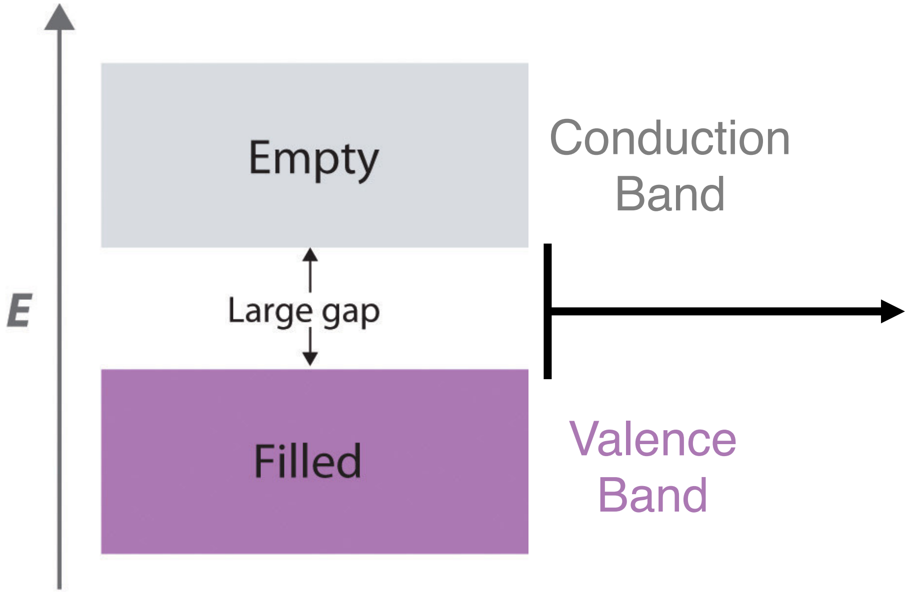
If you remember your orbitals from physics/chemistry:
1s, 2s, 2p, 3s, 3p…



All solids have an energy band structure
Electrons can only occupy these bands
Bands can be full, partially full, empty

Band theory helps us distinguish metals from non-metals

Insulators



To conduct electricty, electrons need to move from valence band to conduction band*

In an insulator, there is a band gap between the bands

Energy needs to be supplied to cross this band gap

Not possible at 0 K

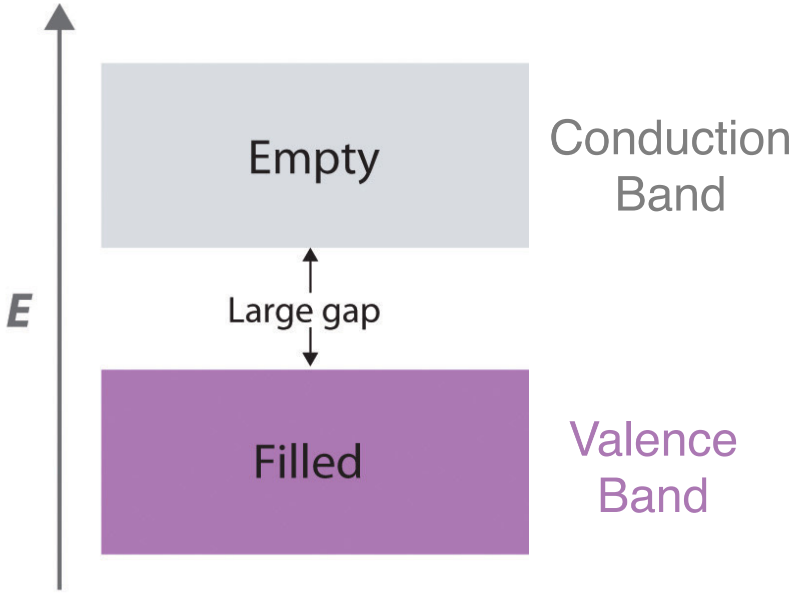
Valence Band: Highest band with electrons in it

Conduction Band: Lowest band with vacant energy levels

*This is a simplification. But this is not a solid-state physics class.

Band theory helps us distinguish metals from non-metals

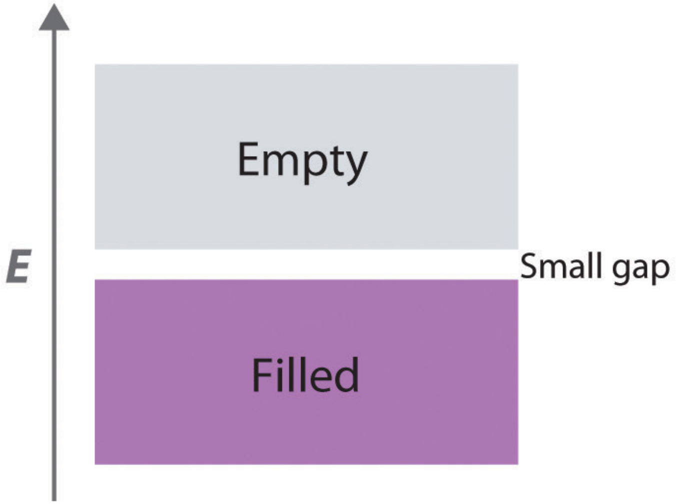
Insulators



Valence Band:
Highest band with electrons in it

Conduction Band:
Lowest band with vacant energy levels

Semiconductors



Partially filled conduction band at room temperature

More energy provided → More electrons can cross the band gap

Increasing temperature → Increasing conducitivity

Key defining property of non-metals

Band gap between valence and conduction band

Electric field not sufficient to promote electrons across gap

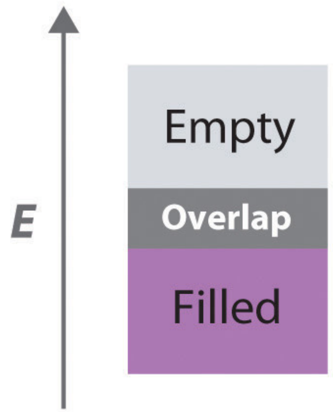
Conductivity increases with temperture

No conductivity at absolute zero (0 K)

Band theory helps us distinguish metals from non-metals

Metals (2 types of band structure)

Partially filled valence band

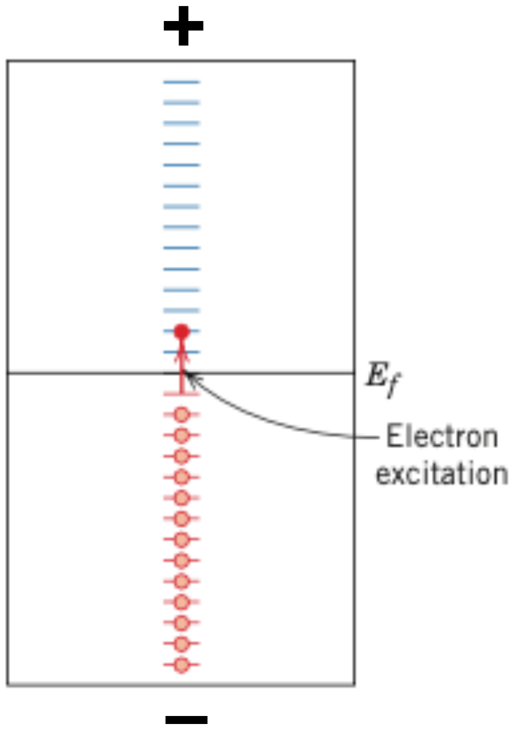


Filled valence band

Conduction band overlaps with valence band

Very little energy needed to promote electron into next available energy state

Electric field can cause electrons to flow



Key defining property of metals

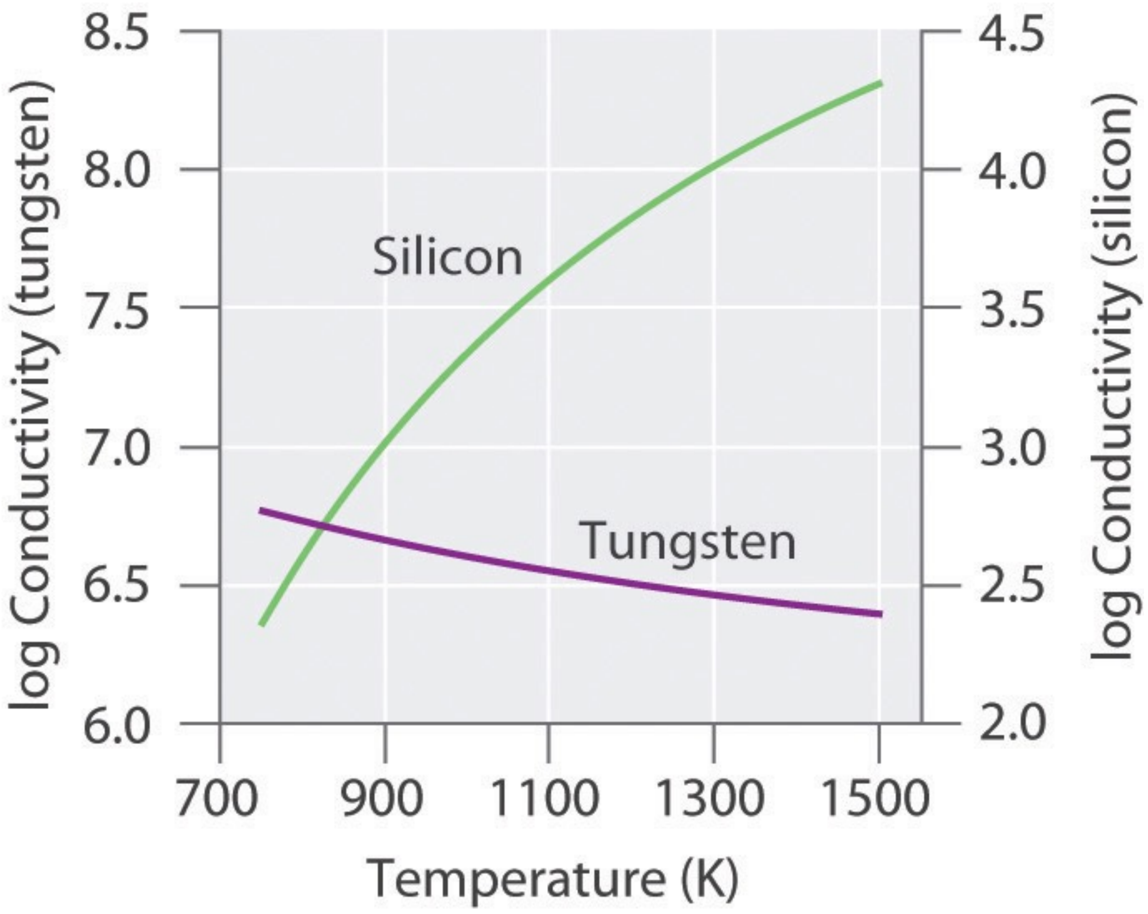
No band gap between valence and conduction band

Electric field sufficient to promote electrons across gap

Conductivity **decreases** with temperture

Conductive even at absolute zero (0 K)

Quick note about temperature dependence



Metals: Decrease conductivity with temperature

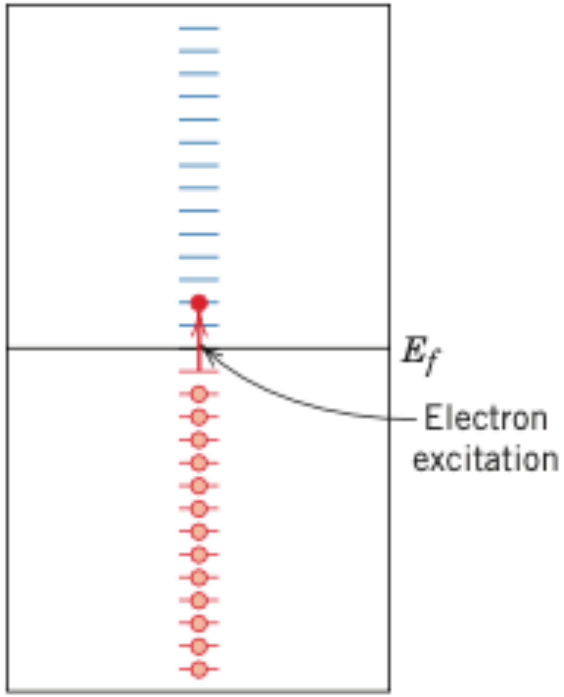
Insulators and semiconductors: Increase conductivity with temperature

Not same rate of change!

Larger temperature dependency for insulators/semiconductors

Band theory can explains some properties of metals

Eg. Why are metals shiny and opaque?



1. Many empty levels above the valence band means that the electrons in the valence band can be excited by photons with low energies

2. Electrons absorb low energy visible light → <u>Opaque</u>

3. Excited electrons release energy as visible light → <u>Reflect light</u>

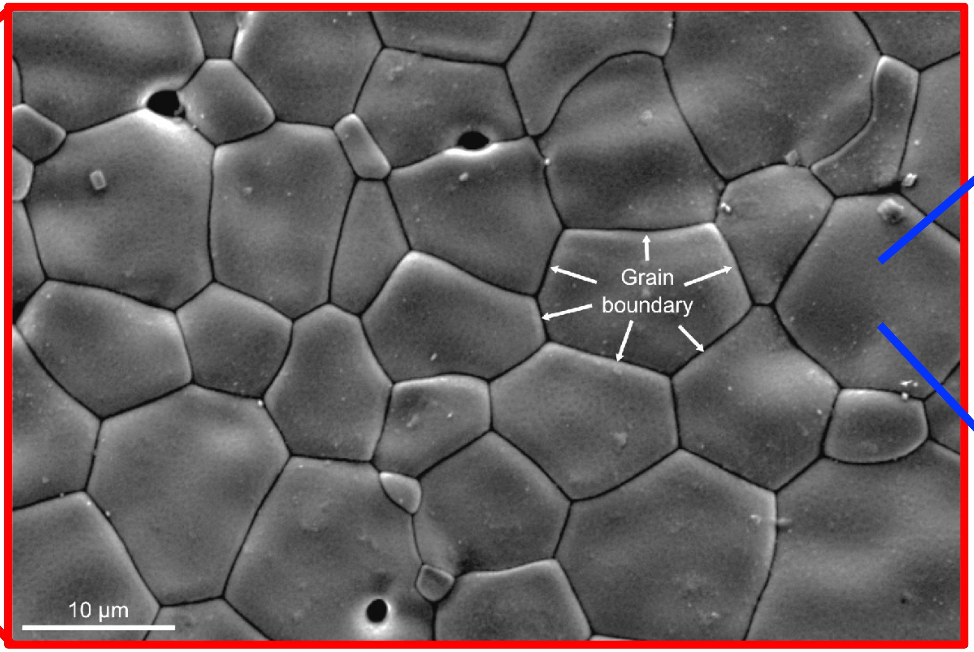
Smooth metal surfaces allow for **specular reflection** → <u>Shiny</u>

Rough surfaces result in **diffuse reflection** → Not shiny (white)

What does a metal look like at different length scales?

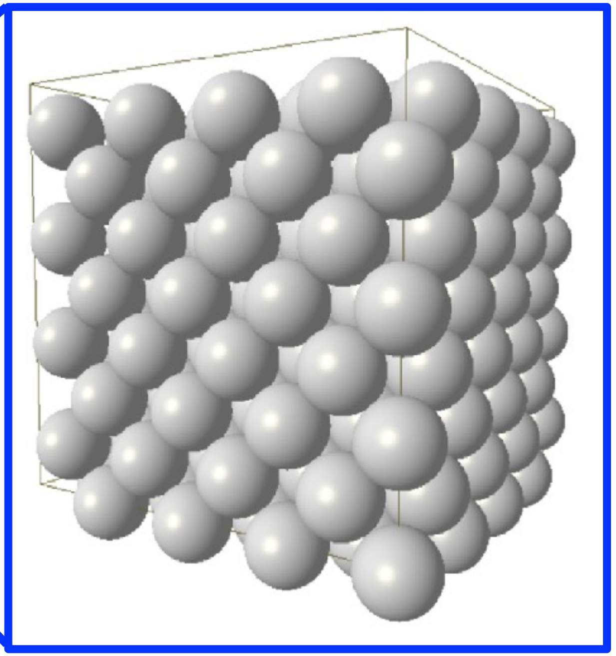
Part / Product

Microstructure



Grains, cracks, precipitates, dislocations, twins, etc.

Crystal Structure



Atoms

Scale: mm – km | nm – cm | Angstrom

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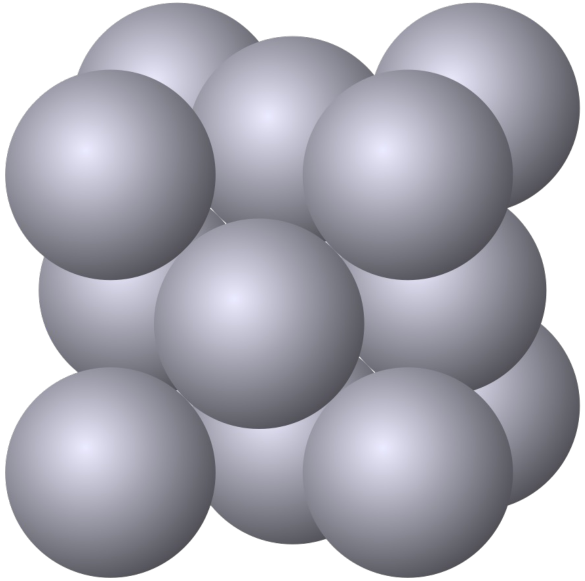
All of you have seen metal microstructure before!

These splotches / patches are metal grains from the microstructure of the metal

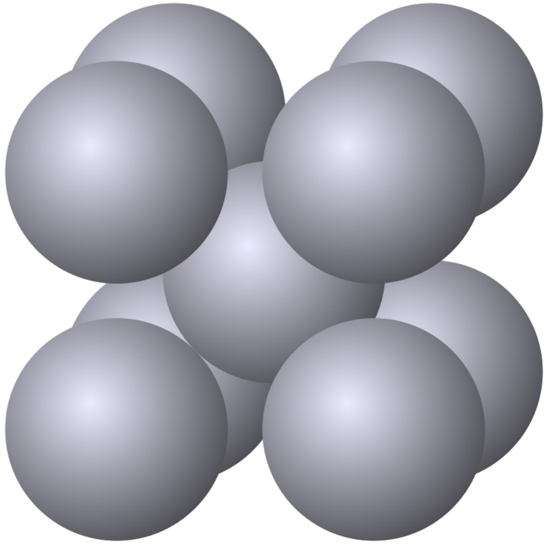
Grains belong to the zinc coating that is applied to steel to prevent rusting. (Galvanized steel)

Most Common Crystal Structures of Metals

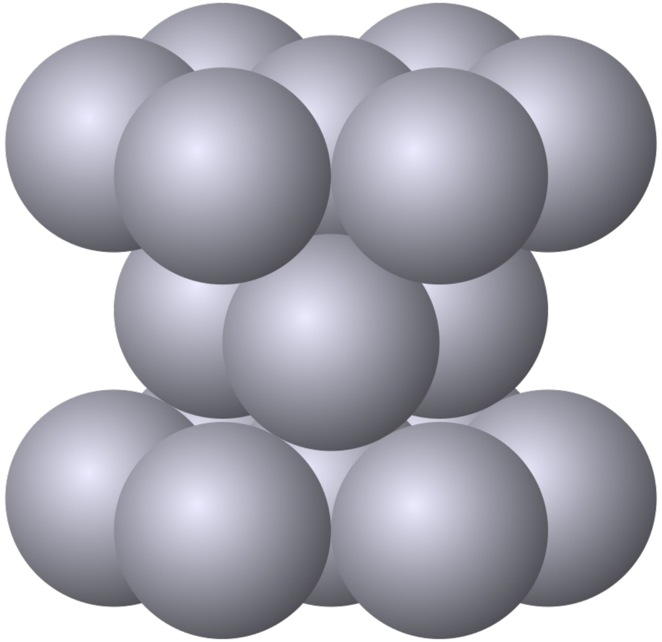
Face-Centered Cubic
(FCC)



Body-Centered Cubic
(BCC)



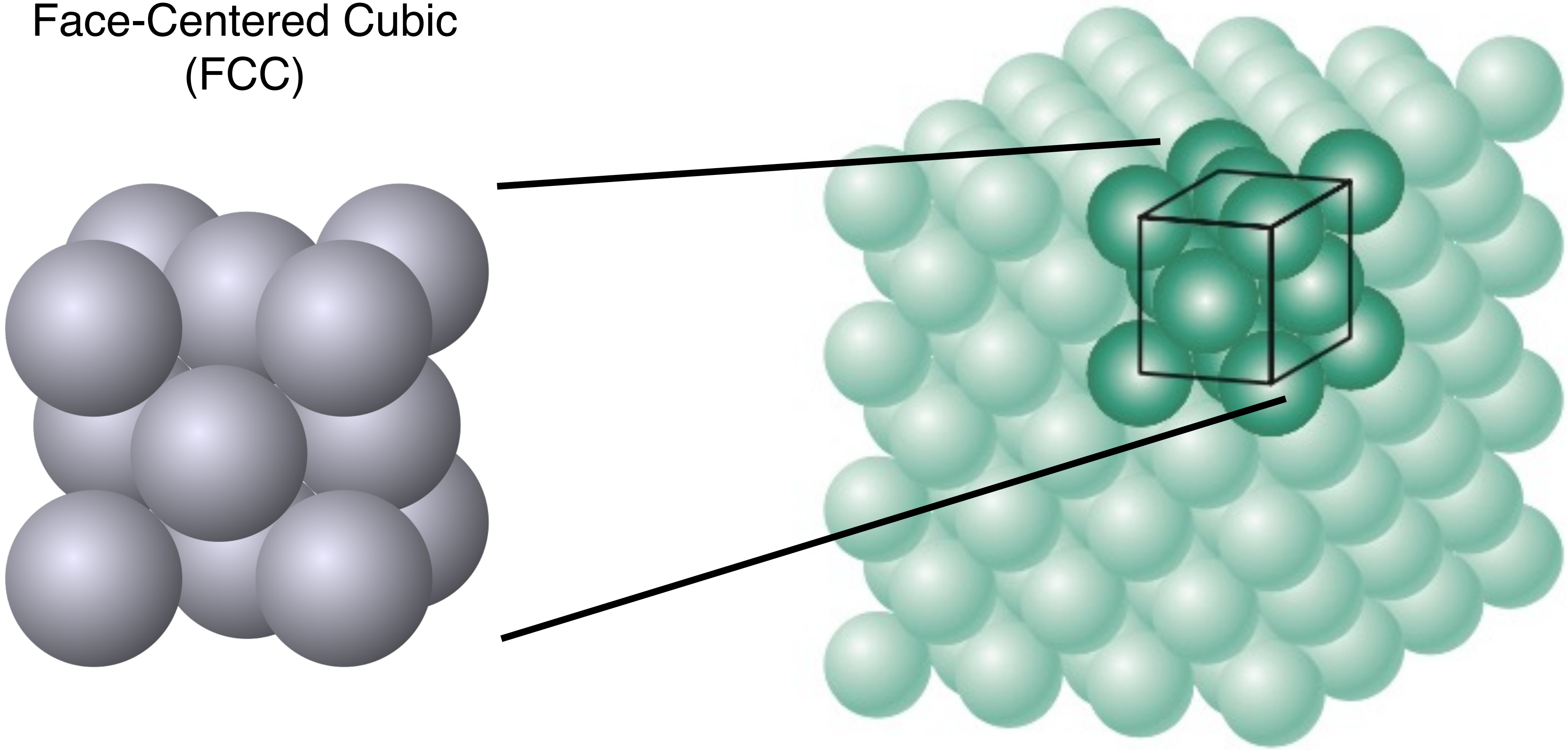
Hexagonal Close-Packed
(HCP)



The crystal structure shows how the metal atoms pack together in the metal

Most Common Crystal Structures of Metals

Face-Centered Cubic
(FCC)



The crystal structure shows how the metal atoms pack together in the metal
Tesselate the unit cell in all directions to obtain the metal

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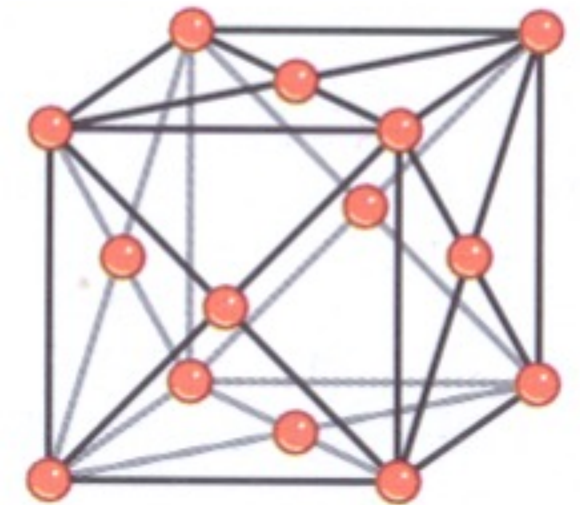
Most Common Crystal Structures of Metals

Face-Centered Cubic
(FCC)



Body-Centered Cubic
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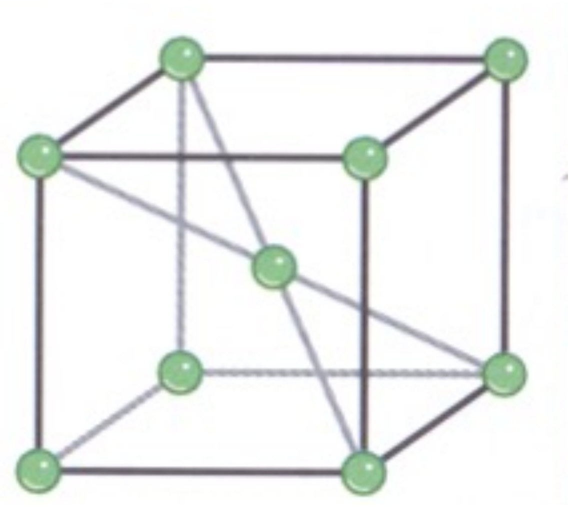
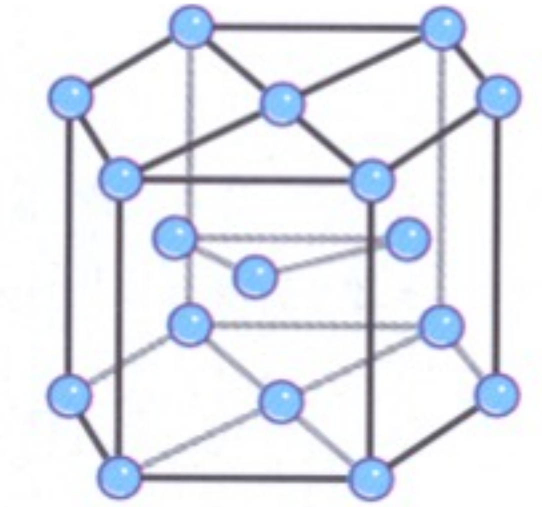


Hexagonal Close-Packed
(HCP)



Easier to represent the crystal structure using a reduced-sphere unit cell

(No need to draw the lines inside the unit cell, they just help guide the placement of the atoms)

How Do We Classify Metals?

Multiple ways of classifying metals — Depends on the information you want to convey

1. Composition: Ferrous or Non-ferrous

Essentially: Is there iron in the metal/alloy or not?

Ferrous

- Heavier
- Often magnetic
- Typically stronger
- Vulnerable to rust (iron oxide)
- Cheap

Non-Ferrous

- Lighter
- Often not magnetic
- Typically weaker
- Does not rust but can corrode
- Expensive

Element	Density (g/cm^3)	Cost ($/kg)
Fe	7.8	0.1
Al	2.7	2.6
Ti	4.5	14.9
Ag	10.5	1120.7

The amount of iron in the metal hints at the types of properties that it has

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How Do We Classify Metals?

Multiple ways of classifying metals — Depends on the information you want to convey

2. Composition: Alloy or Pure metals

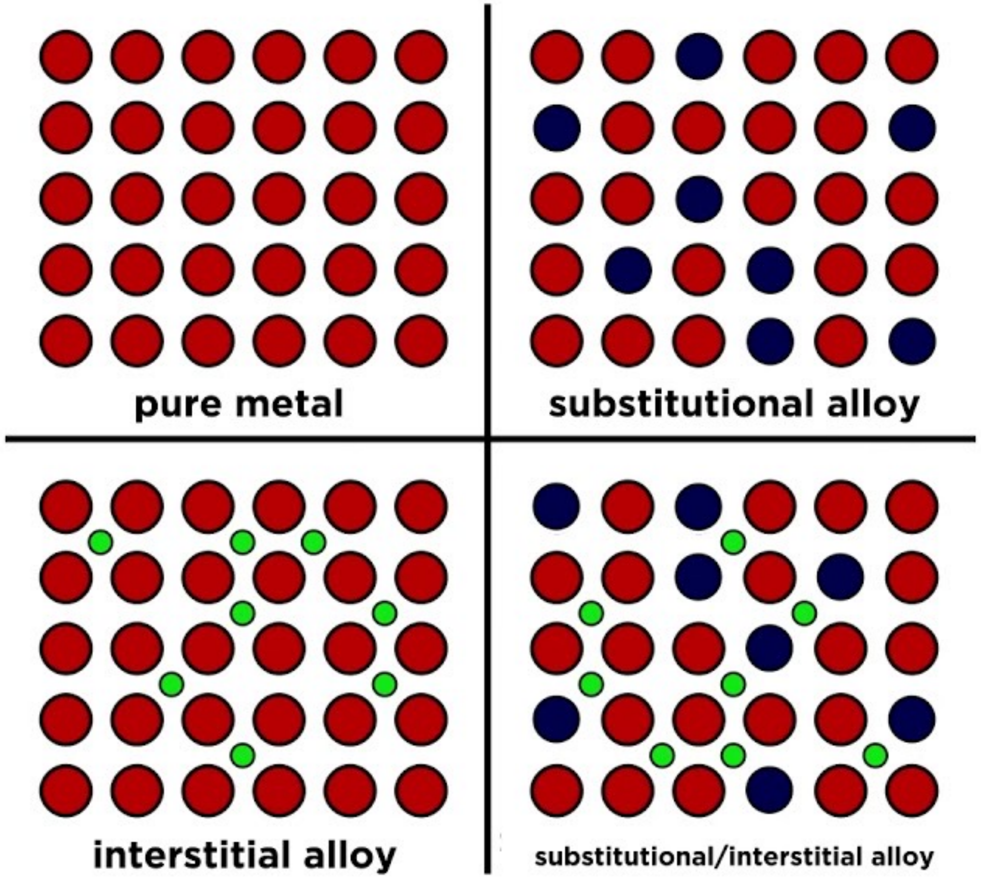
An alloy is a mixture of chemical elements, in which at least one is a metallic element.

The majority of elements should be metallic elements

Most metals used today are alloys!

Very few pure metals are used:
Cu, Ag, Au, Pt

Atomic representation of alloying

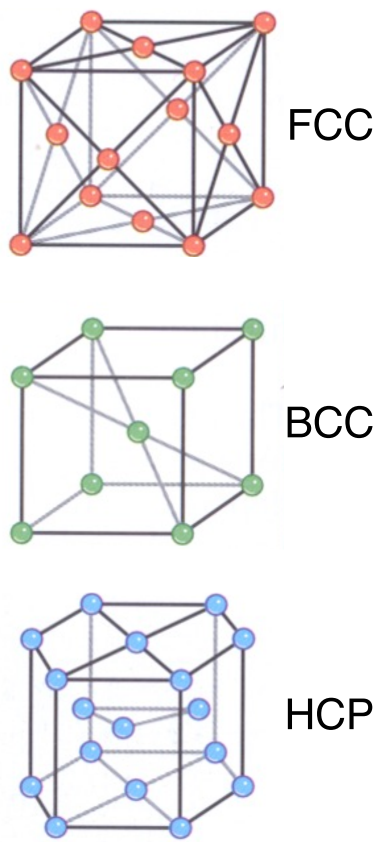


How Do We Classify Metals?

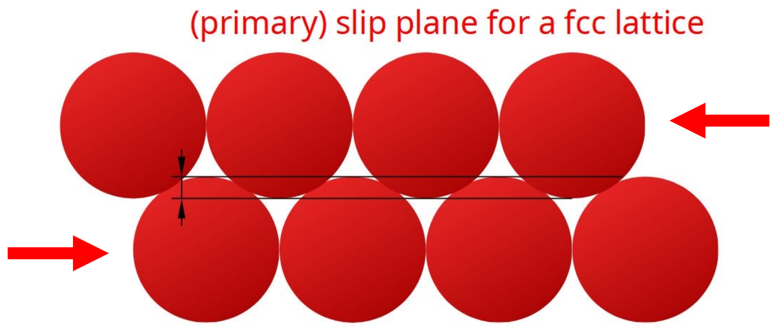
Multiple ways of classifying metals — Depends on the information you want to convey

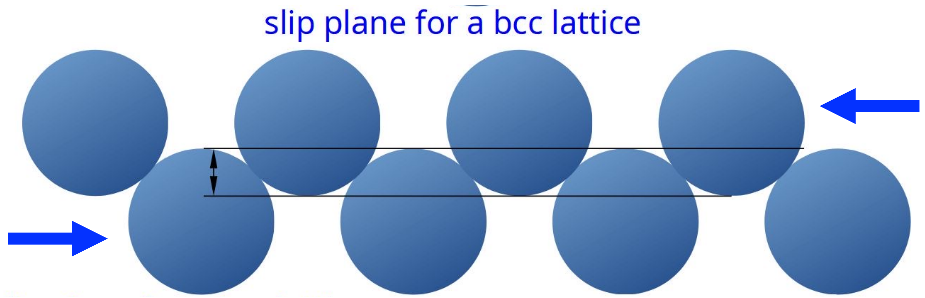
3. Crystal structure

Properties of crystal structure → Properties of metal



Example 1: Ductility





Ease of slip is related to ductility in the metal (Covered in Lecture 9 or 10)

The number of slip systems and the energy needed to activate them depends on the crystal structure

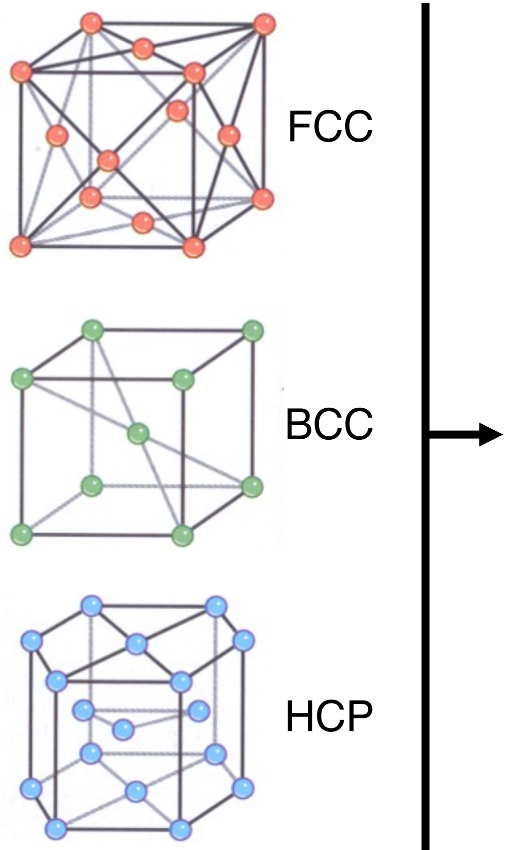
Ease of slip: FCC > BCC > HCP → **Ductility**: FCC > BCC > HCP

How Do We Classify Metals?

Multiple ways of classifying metals — Depends on the information you want to convey

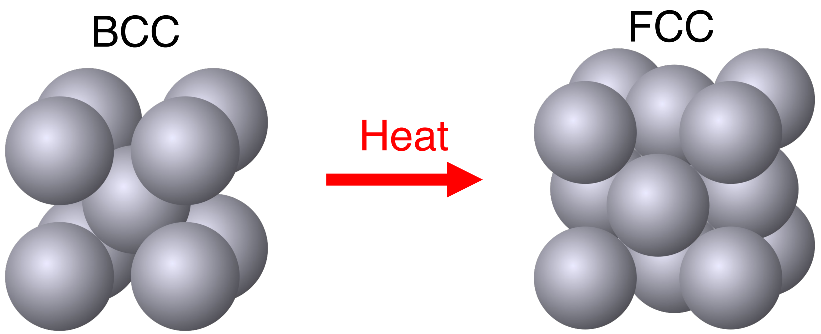
3. Crystal structure

Properties of crystal structure → Properties of metal



Example 2: Density

Past a certain temperature, heating an iron rod causes it to **shrink** rather than expand



FCC unit cell is denser than BCC

For the same mass, increasing density decreases volume → Shrinkage!

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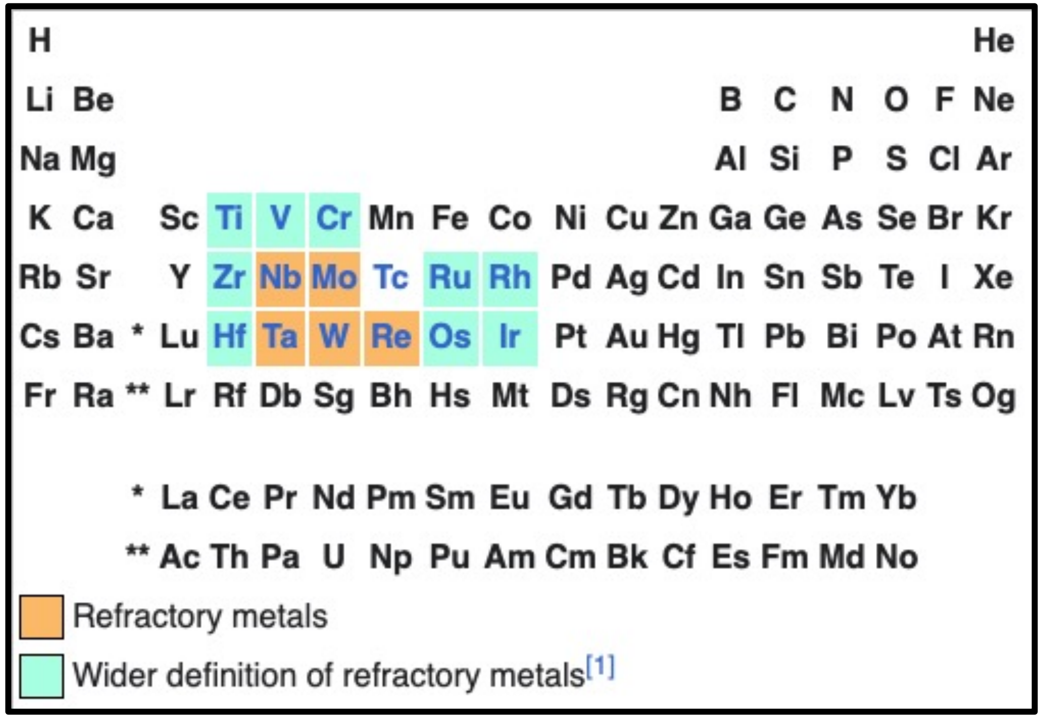
How Do We Classify Metals?

Multiple ways of classifying metals — Depends on the information you want to convey

<u>4. Refractory or not?</u>

Refractory metals are a class of metals that extremely resistant to heat and wear



Element	Melting Point (˚C)	Vickers Hardness (GPa)
W	3422	3.4
Mo	2623	1.5
Cr	1907	1.0

Often means a melting point above 2200˚C but some definitions require a melting point above 1800˚C

Challenge with refractory metals

Hard to manufacture since forming temperatures are high

Highly susceptible to oxidation at high temperatures

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How Do We Classify Metals?

Multiple ways of classifying metals — Depends on the information you want to convey

5. Base metal vs. Precious metal

Base Metal

- Common
- Inexpensive
- *Oxidizes / Corrodes easily*

→ Iron, Nickel, Zinc, Copper, Etc.

Precious Metal

- Rare
- Expensive
- *Resistant to oxidation / corrosion*

→ Gold, Silver, Platinum, Palladium, Etc.

Oxidation of copper

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How Do We Classify Metals?

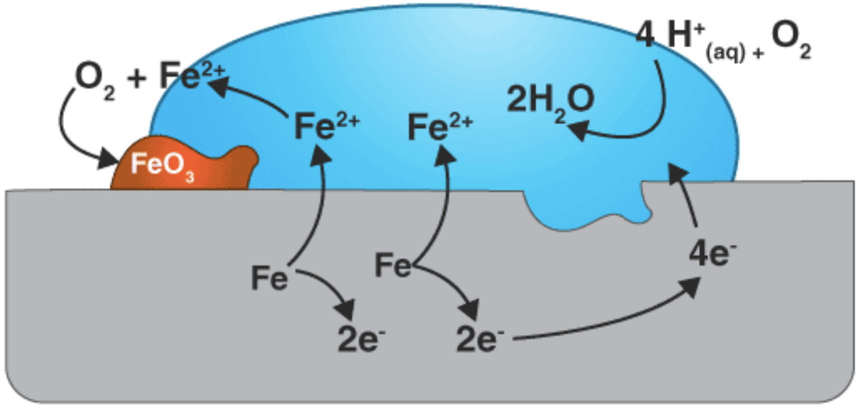
Multiple ways of classifying metals — Depends on the information you want to convey

6. Corrosion resistance

What is corrosion?

Corrosion in metals costs about US $2.5 trillion each year, about 3% of the world's GDP!

Corrosion in metals often refers to the conversion of the metal to a metal oxide



Impacts performance and also aesthetics

Corrosion is often an electrochemical process! *(not covered in this course)*

How Do We Classify Metals?

Multiple ways of classifying metals — Depends on the information you want to convey

6. Corrosion resistance

Strong corrosion resistance:

- Stainless steel
- Titanium
- Copper
- Aluminium

Poor corrosion resistance:

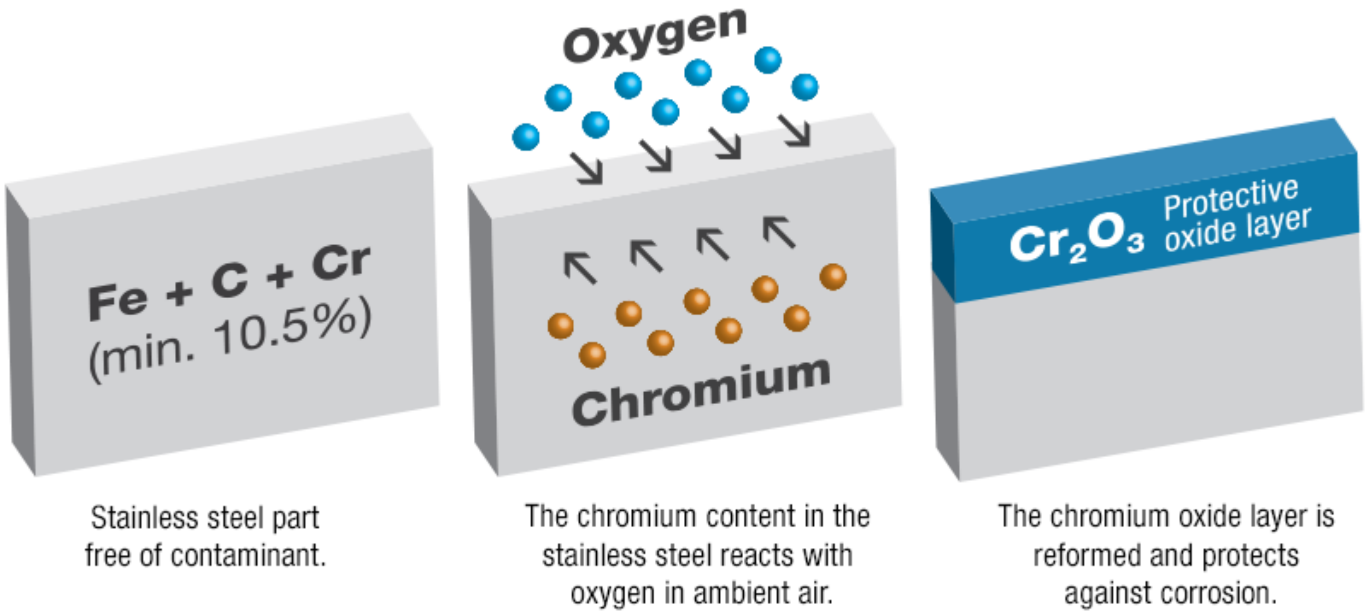
- Carbon steels
- Magnesium
- Lead

How to introduce corrosion resistance?

The metal oxide formed protects the metal from further corrosion

Natural: Al, Ti

Engineered: High Cr steels



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How Do We Classify Metals?

Multiple ways of classifying metals — Depends on the information you want to convey

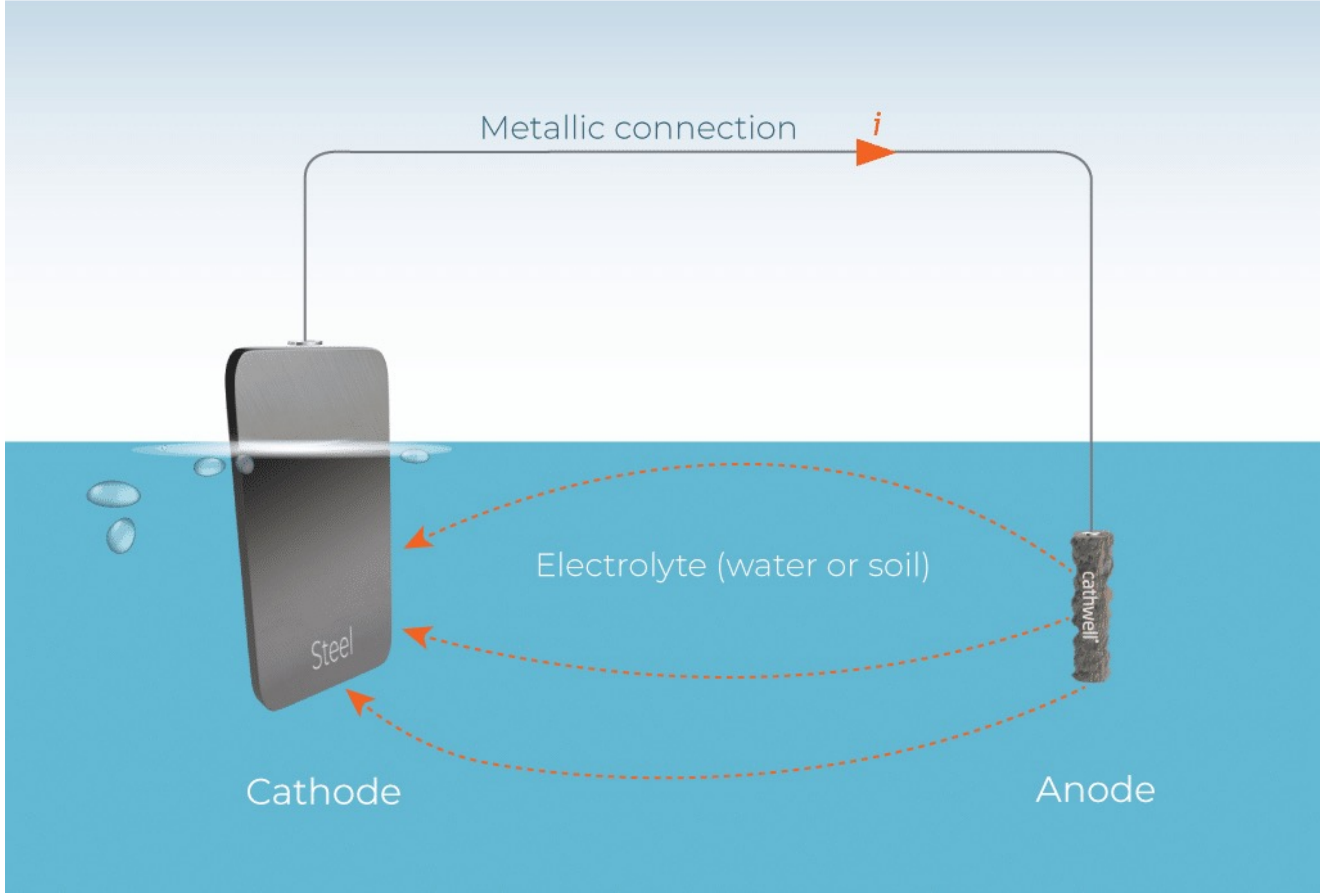
6. Corrosion resistance

Another way to introduce corrosion resistance: **Cathodic protection**

Idea: Protect a metal (the cathode) by sacrificing another one (the anode)

Since it's an electrochemical system (think battery), need to have a "circuit".

Metals in electrical contact with an electrolyte



How Do We Classify Metals?

Multiple ways of classifying metals — Depends on the information you want to convey

6. Corrosion resistance

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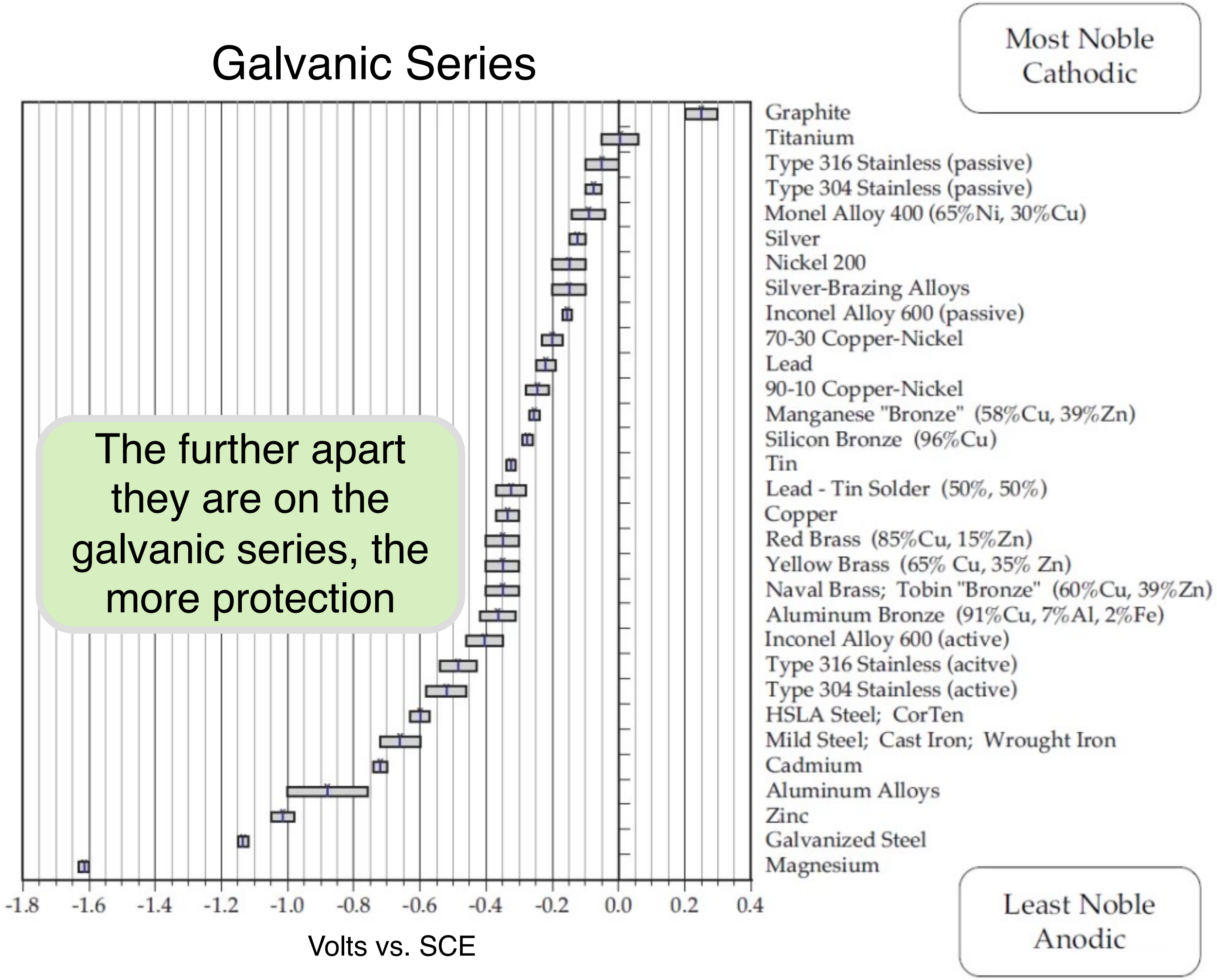
Metals in electrical contact with an electrolyte

Galvanic Series



How Do We Classify Metals?

Multiple ways of classifying metals — Depends on the information you want to convey

6. Corrosion resistance

Another way to introduce corrosion resistance: **Cathodic protection**

Idea: Protect a metal (the cathode) by sacrificing another one (the anode)

Since it's an electrochemical system (think battery), need to have a "circuit".

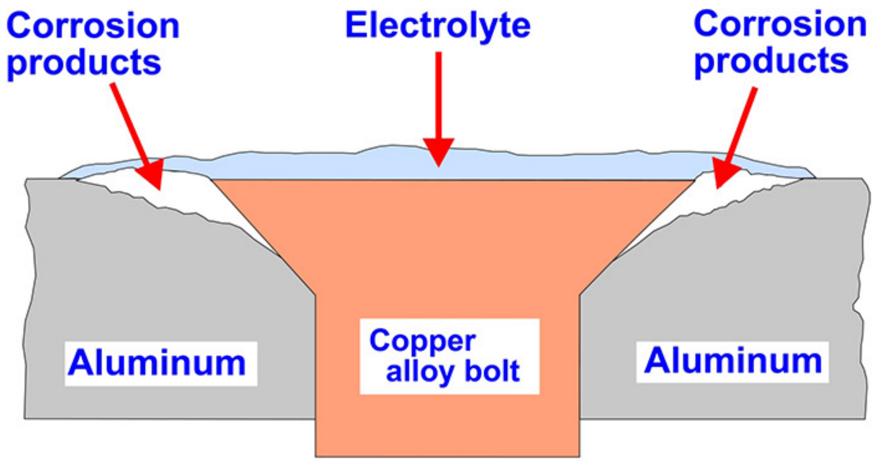
Metals in electrical contact with an electrolyte

Galvanic corrosion

If unintentional → Sacrifice the wrong metal!

Corrode something that is corrosion resistant

Copper bolt in aluminum



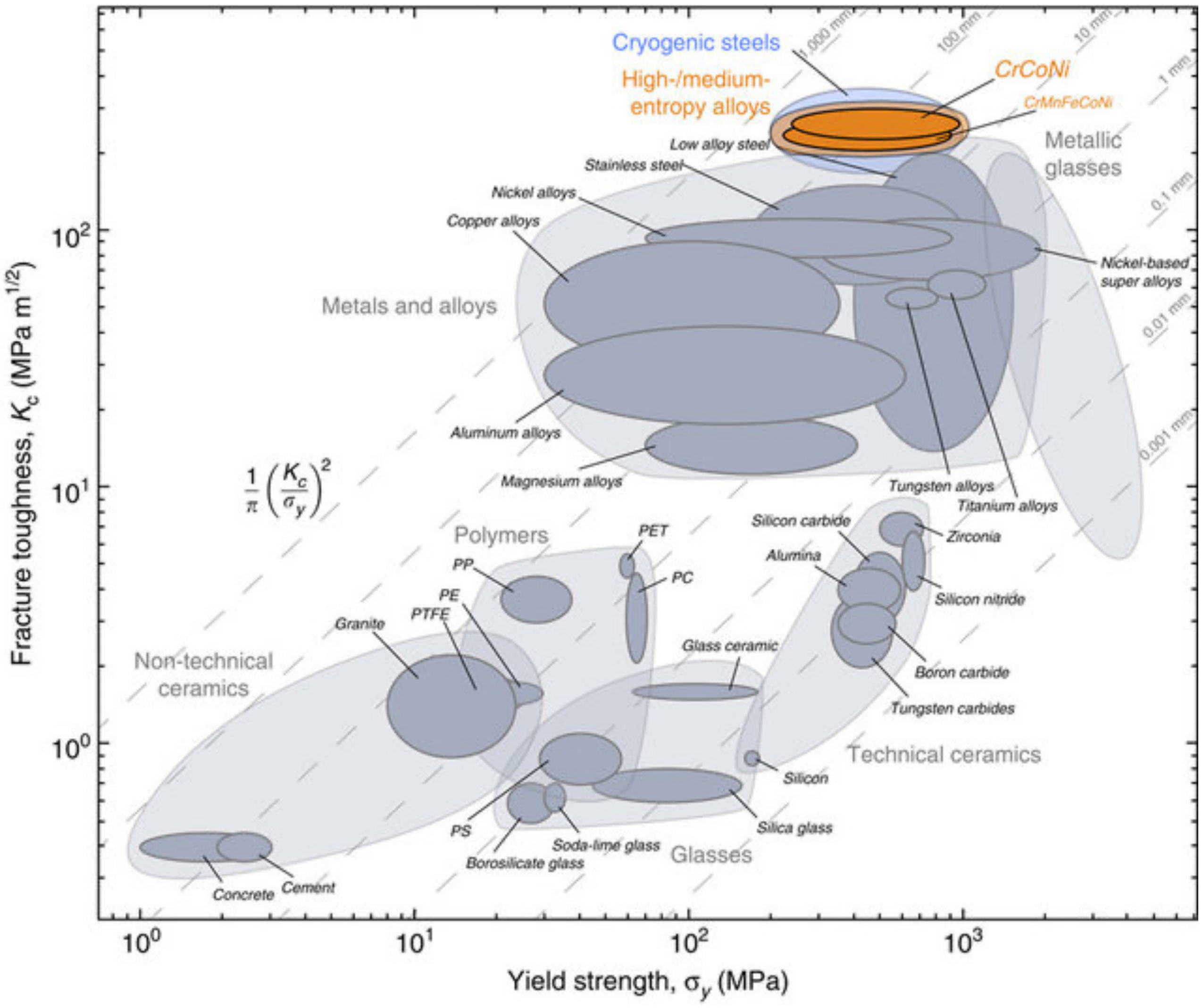
Aluminum protected the copper
Aluminum corroded

How Do We Classify Metals?

Multiple ways of classifying metals — Depends on the information you want to convey

7. Mechanical Properties

- Strength
- Ductility
- Young’s modulus
- Shear modulus
- Hardness
- Toughness
- Fatigue resistance
- Creep resistance



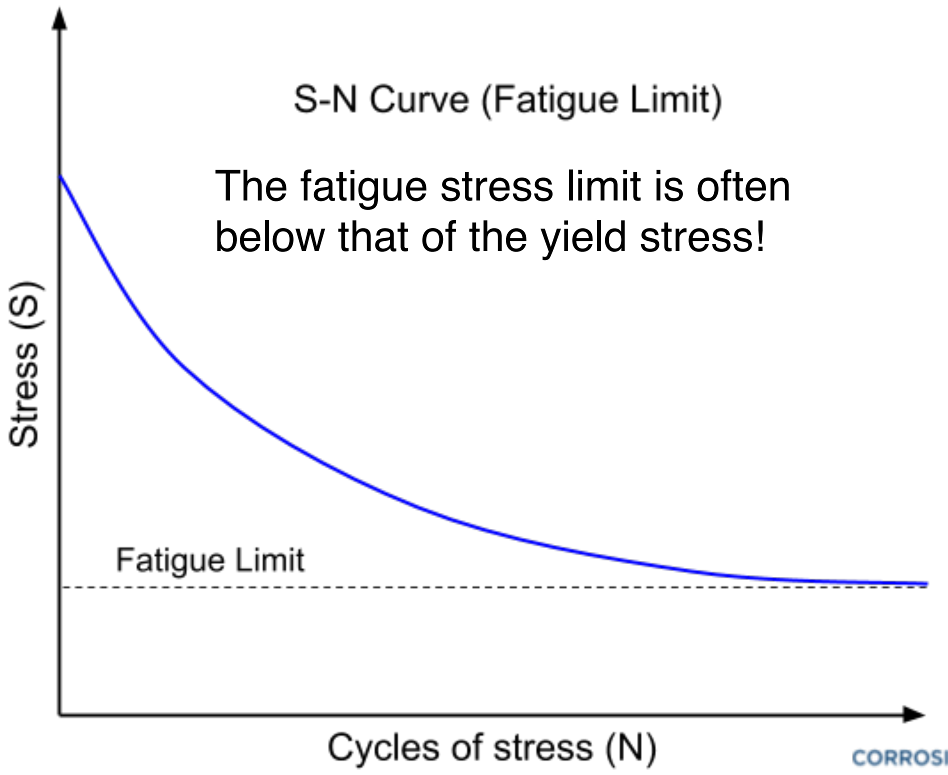
How Do We Classify Metals?

Multiple ways of classifying metals — Depends on the information you want to convey

7. Mechanical Properties

- Strength
- Ductility
- Young's modulus
- Shear modulus
- Hardness
- Toughness
- Fatigue resistance
- Creep resistance

Fatigue is the initiation and propagation of cracks in a material due to cyclic loading



CORROSIONPEDIA

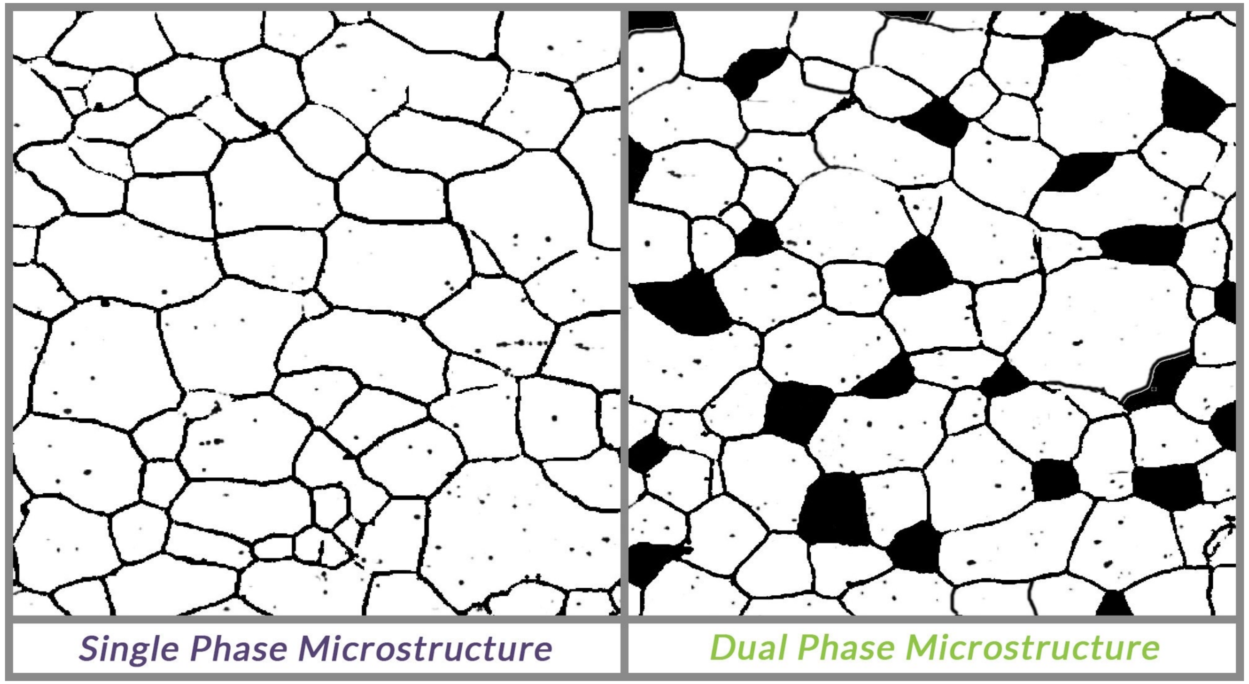
Classic example: Aloha Airlines Flight 243

How Do We Classify Metals?

Multiple ways of classifying metals — Depends on the information you want to convey

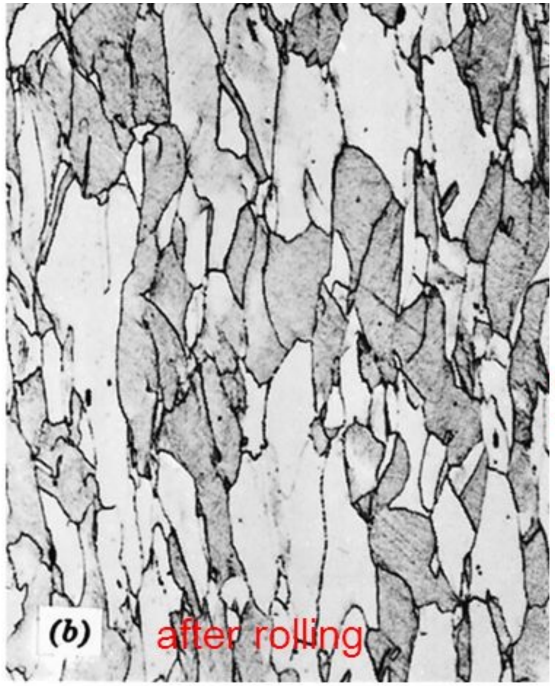
8. Microstructure

Homogeneous | Heterogeneous



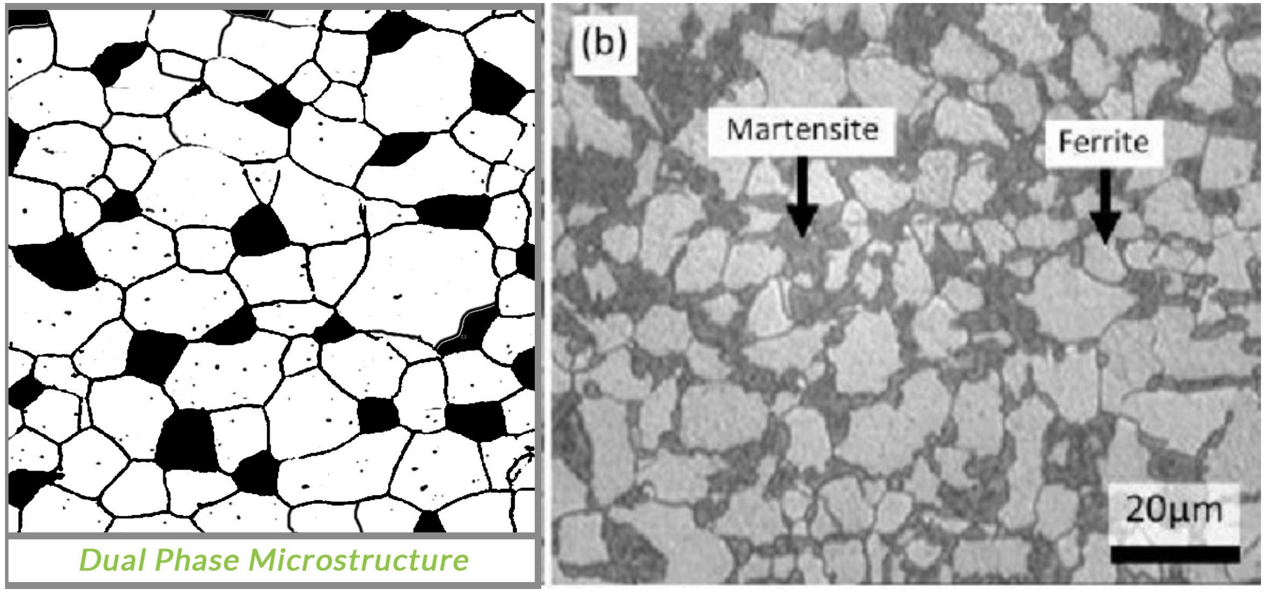
Isotropic grains

Anisotropic grains

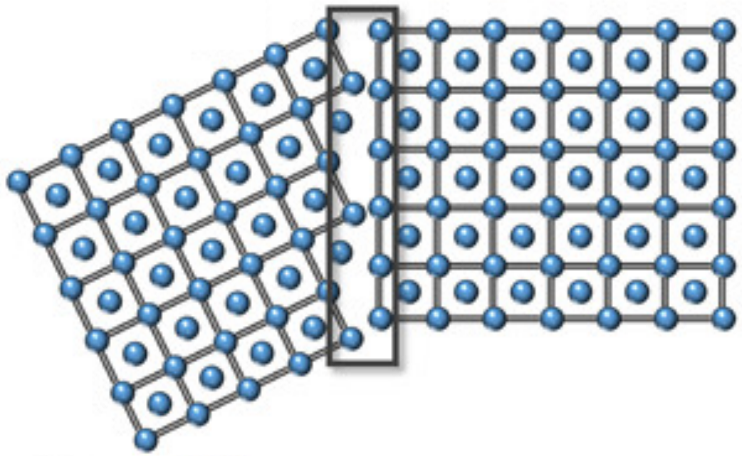


Microstructure impacts the mechanical properties of the metal

Before we proceed: What is a phase?

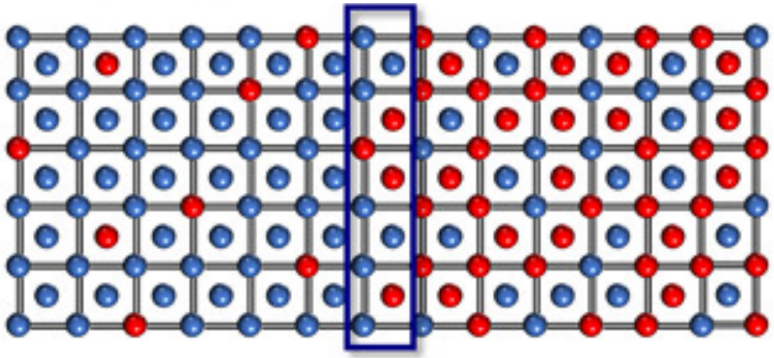


Two grains with same composition and crystal structure → Single phase



A phase is a state of matter that has uniform physical and chemical characteristics

Two grains with different composition but same crystal structure → Dual phase



Syrup → Sugar + Water (Single phase)

Ice + Water (Two phases)

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What is an Alloy?

An alloy is a mixture of chemical elements, in which at least one is a metallic element.

The majority of elements should be metallic elements

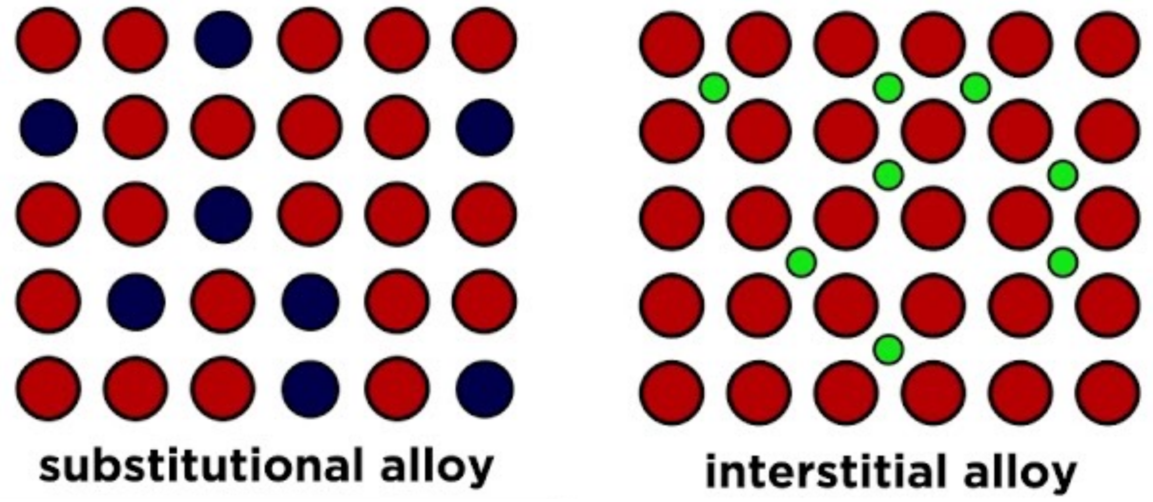
Alloys in your daily life:

Brass: Cu, Zn

Al 3004: Al, Mg, Si, Fe, Cu, Zn, Mn

Inconel 718: Ni, Fe, Cr, Cb, Ta, Mo, Ti, Al, Co

Atomic representation of alloying

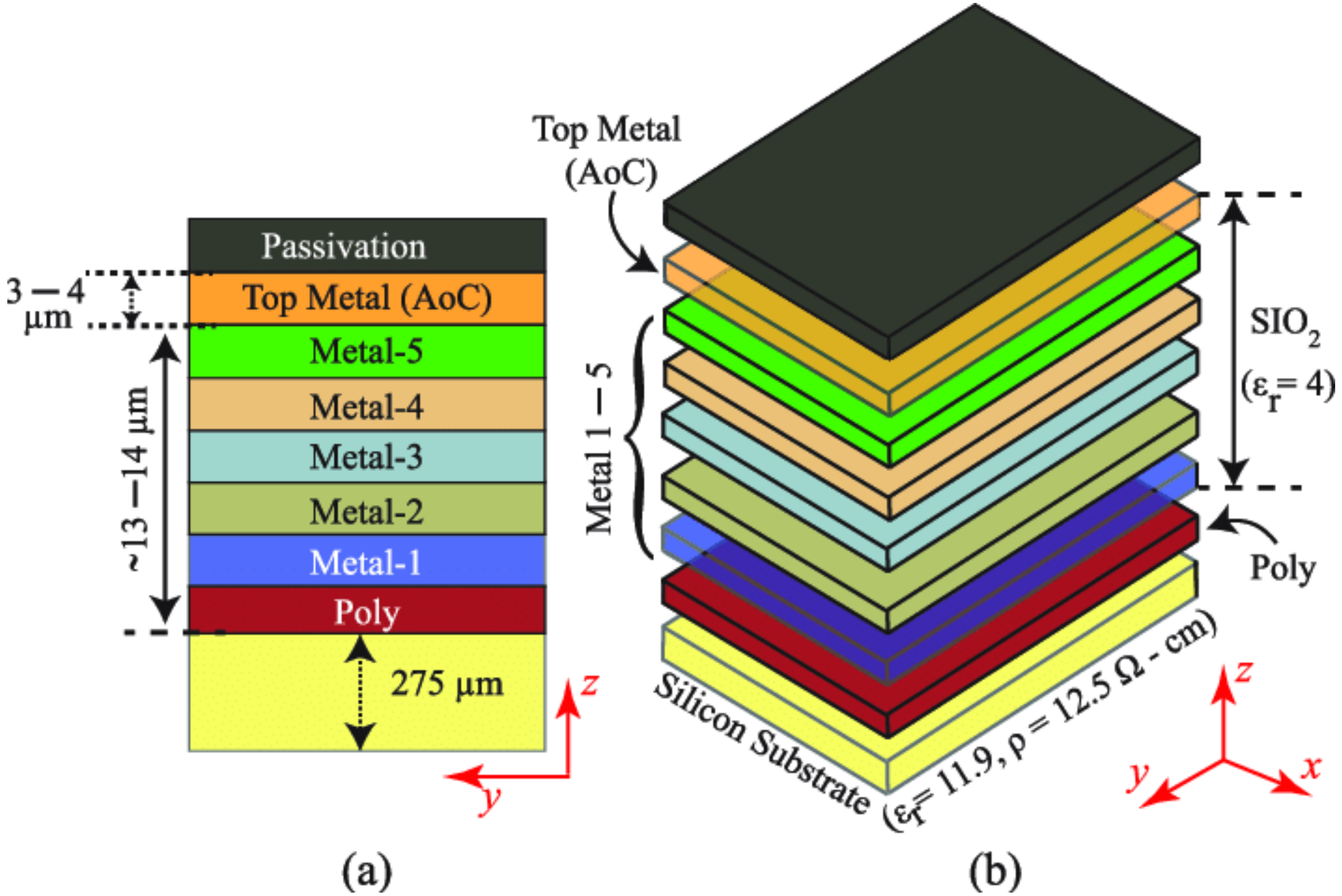


Qn1: Why do we need to know if something alloys?

Qn2: Why do some elements form substitutional alloys and some form interstitial alloys?

Why do we need to know if something alloys?

How will two metals behave if they are in contact?



What happens at the interface when I join two metals together?

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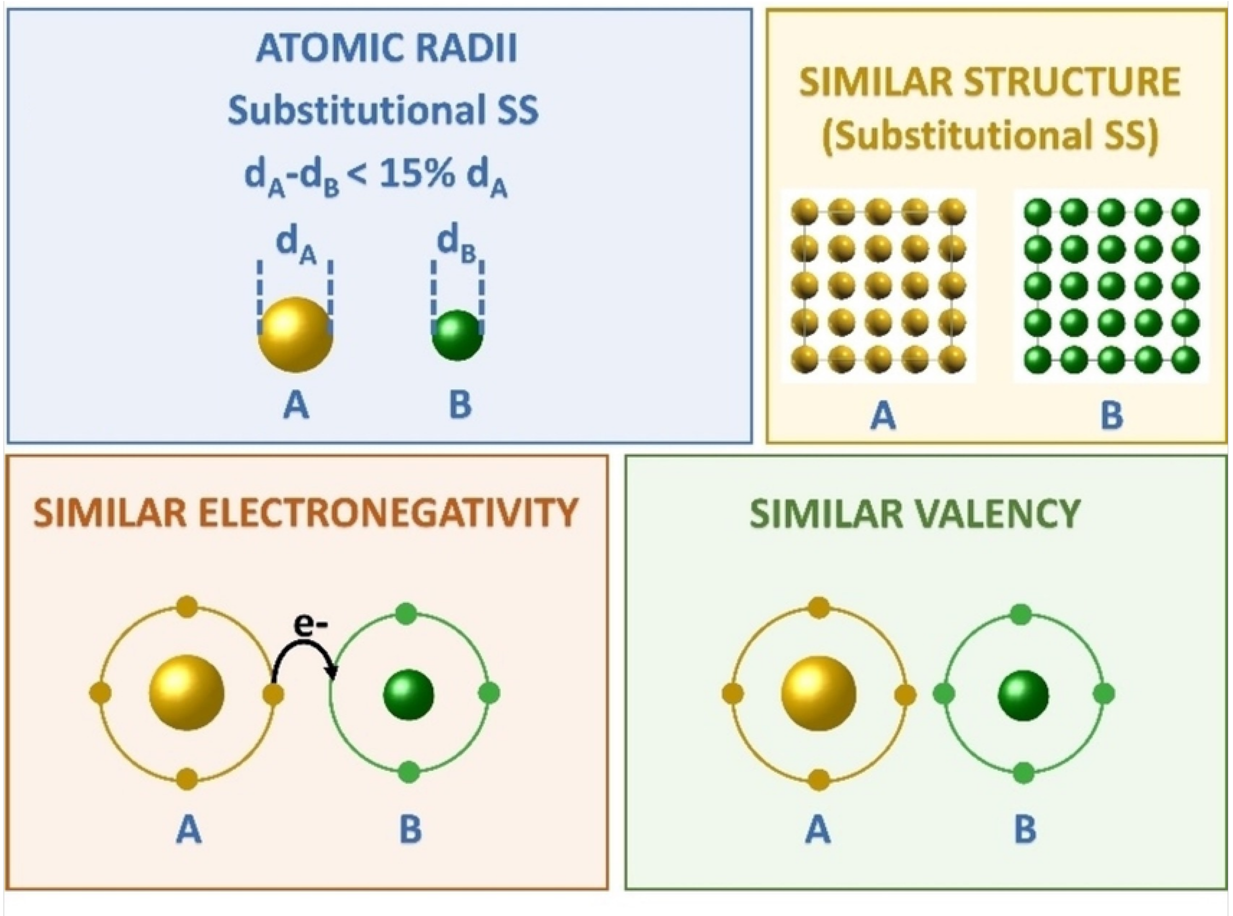
Hume-Rothery Rules for Binary Solid Solutions

Solid solution: Crystal structure is maintained and no new structures form (Single phase)

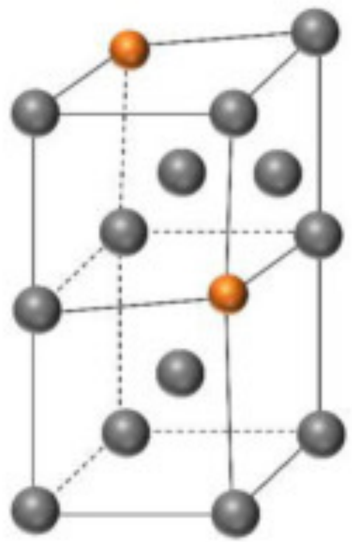
Simple analogy: Mix water and alcohol together. Compositionally homogenous



For substitutional solid solutions

1. Difference in atomic radii is < 15%
2. Crystal structures have to be the same
3. Similar electronegativity
4. Similar valency

Can think of it as the conditions needed to replace one atom in the crystal with another atom.



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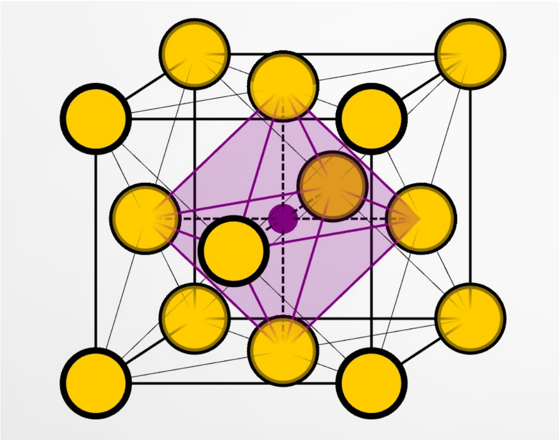
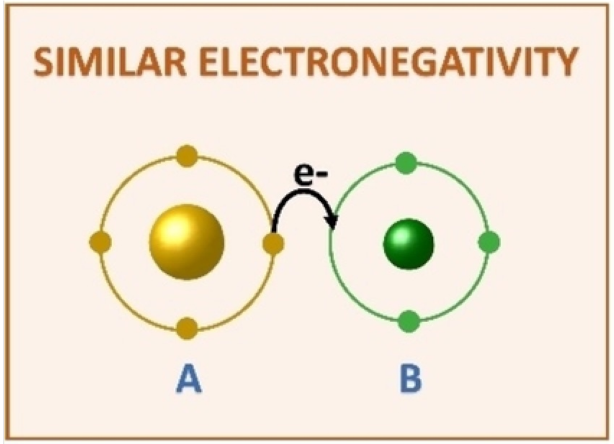
Hume-Rothery Rules for Binary Solid Solutions

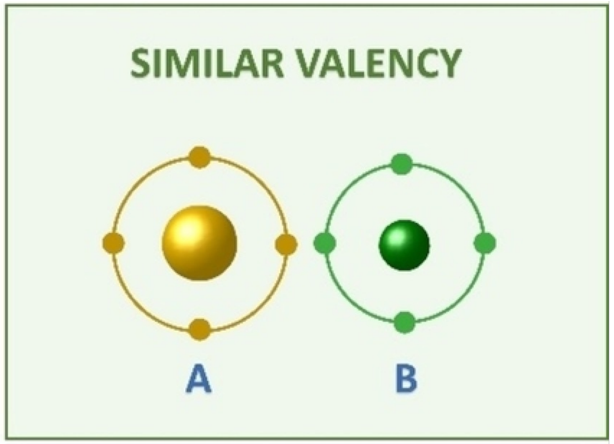
Solid solution: Crystal structure is maintained and no new structures form (Single phase)

Simple analogy: Mix water and alcohol together. Compositionally homogenous

Octahedral interstitial site in FCC



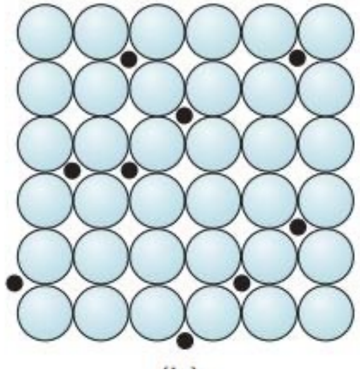




For interstitial solid solutions

1. Solute atom has to fit within ”pore” space of the unit cell
2. Similar electronegativity
3. Similar valency

Can think of it as the conditions needed to squeeze in one atom into the free space of the unit cell



Hume-Rothery Rules for Binary Solid Solutions

For substitutional solid solutions

1. Difference in atomic radii is < 15%
2. Crystal structures have to be the same
3. Similar electronegativity
4. Similar valency

For interstitial solid solutions

1. Solute atom has to fit within ”pore” space of the unit cell
2. Similar electronegativity
3. Similar valency

If Hume-Rothery rules are not fulfilled → Low to no solubility of element in the metal

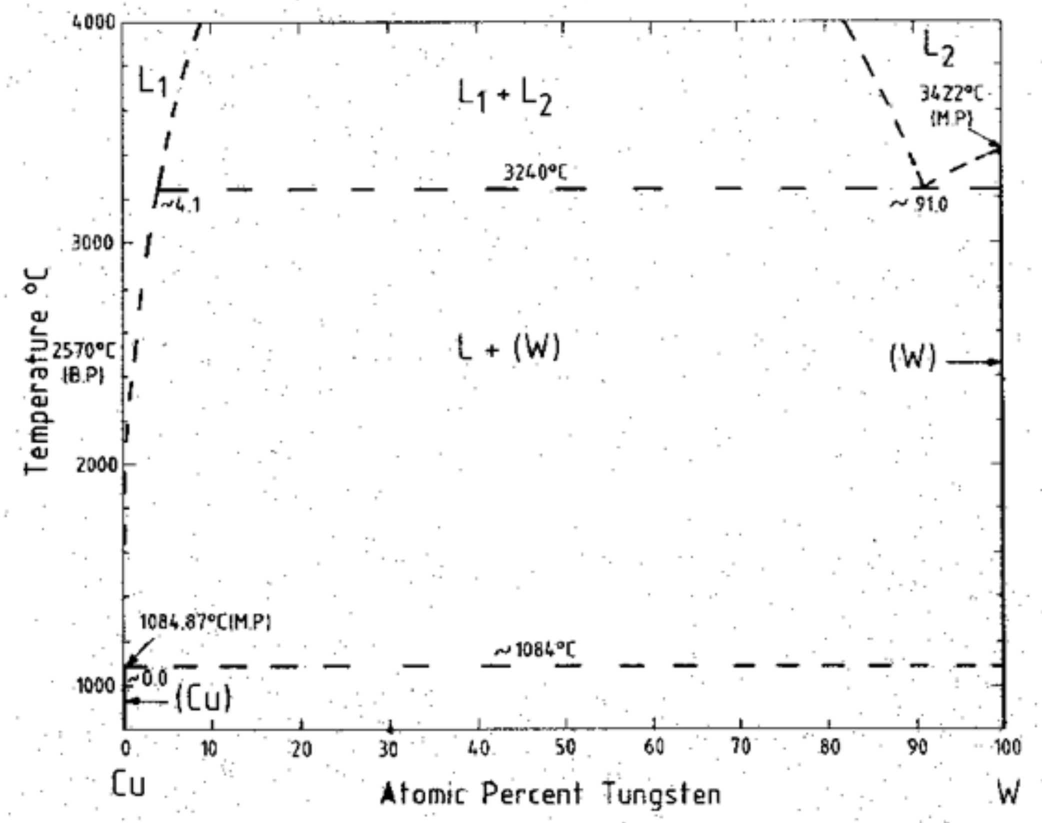
Hume-Rothery rules only tell you if elements mix, not how much they mix

Hume-Rothery Rules for Binary Solid Solutions (Examples)

Copper and Tungsten

Will they form a solid solution?

Element	Atomic Radius (nm)	Crystal Structure	Electronegativity	Valency
W	0.141	BCC	2.36	2
Cu	0.128	FCC	1.90	6



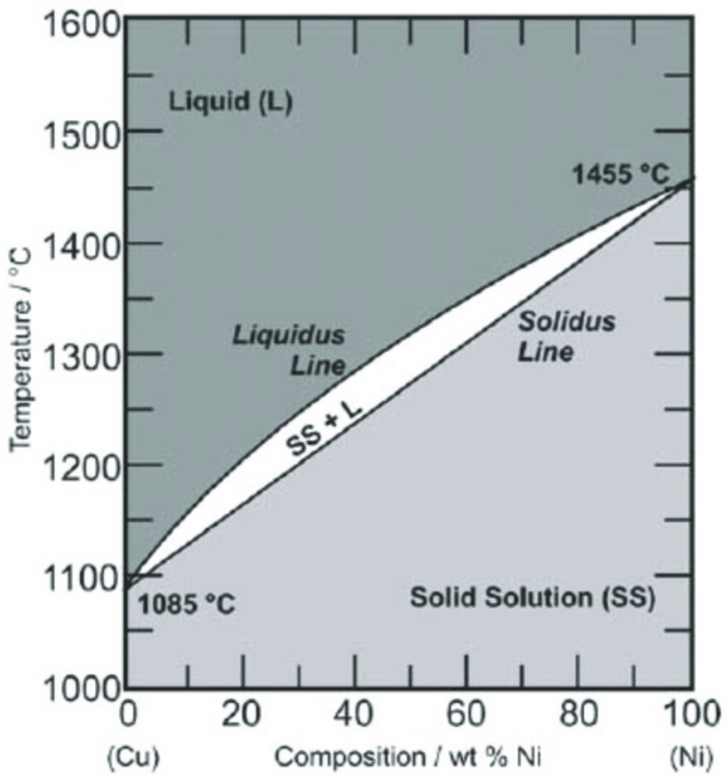
We'll go over how to read this next lecture but the main takeaway is that Cu and W are not miscible (they do not mix)

Hume-Rothery Rules for Binary Solid Solutions (Examples)

Copper and Nickel

Will they form a solid solution?

Element	Atomic Radius (nm)	Crystal Structure	Electronegativity	Valency
Ni	0.125	FCC	1.80	2
Cu	0.128	FCC	1.90	2



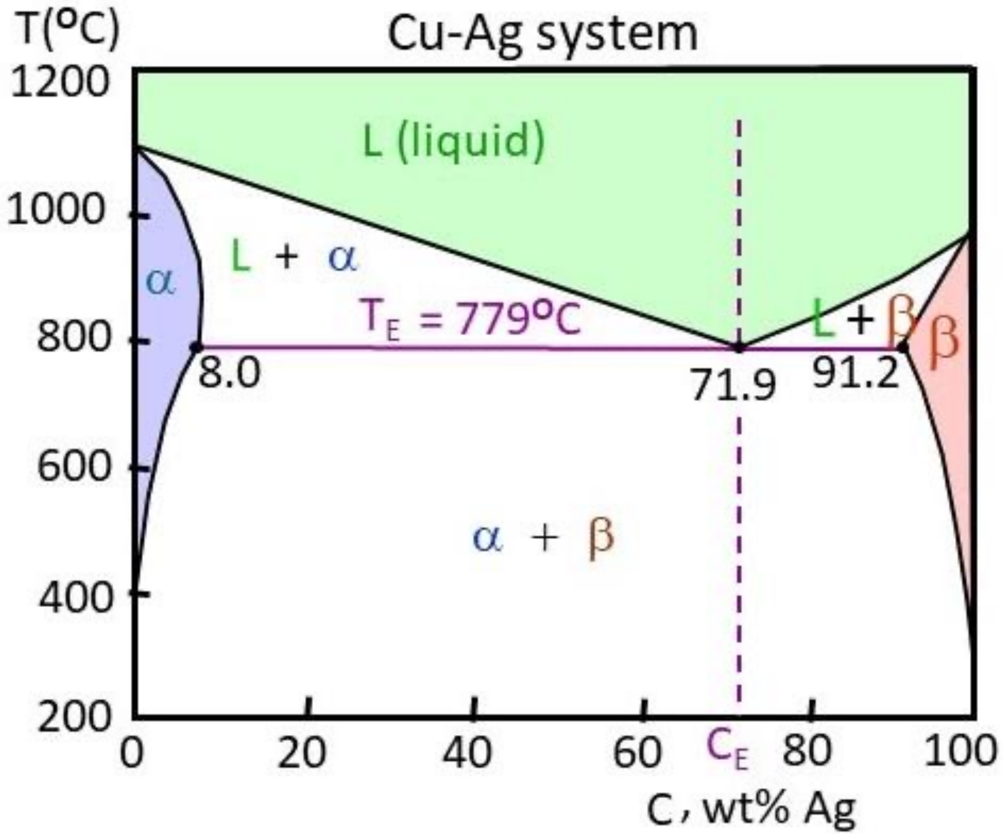
Cu and Ni are completely soluble with each other and just form a single phase prior to melting

Hume-Rothery Rules for Binary Solid Solutions (Examples)

Copper and Silver

Will they form a solid solution?

Element	Atomic Radius (nm)	Crystal Structure	Electronegativity	Valency
Ag	0.144	FCC	1.93	1
Cu	0.128	FCC	1.90	2



Ag has limited solubility in Cu (α)
Cu has limited solubility in Ag (β)

Two phase mixture of α and β to form for most compositions of Cu-Ag

Why do we alloy metals?

Some common reasons:

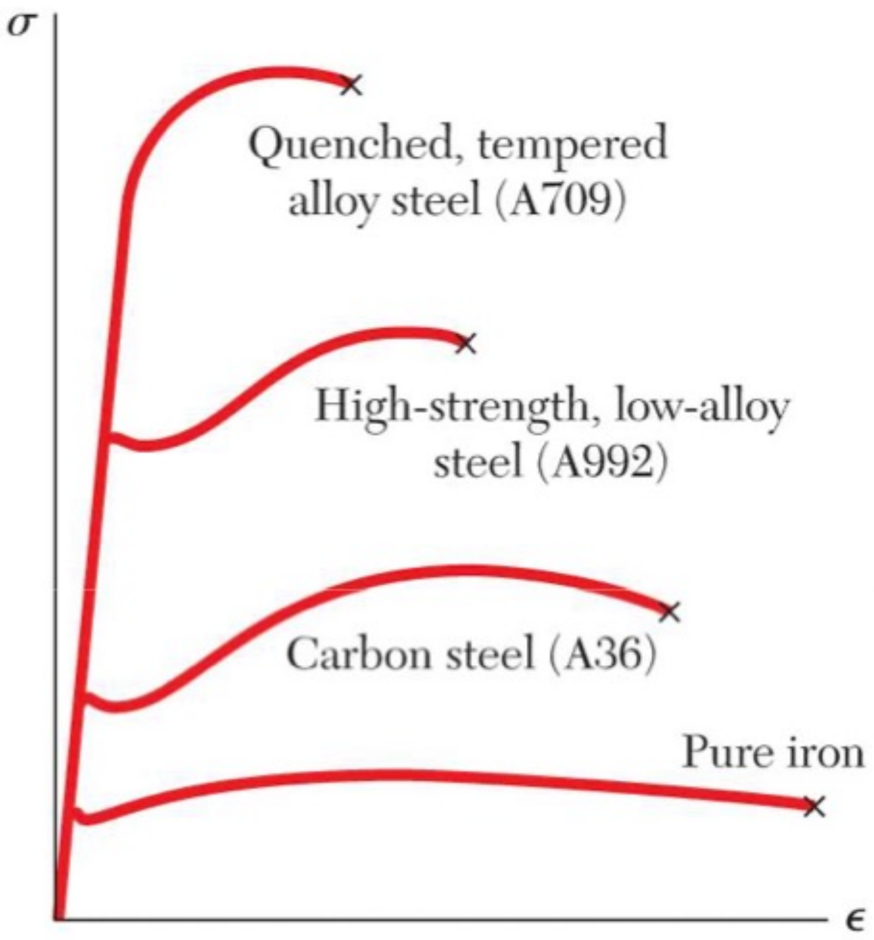
Improve mechanical properties

Improve corrosion resistance

Property enhancement

Reduce melting point for easier processing

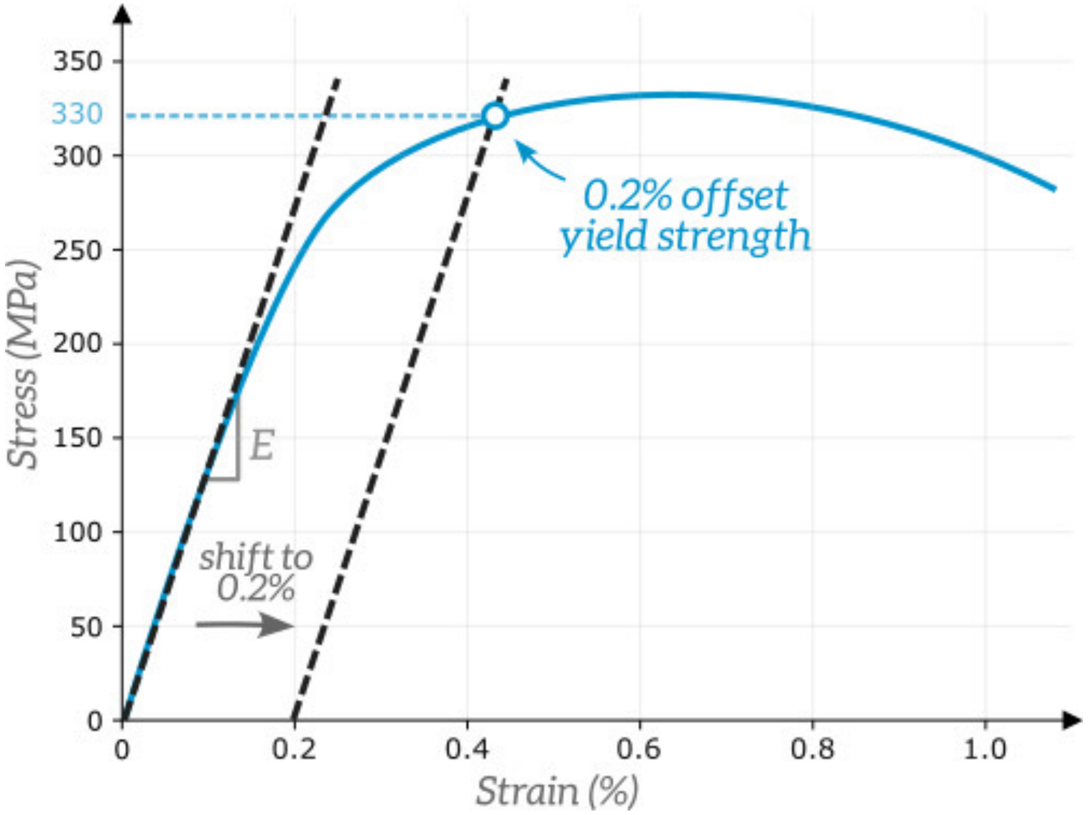
Reduce cost while maintaining properties



Just 1wt% of carbon can increase its mechanical properties significantly!

What dictates the strength of a metal?

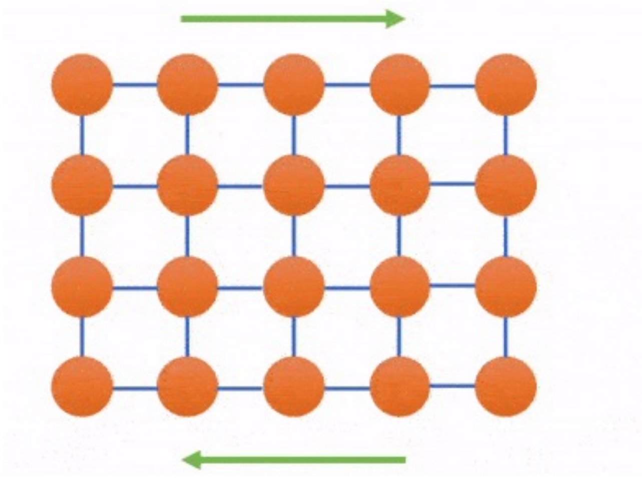
Recap: Yield strength, 0.2% offset yield strength, ultimate tensile strength (UTS)



Yield strength, 0.2% offset yield strength, UTS all measure the **extent of plastic deformation**

How to deform a crystal structure?

One way is to slide a plane of atoms across



Theoretical shear stress (τ_{theory}) needed to do this

$$\tau_{theory} = \frac{G}{2\pi}$$

G = Shear modulus

τ_{theory} for iron is ~ 12 GPa
$\tau_{observed}$ is ~ 0.5 GPa

$\tau_{observed}$ is usually significantly lower than τ_{theory}
→ This is not how deformation occurs

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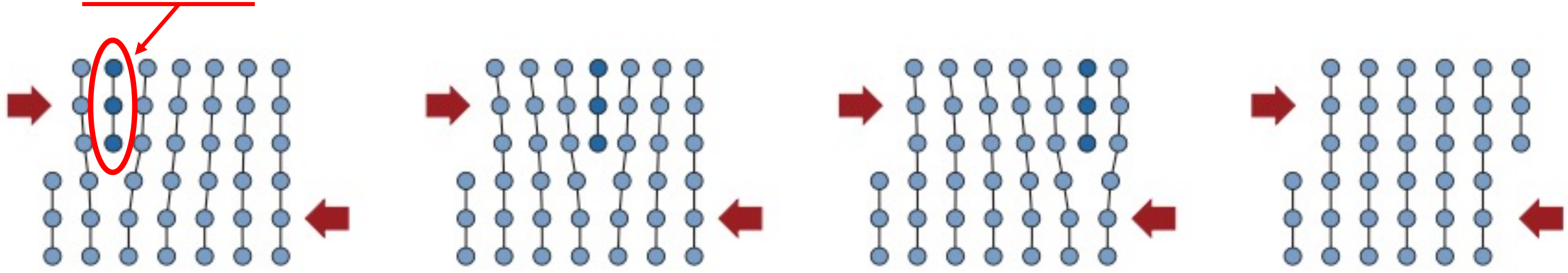
A brief look into dislocations

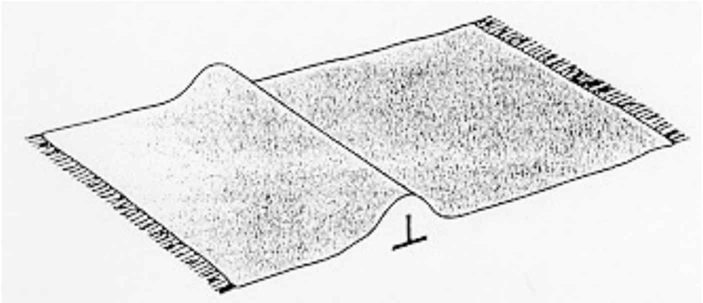
The strength of a metal depends on the ability of its **dislocations** to move.

A dislocation is a line defect in the crystal where the atoms are arranged anomalously



With a dislocation, only one bond needs to be broken at a time!

If you don't like bugs, it's like a ruck in a carpet →

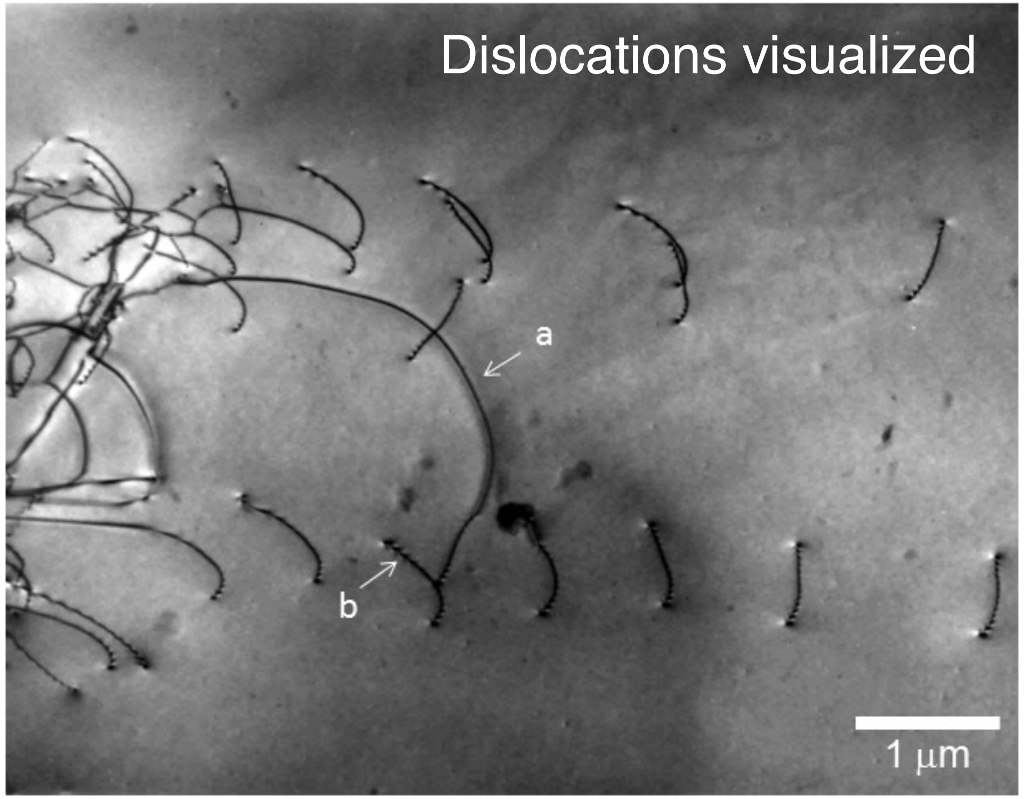


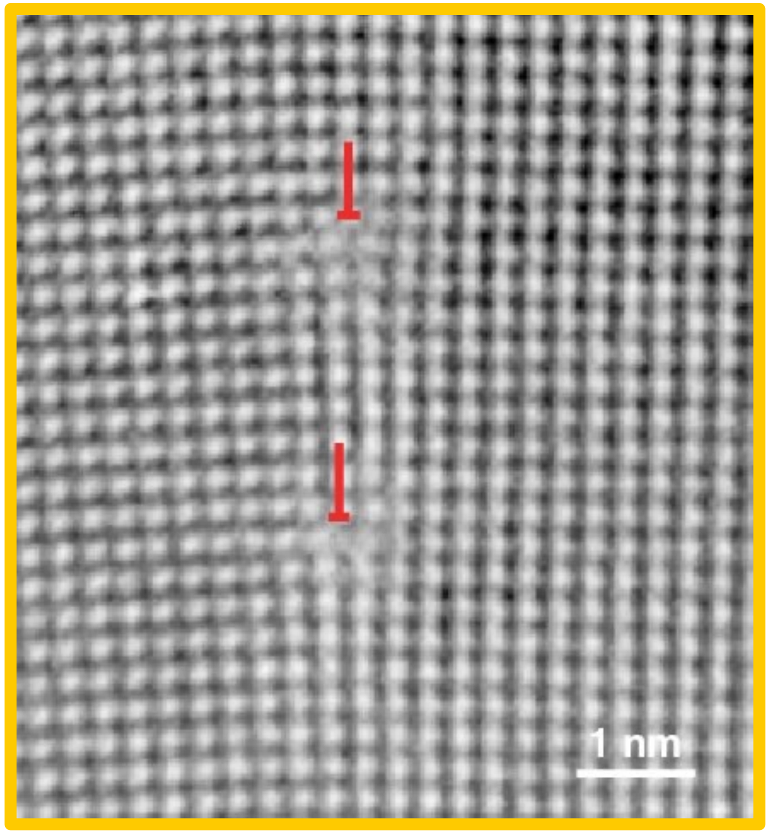
A brief look into dislocations

The strength of a metal depends on the ability of its **dislocations** to move.

Movement of dislocations causes plastic deformation

Easy to move → Low strength ; Hard to move → High strength





⊥ This is used to denote an **edge** dislocation

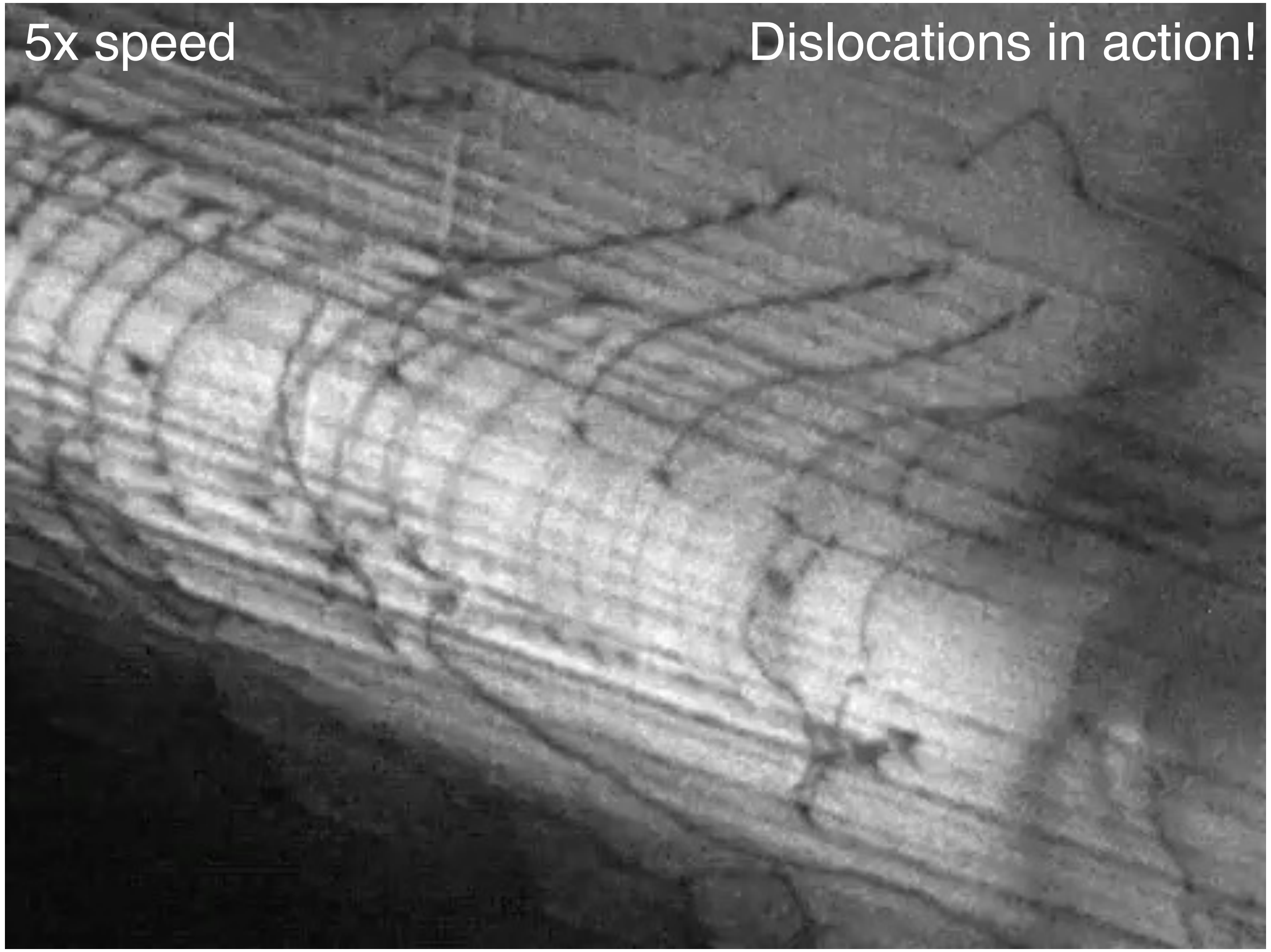
Two types: Edge and screw dislocations

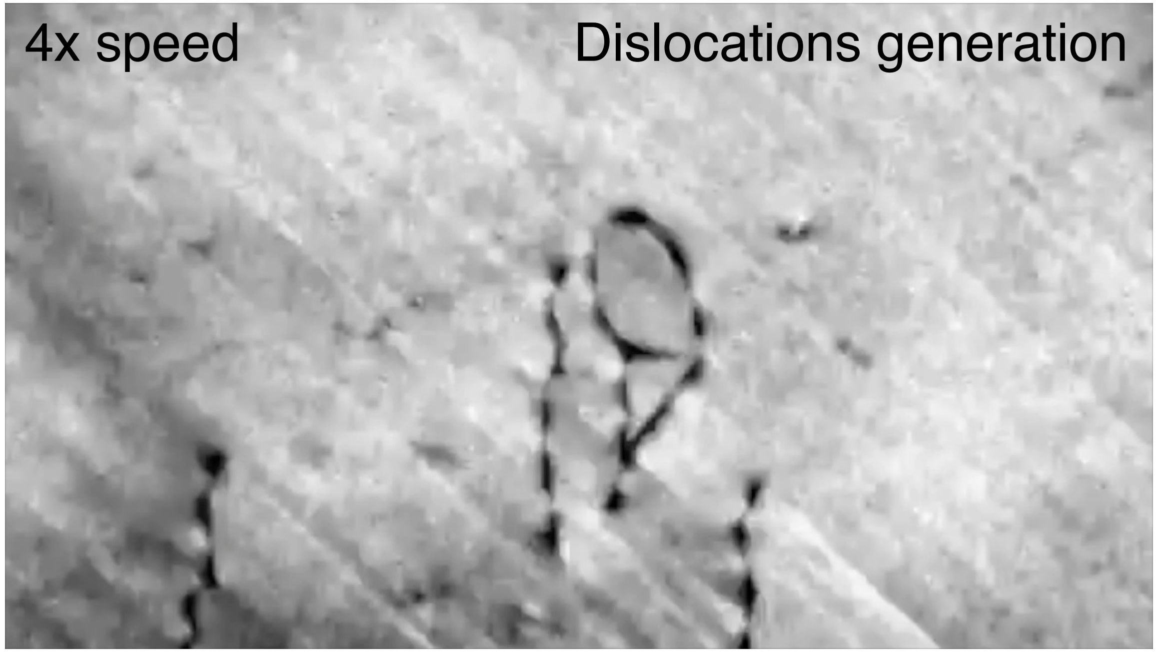
For this course, we will only briefly discuss edge dislocations

Just know that screw dislocation exist and they also enable deformation

A brief look into dislocations

The strength of a metal depends on the ability of its **dislocations** to move.





Key takeaway: Deformation in metals is mediated by dislocation movement

Alloying impedes dislocation movement!

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Week 7 Learning Objectives

- **Understand what a metal is**
  - Terms: band theory, valence band, conduction band, band gap, crystal structure
- **Know how to classify metals**
  - Composition, crystal structure, mechanical properties, temperature stability, density, corrosion resistance, microstructure
- **Understand what an alloy is and how the Hume-Rothery rules can be used to predict its formation**
- **Understand what a dislocation is and why it enables deformation of metals**