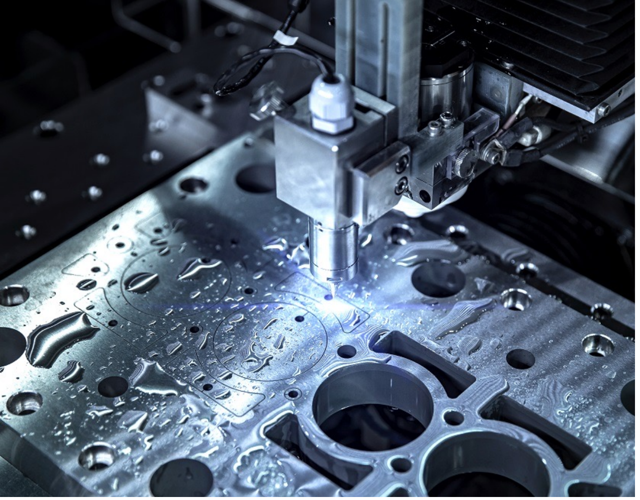

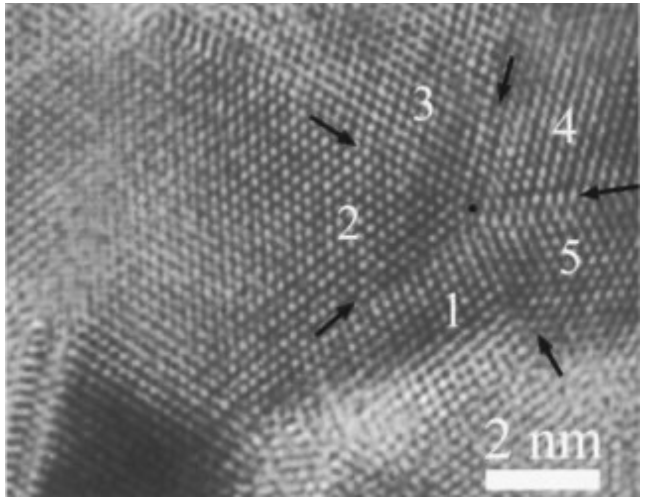

Materials Engineering I (MSE 214)

Lecture 8: Metals – Properties and Phase Diagram (I)

Prof. Daryl W. Yee

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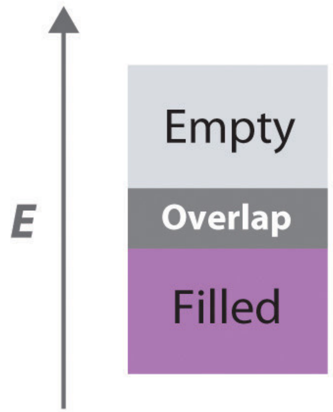
Recap: What are metals?

Metals (2 types of band structure)

Partially filled valence band

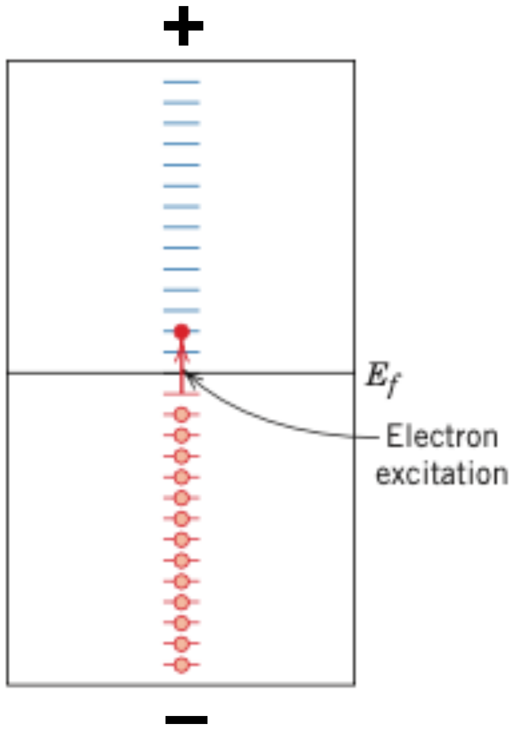


Filled valence band

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

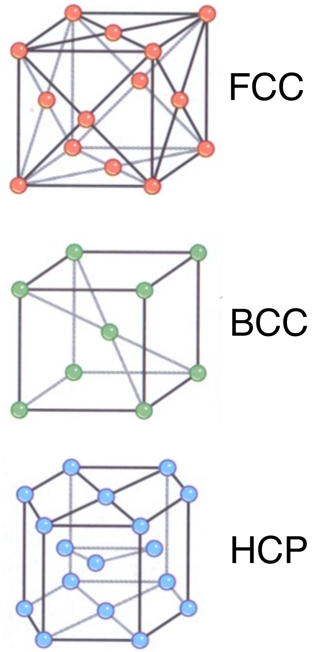
Conductive even at absolute zero (0 K)

Recap: How Do We Classify Metals?

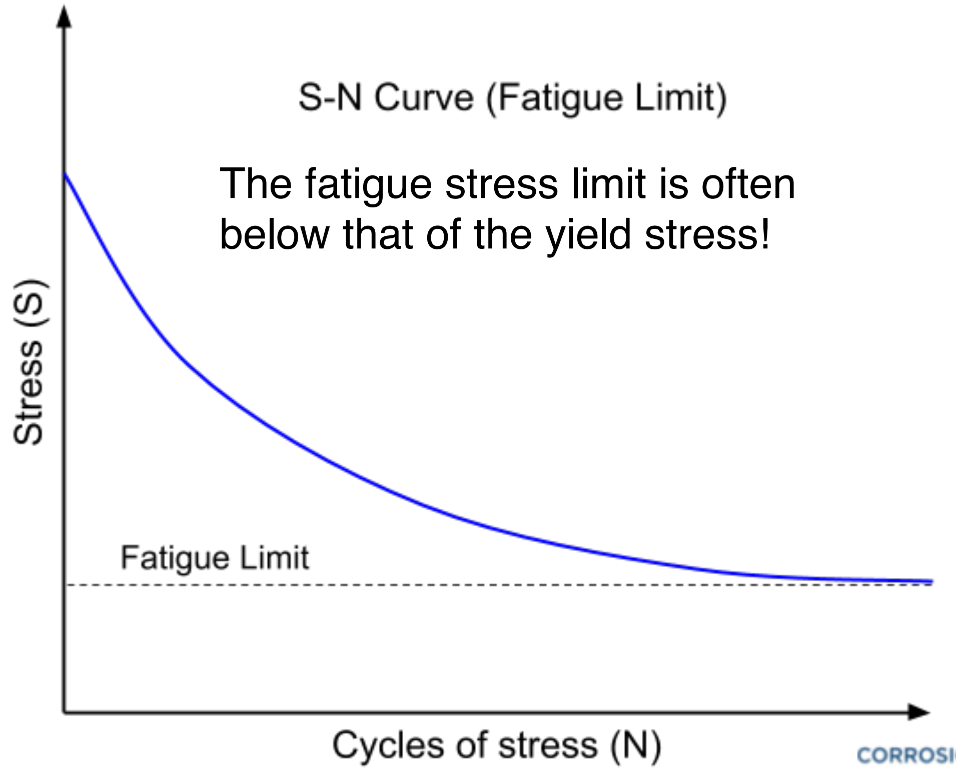
Multiple ways of classifying metals — Depends on the information you want to convey

1. Composition: Ferrous or Non-ferrous
2. Composition: Alloy or Pure metals
3. Crystal structure
4. Refractory or not?
5. Base metal vs. Precious metal
6. Corrosion resistance
7. Mechanical Properties
8. Microstructure

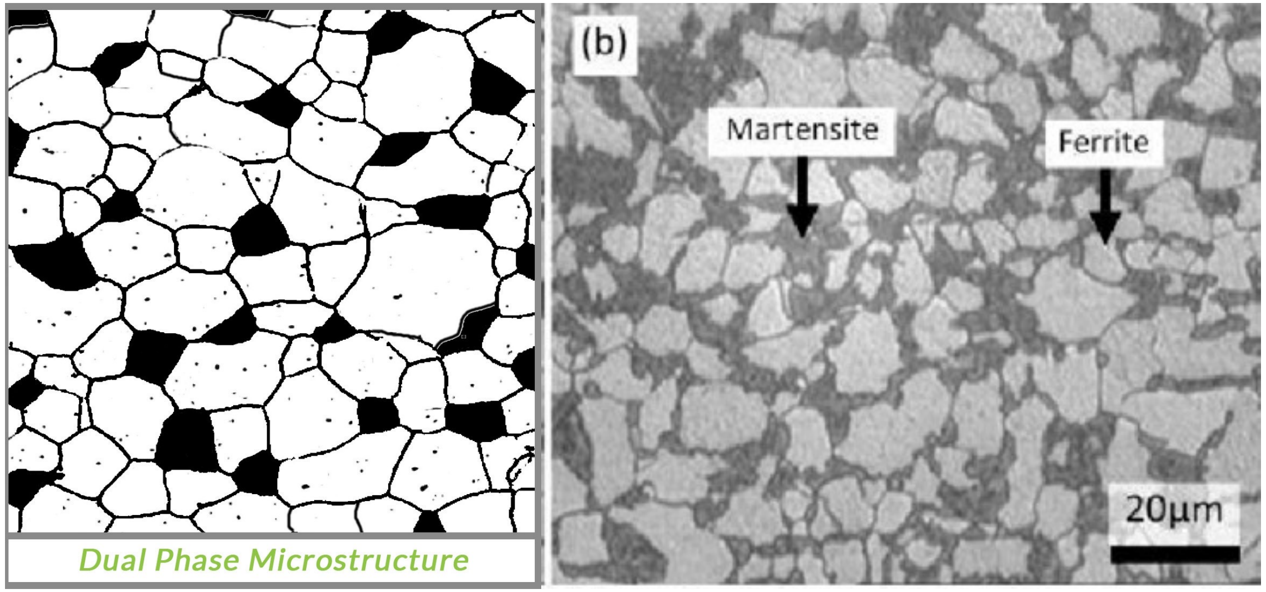
Crystal Structure



Mechanical Properties



Recap: What is a phase?

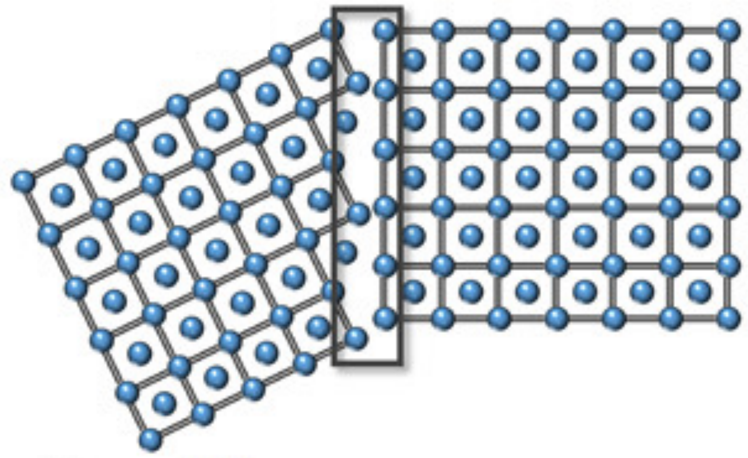


A phase is a state of matter that has uniform physical and chemical characteristics

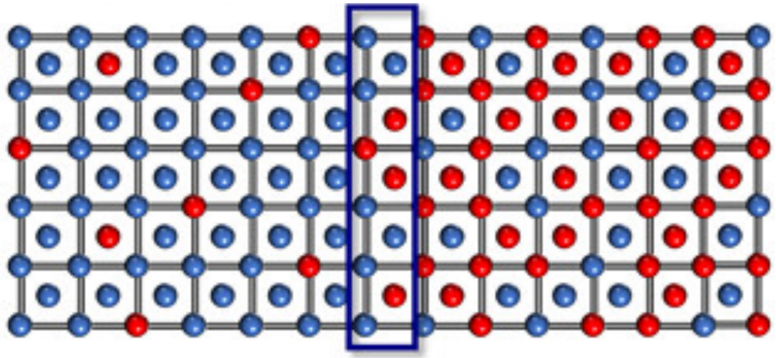
Syrup → Sugar + Water (Single phase)

Ice + Water (Two phases)

Two grains with same composition and crystal structure → Single phase



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



Recap: 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

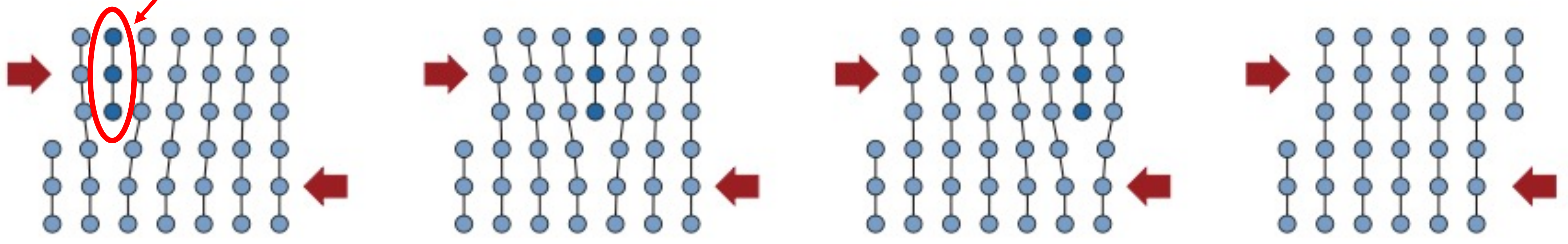
If Hume-Rothery rules are not fulfilled → Low to no solubility of element in the metal

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

Recap: A brief look into dislocations

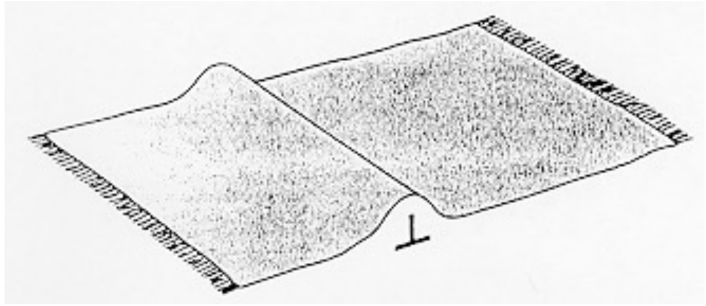
The strength of a metal depends on the ability of its **dislocations** to move.

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

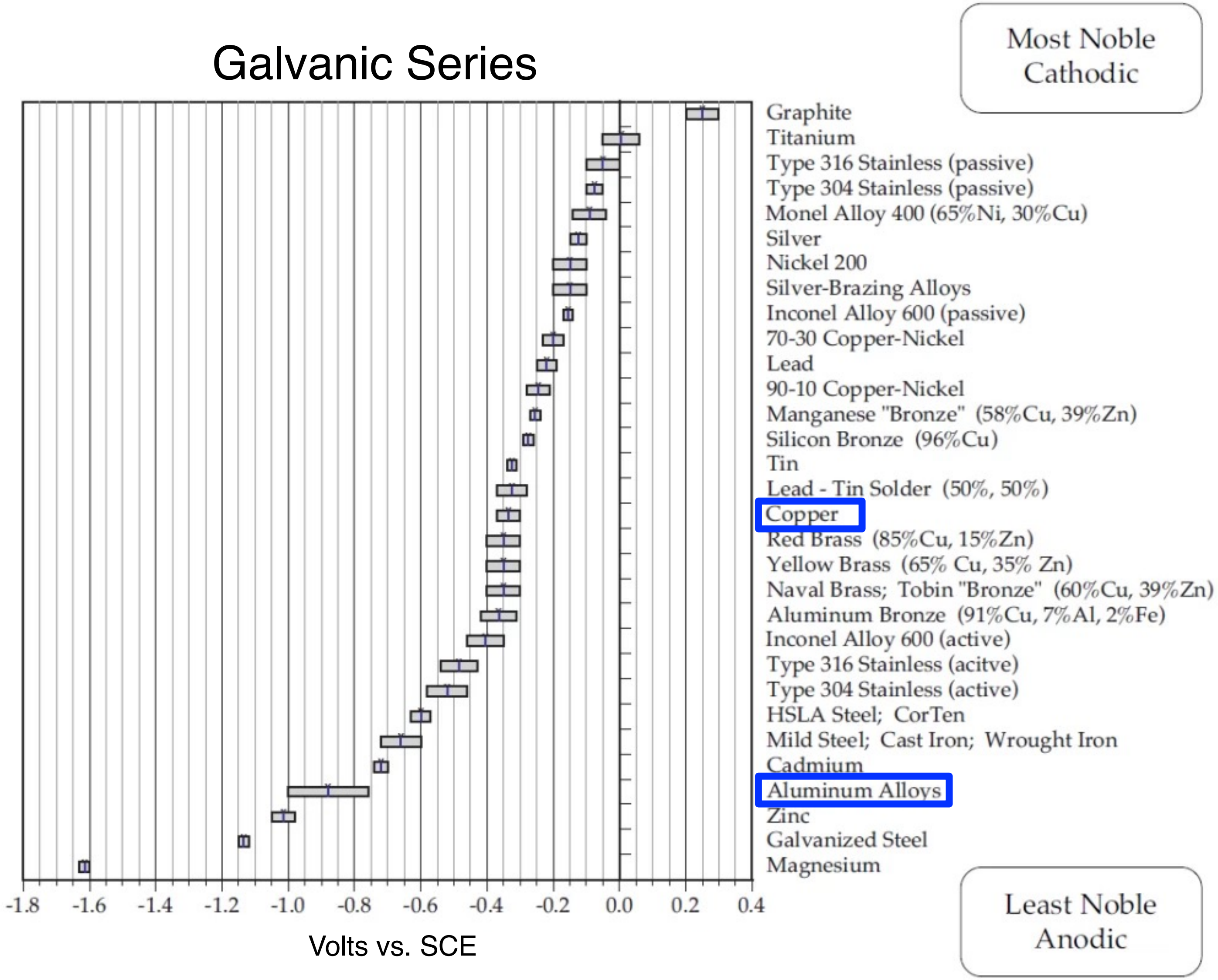


With a dislocation, only one bond needs to be broken at a time!

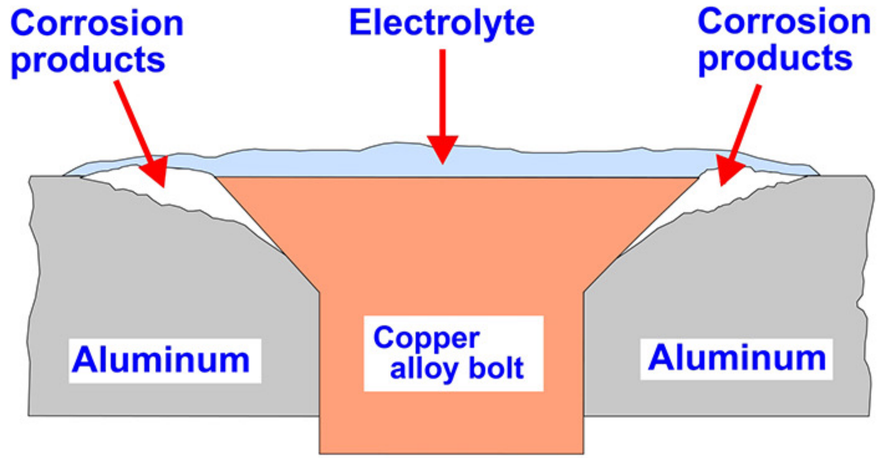
If you don't like bugs, it's like a ruck in a carpet →



Common question: How to pick metal for cathodic protection?



The anode must possess a more negative electrode potential than that of the cathode (the target structure to be protected)



Exercise 6 Question 4: Vat Photopolymerization

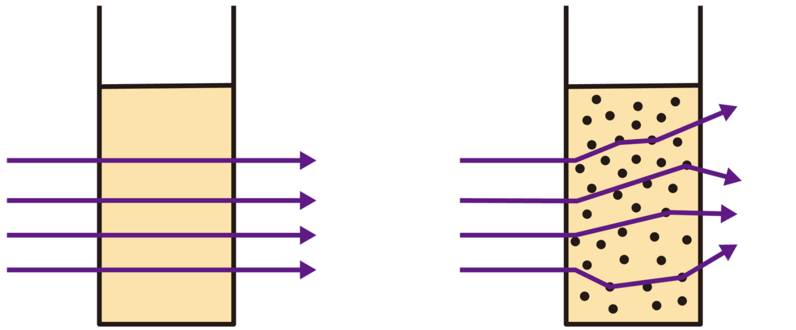
Vat photopolymerization can also be used to make composite structures (polymers + ceramic / metal particles).

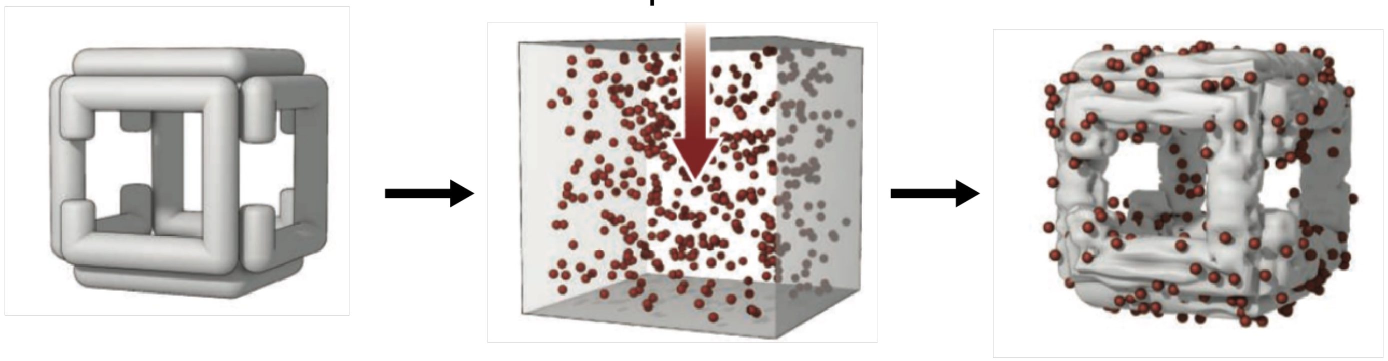
To do so, a slurry is first prepared by mixing the photoresin with ceramic / metal particles.

This slurry is then used with a vat photopolymerization process to make the composite structure.

Unfortunately, this process is very challenging and often results in inaccurate and / or inhomogeneous parts.

Give 2 reasons why you think this is the case.





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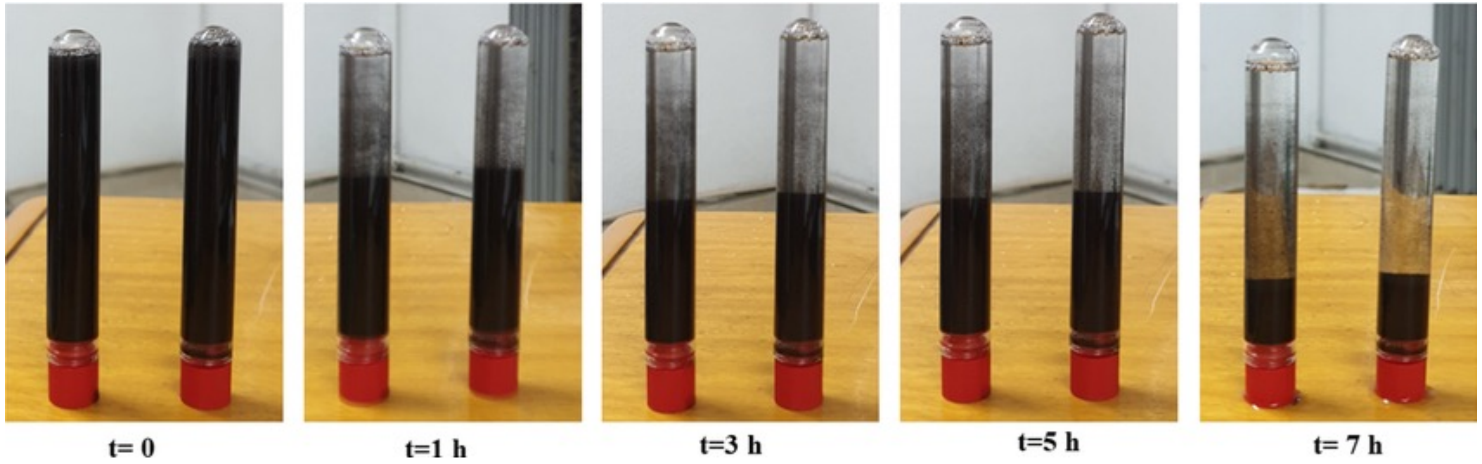
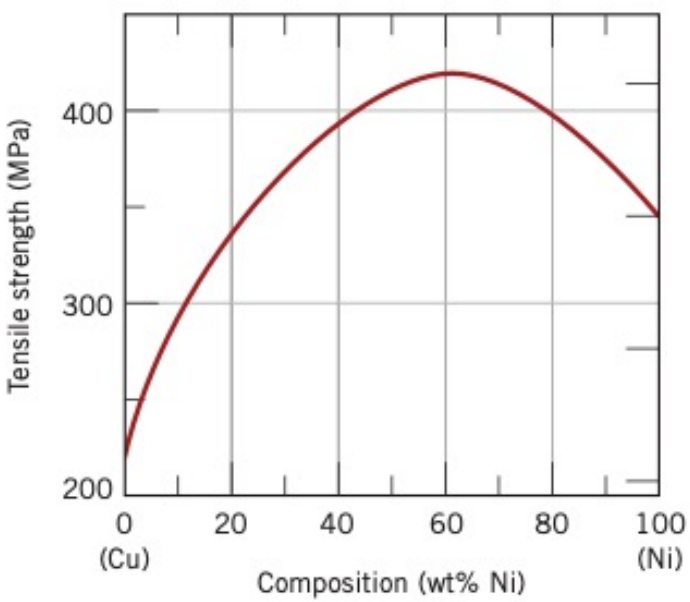


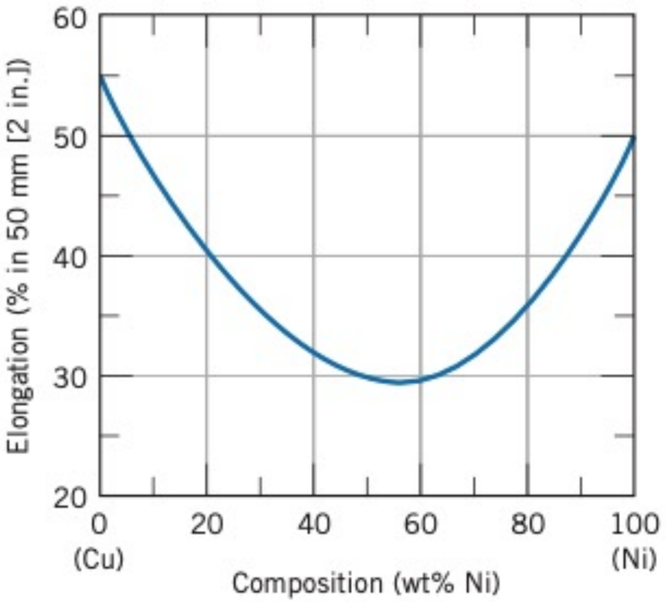
Layer-by-layer printing process means that the composition of each layer will change with time!

Week 8 Learning Objectives

- **Understand why alloying strengthens a metal**
- **Understand what a phase diagram is**
- **Understand how to read a binary phase diagram for:**
  - **Isomorphous systems**
  - **Eutectic systems**
- **Be able to predict alloy microstructure from the phase diagram**
- **Be able to use tie lines and the lever rule to calculate the amount and composition of the phases formed in a two-phase region.**

Why does alloying increase the strength of a material?





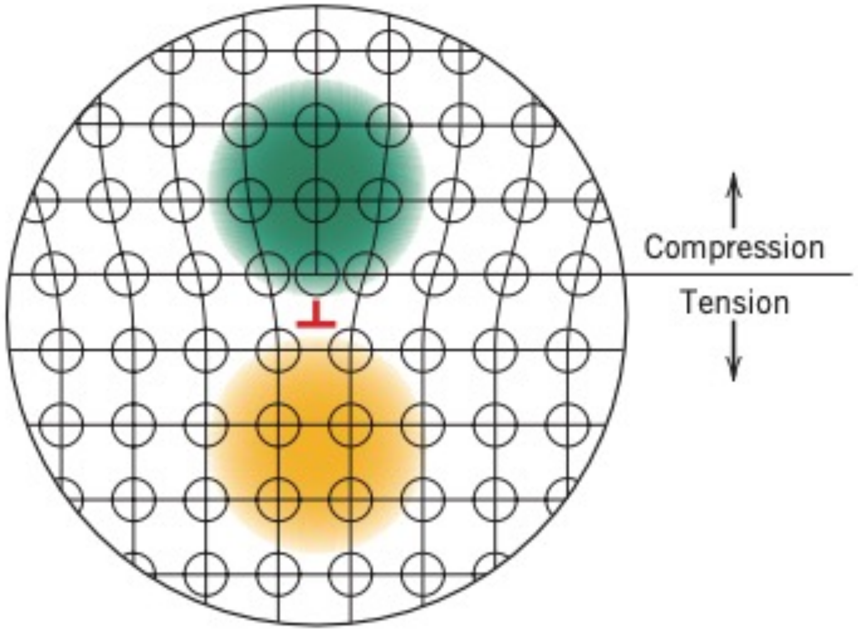
Adding Ni to Cu increases tensile strength and decreases ductility

But see a flip in behavior above 60 wt% Ni. Why?

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

How does alloying change dislocation mobility?

First, let's take a closer look at dislocations



<u>Dislocations have a strain field around them</u>

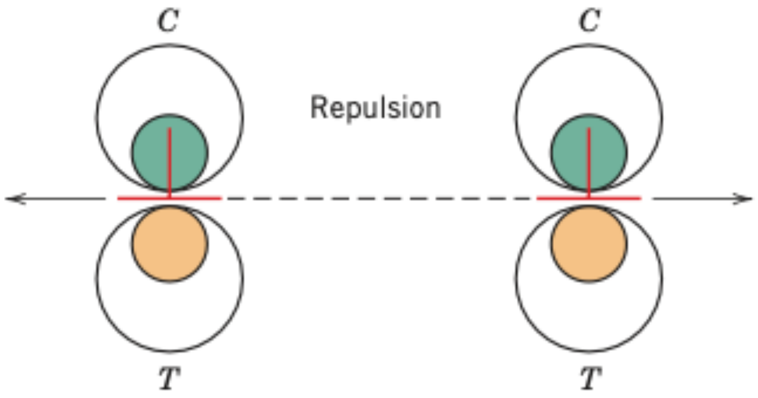
The extra half-plane of atoms distorts the surrounding lattice

Atoms directly **above** the dislocation line are being squeezed together by the additional plane (2→3)

Atoms directly **below** the dislocation line are being pulled together by the missing plane (3→2)

<u>**Implication:**</u>

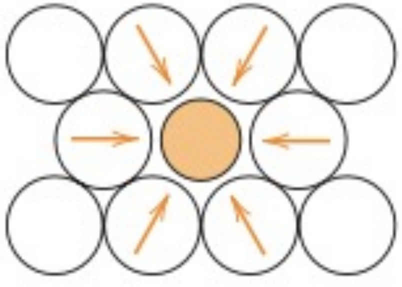
Dislocation mobility is impacted by its surrounding strain field



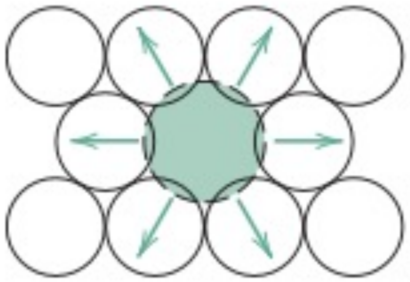
Solid-solution strengthening

Size mismatch of atoms strains the lattice

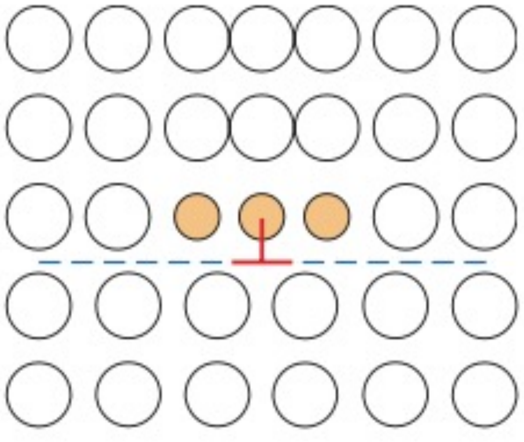
Smaller substitutional atom imposes **tensile** strains on the host lattice

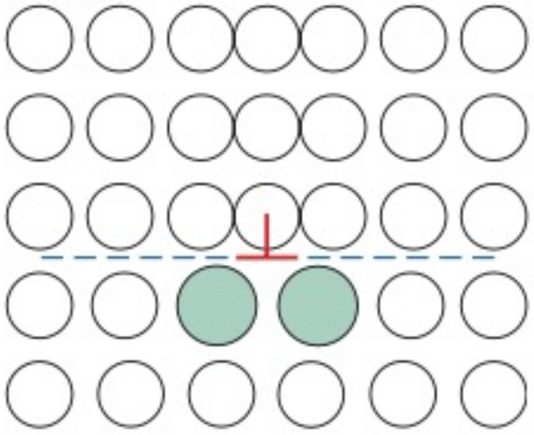


Larger substitutional atom imposes **compressive** strains on the host lattice



Strain field between dislocation and substitutional atoms can interact





Effect 1

Solute atoms moves to cancel the strain field of the dislocation (lower energy state)

↓

Pins the dislocation

↓

Moving the dislocation will increase the energy state

↓

More energy needed to move

↓

Stronger

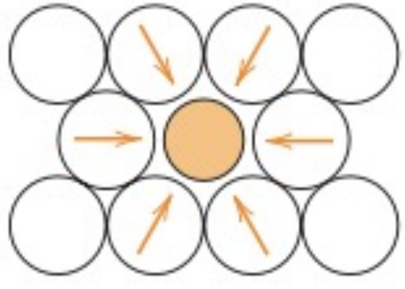
Solid-solution strengthening

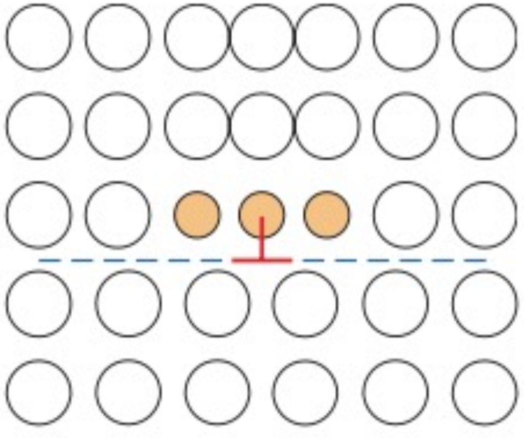
<u>Size mismatch of atoms strains the lattice</u>

<u>Strain field between dislocation and substitutional atoms can interact</u>

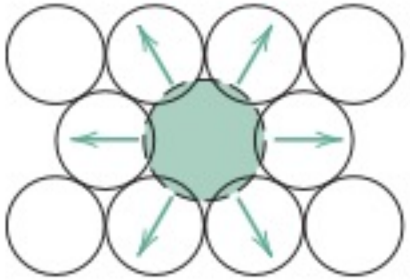
<u>Effect 2</u>

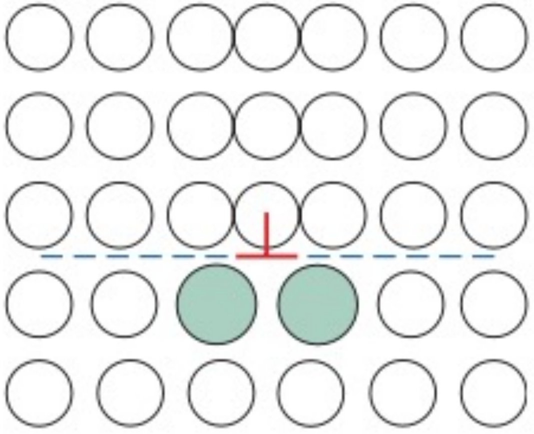
Smaller substitutional atom imposes **tensile** strains on the host lattice





Larger substitutional atom imposes **compressive** strains on the host lattice





Moving dislocations need to overcome the strain fields from the substitutional atoms

↓

More energy needed to move

↓

Stronger

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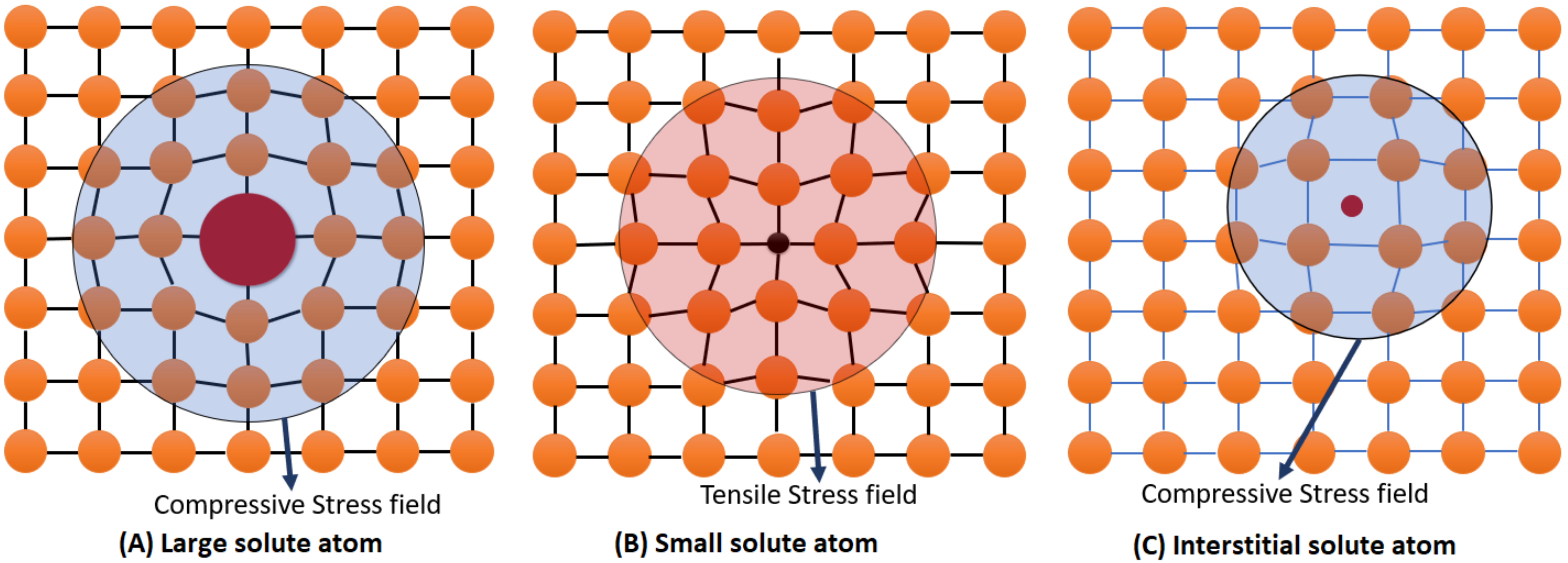
Solid-solution strengthening

Same concept applies to interstitial solutes

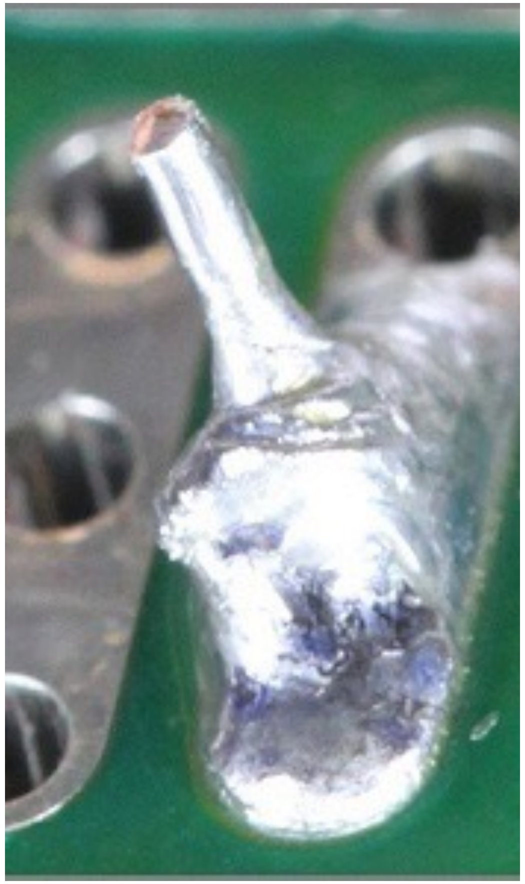


Main take away: Alloying strains the lattice → Dislocation mobility reduced by lattice strains → Harder to move them → Stronger

Where do we see metals in SMT? — Soldering!

Good solder joint

Cold solder joint



Can lead to cracking

→

Increased electrical resistance
Etc.

Cracked solder joint

Why does cold soldering happen?

How do we understand this?

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What is cold soldering?

Happens when the solder does not **melt** properly

And/or

When the board is moved during **cooling**

Understanding the behavior of a metal during thermal transitions is important

Let's look at some popular soldering compositions:

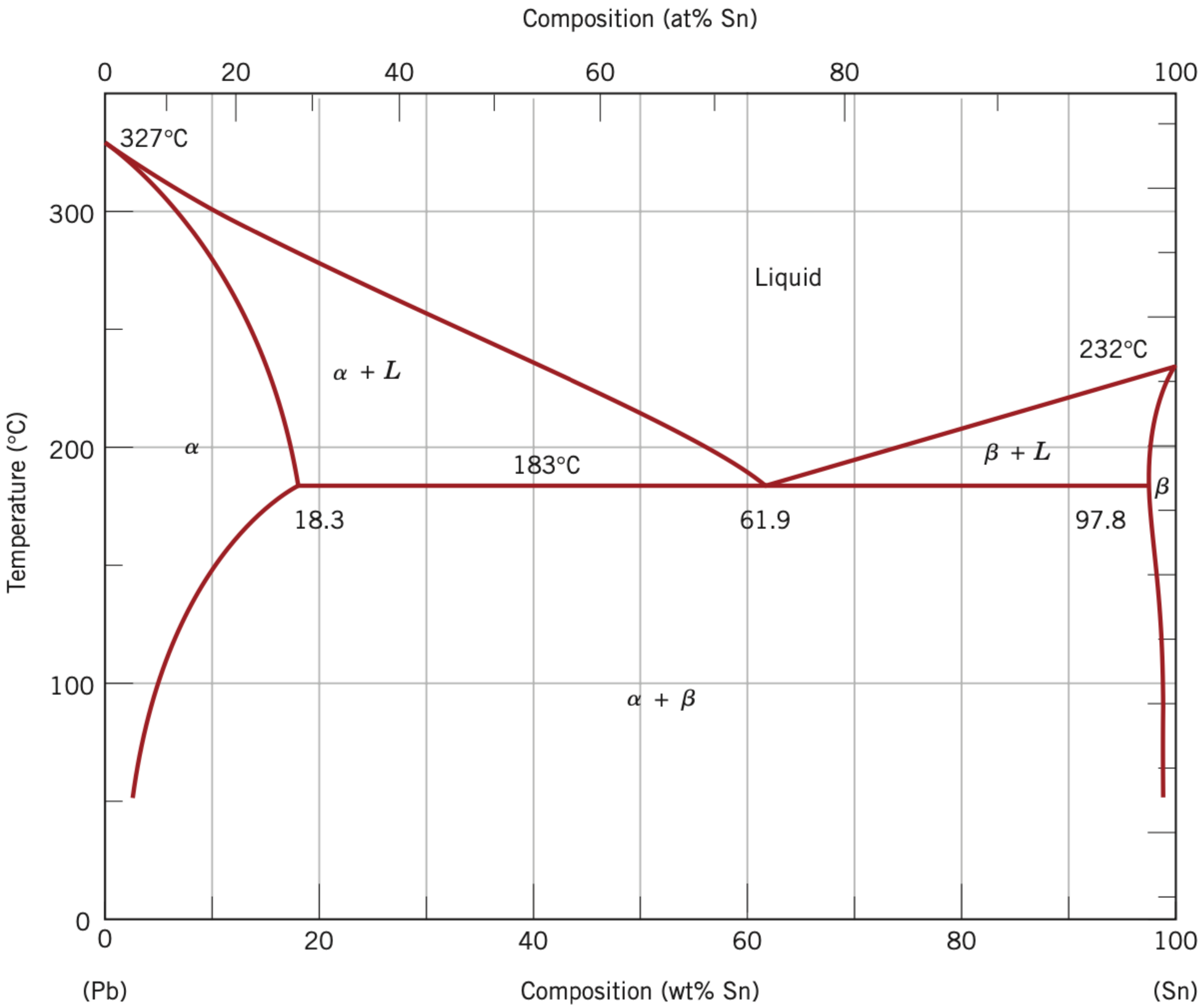
63% tin / 37% lead **(63/37)**	60% tin / 40% lead **(60/40)**
$T_m = 183^{\circ}C$	$T_m = 183 – 191^{\circ}C$
Less susceptible to cold soldering	Susceptible to cold soldering

The larger melting window makes it easier for cold soldering to happen!

How does the composition of an alloy impact its thermal behavior?

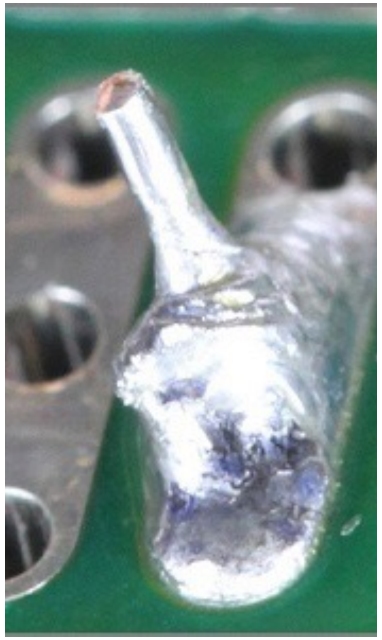
To figure this out, we need to look at a phase diagram!

Pb-Sn phase diagram explains cold soldering!



Good solder joint

Cold solder joint



Today's goal: Understand how to read and intepret this

Phase Diagrams — Parameters that dictate phase at equilibrium

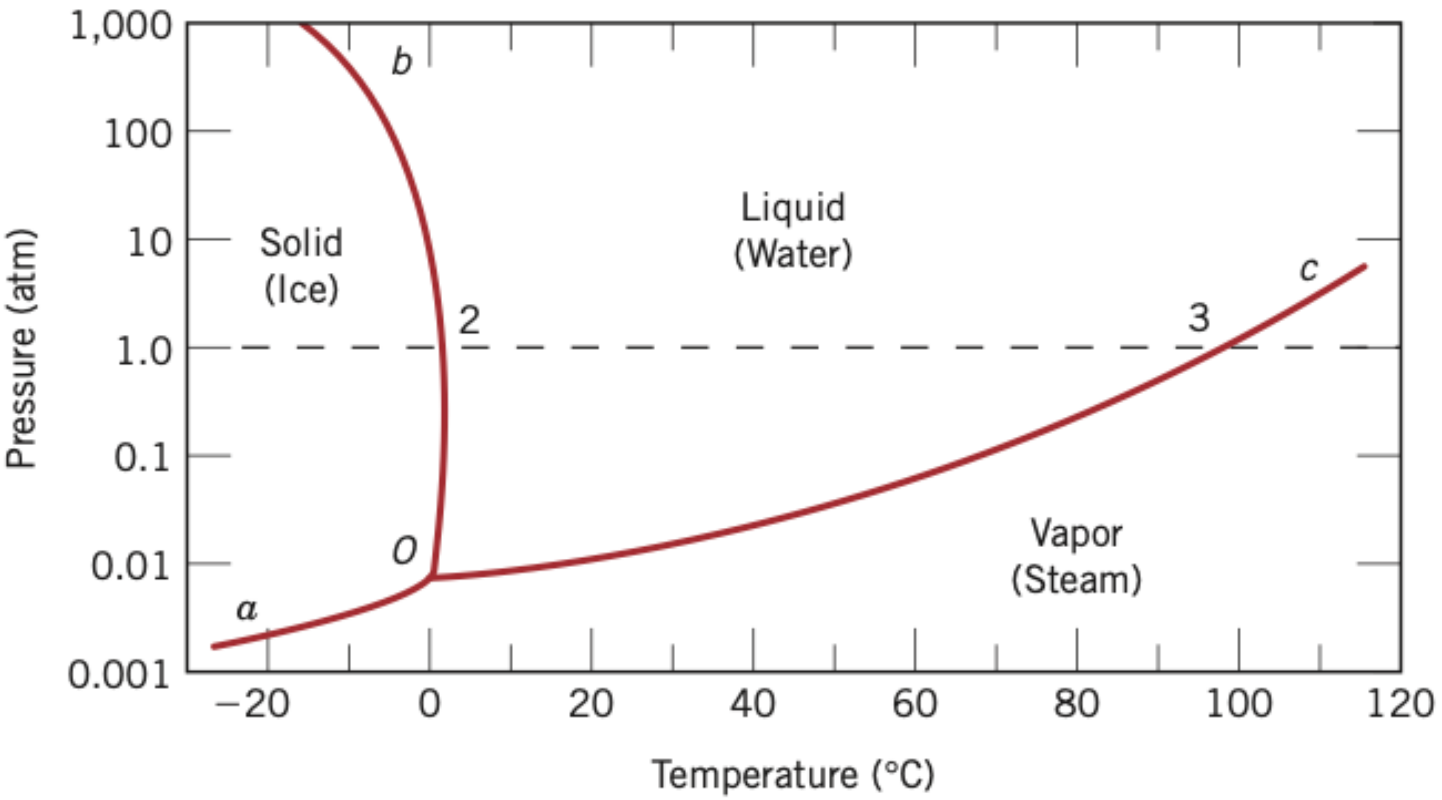
A phase diagram shows the equilibrium phases that are formed at a particle set of parameters

The most common parameters:

- Temperature (T)
- Pressure (P)
- Composition (C)

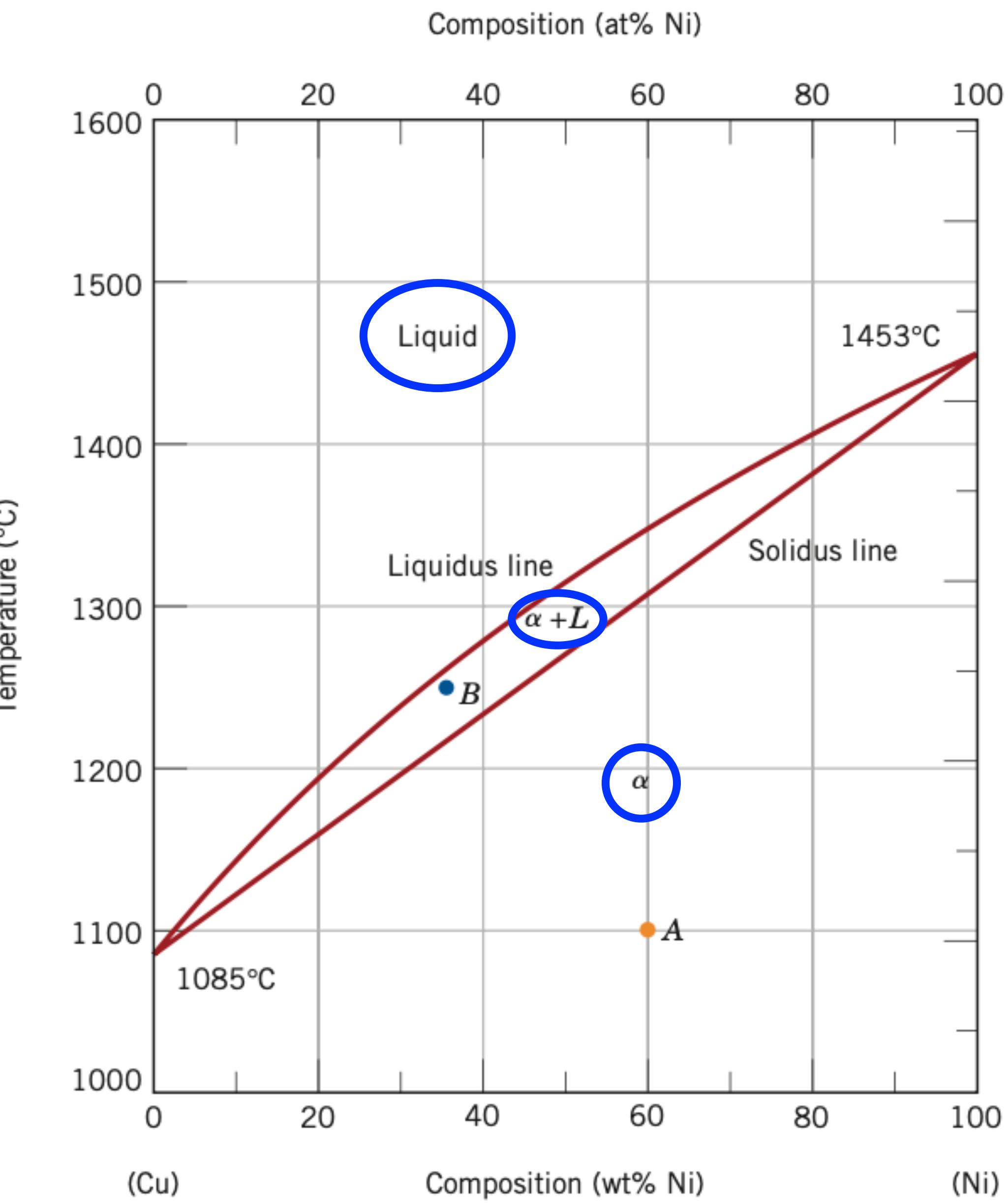
Important: Equilibrium!
Assume no kinetic limitation
Enough time given to form the phase

Pressure-temperature phase diagram for H_2O



The solid lines indicate phase boundaries
→ Conditions where one phase changes to another

Binary phase diagrams — P constant, vary T and C



Simplest system: Binary **isomorphous** system

Elements that are completely miscible at all T and C

Classic example: Cu – Ni system

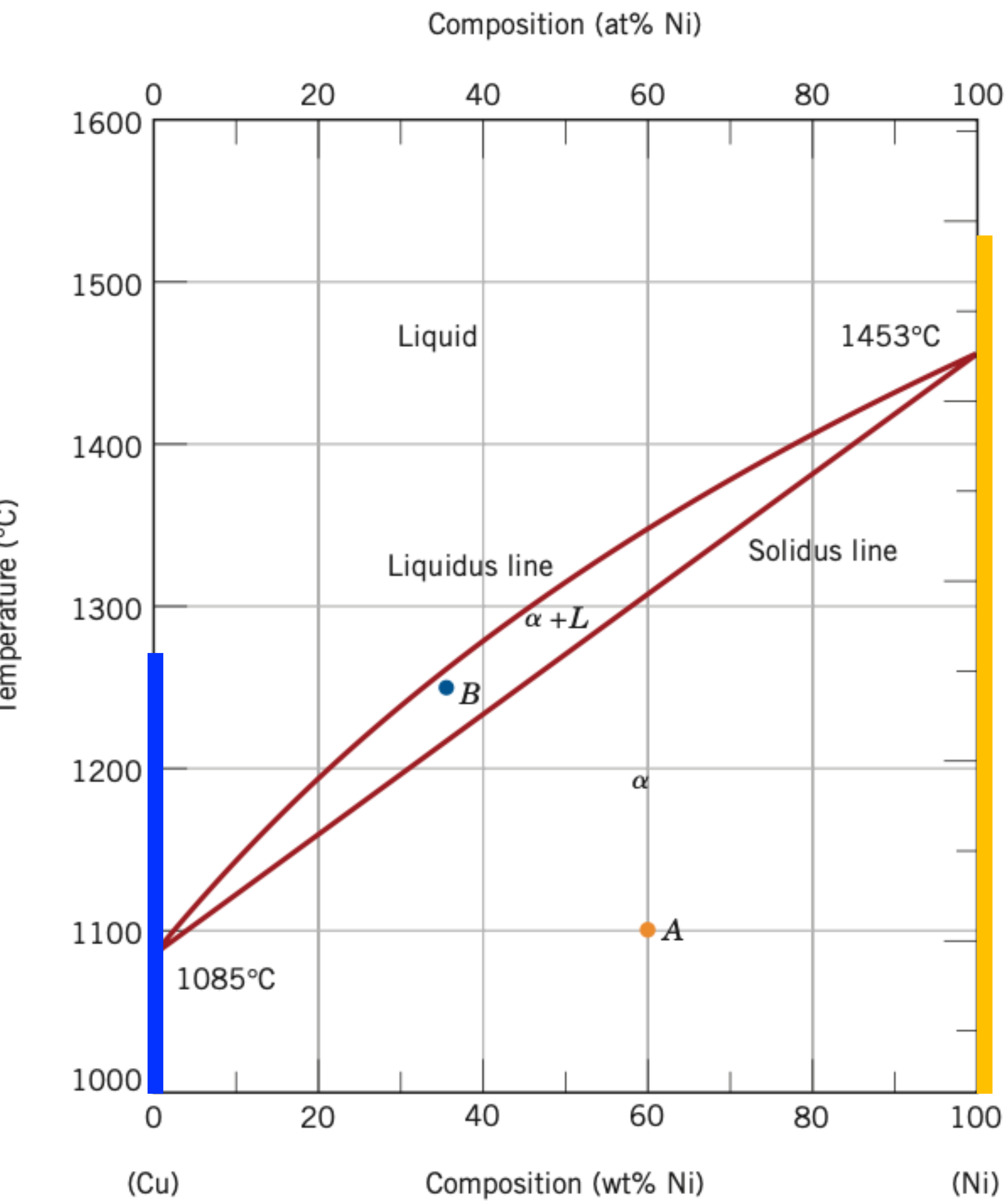
Three phase regions: α , liquid (L), α + L

Liquid (L) region is a homogenous liquid composed of Cu and/or Ni atoms (single phase)

α region is a substitutional solid solution consisting of Cu and Ni atoms (single phase called α)

α + L region consists of both α and liquid (two phase)

Binary phase diagrams — P constant, vary T and C



<u>Liquidus line</u>: Only liquid above this line at all T and C

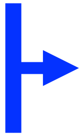
<u>Solidus line</u>: Only solid below this line at all T and C

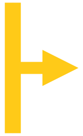
How to read a phase diagram:

1. For a specific composition, draw a vertical line through the temperatures of interest

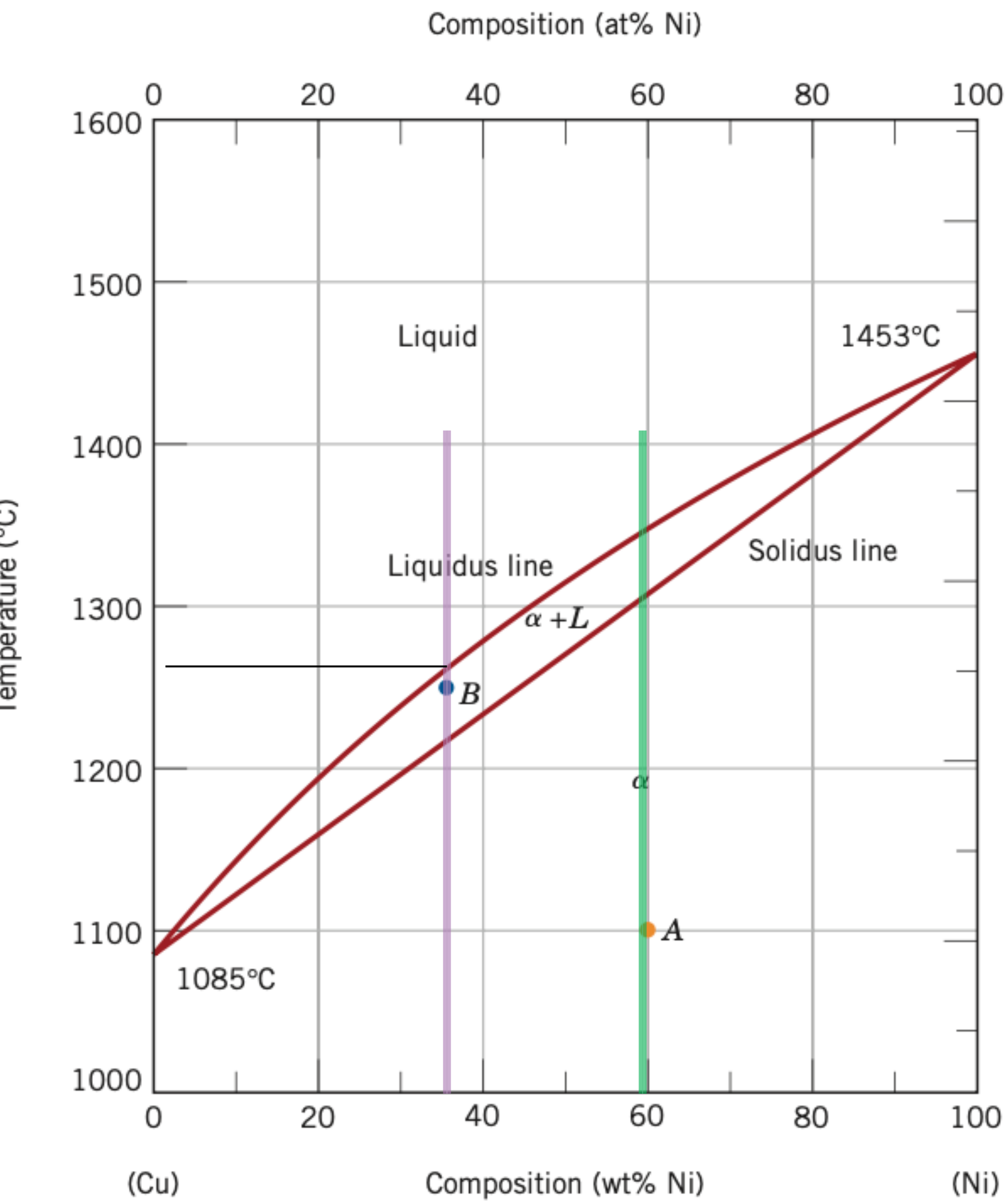
2. Note the regions it passes through

3. Note the transition temperatures

Example 1: Pure Cu  Solid Cu below 1085˚C
Liquid above 1085˚C

Example 2: Pure Ni  Solid Ni below 1453˚C
Liquid above 1453˚C

Binary phase diagrams — P constant, vary T and C



Pure metals are easy, what about alloys?

Example 3: $Cu_{40}Ni_{60}$

Solid α below ~1310˚C
α + L between 1310˚C and 1350˚C
L above 1350˚C

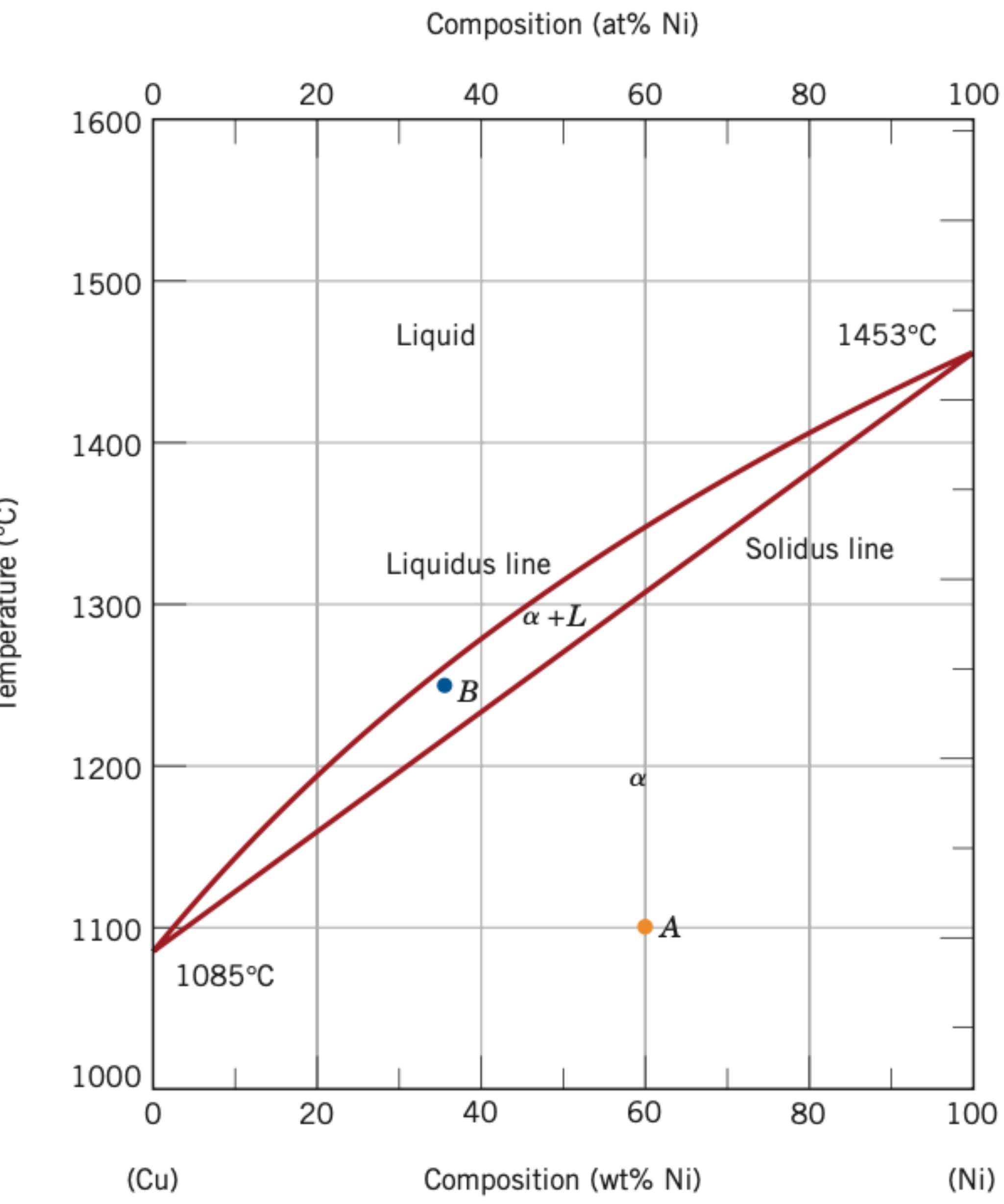
Example 4: $Cu_{65}Ni_{35}$

Solid α below ~1220˚C
α + L between 1220˚C and 1270˚C
L above 1270˚C

Take away 1: Phase diagram can provide information about the thermal transitions of a metal/alloy

Take away 2: Alloying changes the thermal behavior of a metal significantly

How do we determine the composition and amount of the phase(s)



Single phase region:

Amount of phase: 100%

Composition of phase: Same as that of the alloy

Point A: $Cu_{40}Ni_{60}$, 100% of the alloy is the α phase

Two phase region:

Amount of each phase: Determine via lever rule

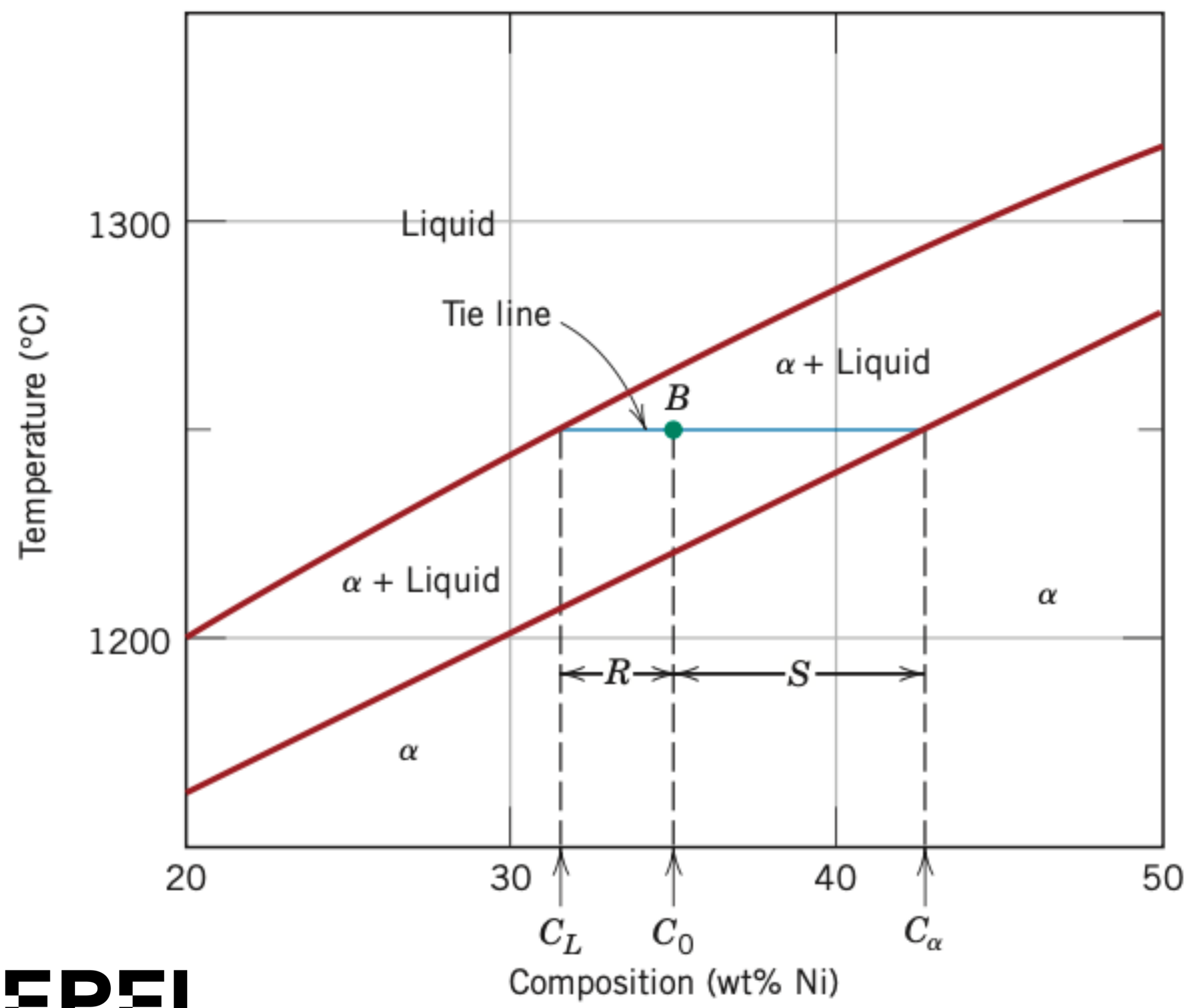
Composition of each phase: Determine via tie line

Point B: Some percent is α phase of some composition
Some percent is the liquid phase of some composition

Why do they need to have different compositions?

Tie lines: Method to determine phase compositions

Let's zoom in to the region around Point B



Step 1: Identify the composition and temperature of interest (Eg. Point B: $Cu_{65}Ni_{35}$ at 1250˚C)

Step 2: Draw a horizontal line through the point until it intersects the phase boundaries

Note: This horizontal line is called a tie line

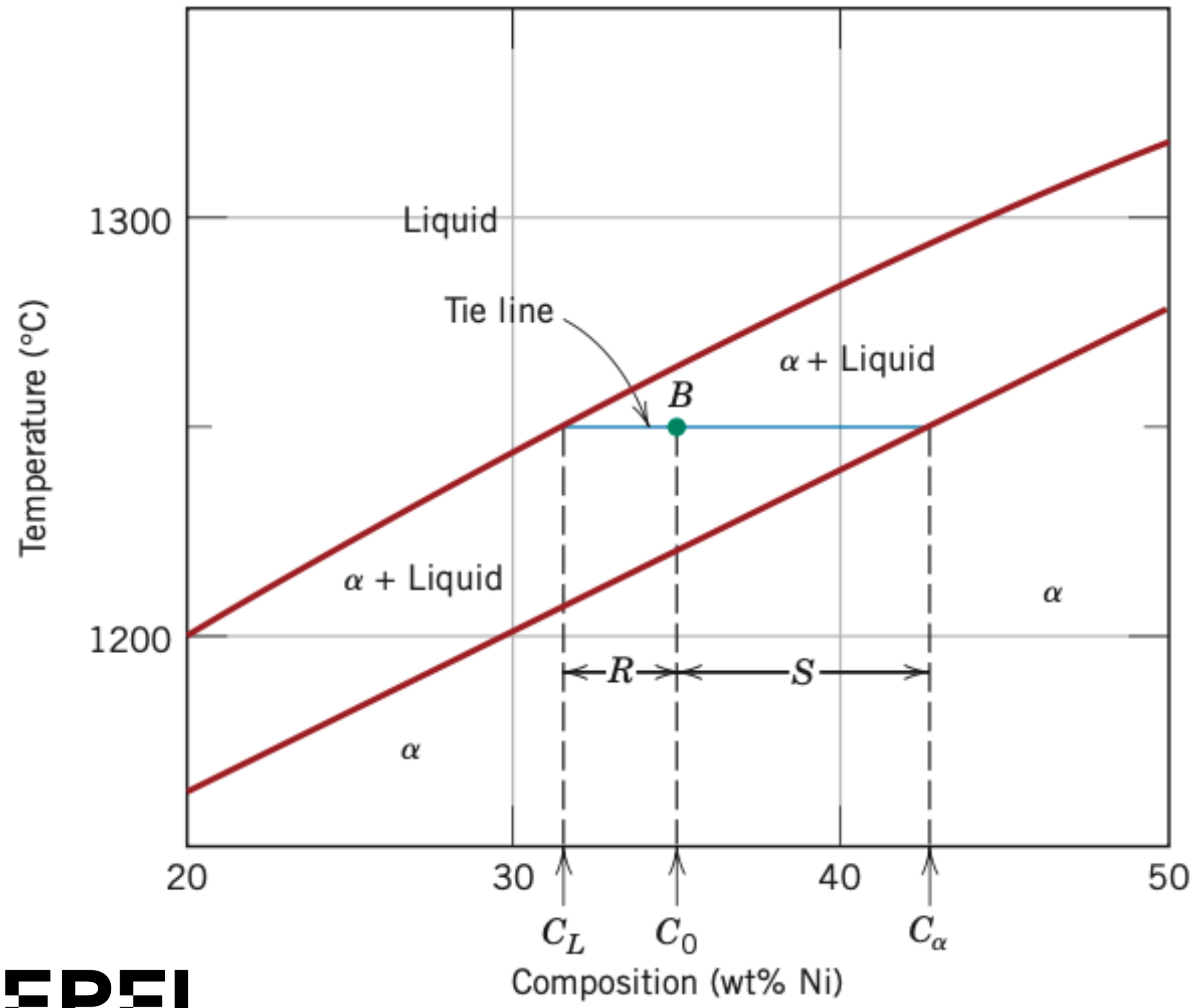
Step 3: From these intersection points, draw vertical lines down to the composition axis

Step 4: Read composition values for each phase

For Point B: $Cu_{65}Ni_{35}$ at 1250˚C
Composition of liquid (C_L) = $Cu_{68.5}Ni_{31.5}$
Composition of α phase (C_α) = $Cu_{57.5}Ni_{42.5}$

Lever rule: Method to determine phase amounts

Let's zoom in to the region around Point B



Step 1: Draw the tie line

Step 2: Fraction of phase 1 is determined by taking the length of the tie line from the overall composition to the phase boundary of phase 2.

Eg. For the L phase, determine *S*

Step 3: Divide this length by the total tie line

Eg. The fraction of L is S / (R+S)

Note: If the composition axis is in wt%, the phase fraction calculated is the mass fraction (mass of a specific phase divided by the total alloy mass)

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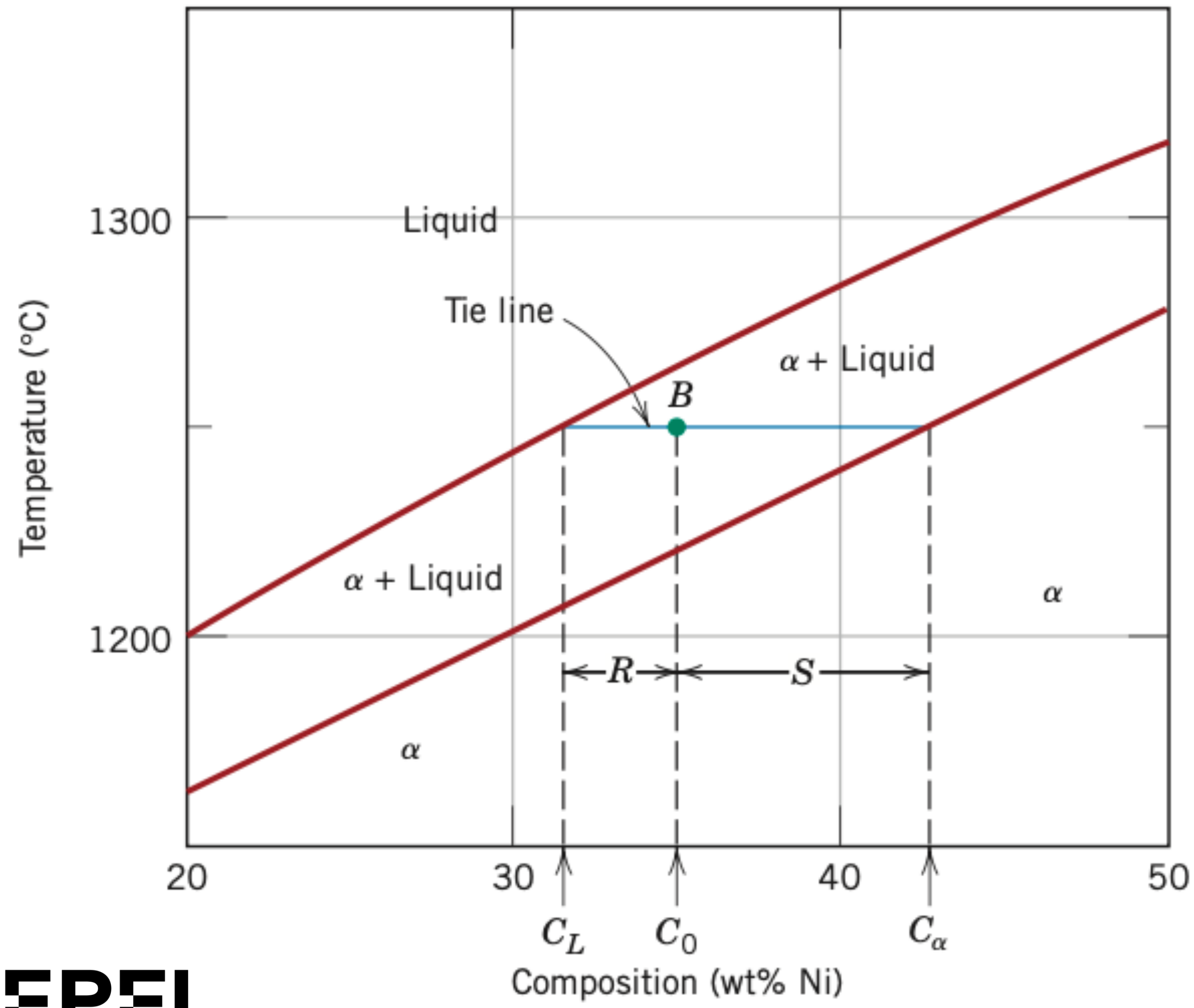
Lever rule: Method to determine phase amounts

Let's zoom in to the region around Point B



How do you measure the length of a tie line?

Old school: If no axis, use a ruler! (It is a ratio afterall)

Precise: Use the compositions on the x axis

$$W_L = \frac{S}{R+S} \quad \text{or} \quad W_L = \frac{C_\alpha - C_0}{C_\alpha - C_L}$$

Only need to use one of the element values to calculate the composition

For Point B:

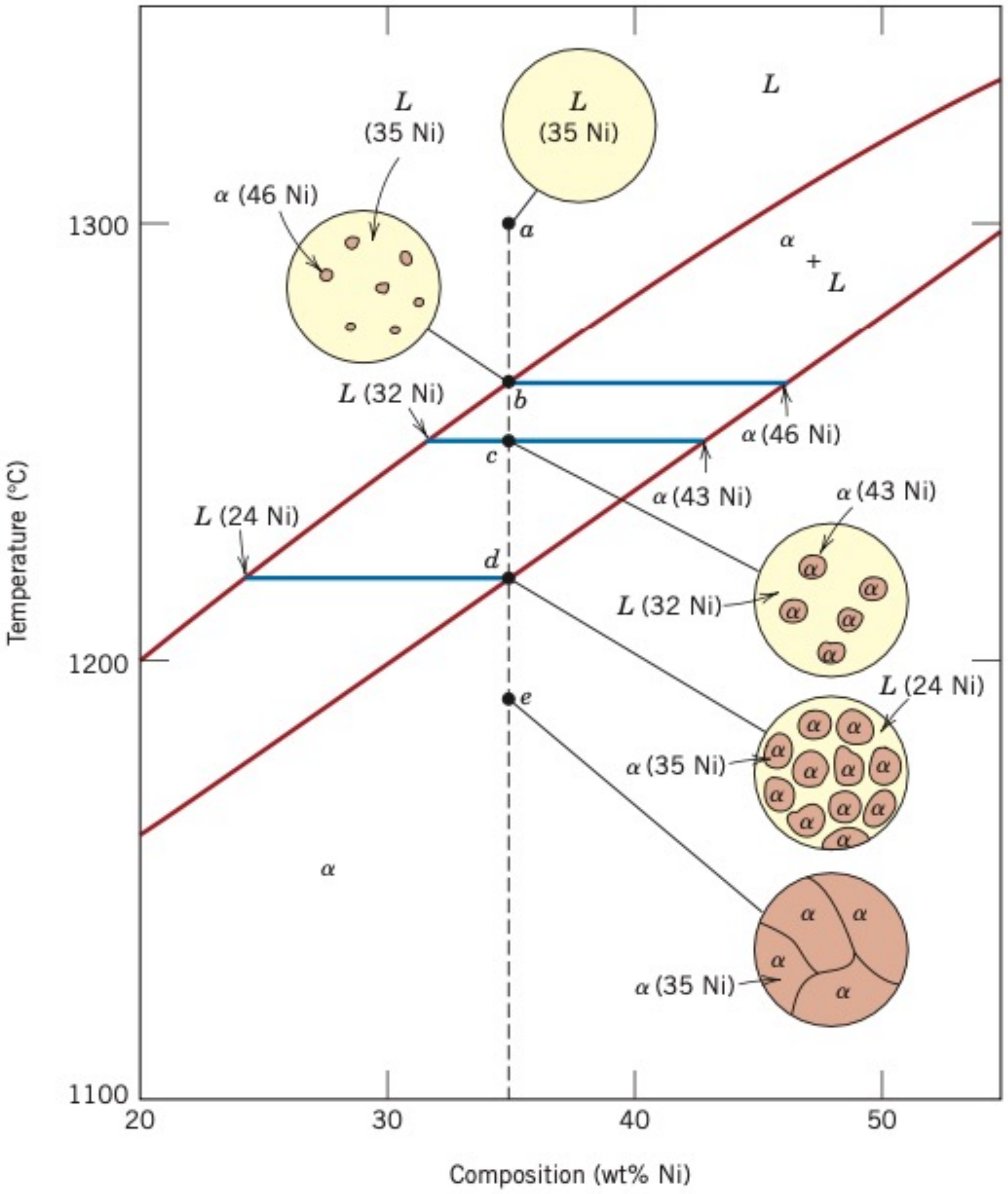
C_0 = 35.0 wt% Ni

C_L = 31.5 wt% Ni

C_α = 42.5 wt% Ni

$$W_L = \frac{42.5 - 35}{42.5 - 31.5} = 0.68$$

At Point B, 68% of the alloy is liquid by mass



Let's cool a $Cu_{65}Ni_{35}$ alloy very slowly from 1300˚C

Very slowly → Equilibrium maintained!

Point *a*: above liquidus → All liquid of $Cu_{65}Ni_{35}$

Microstructure is that of a liquid

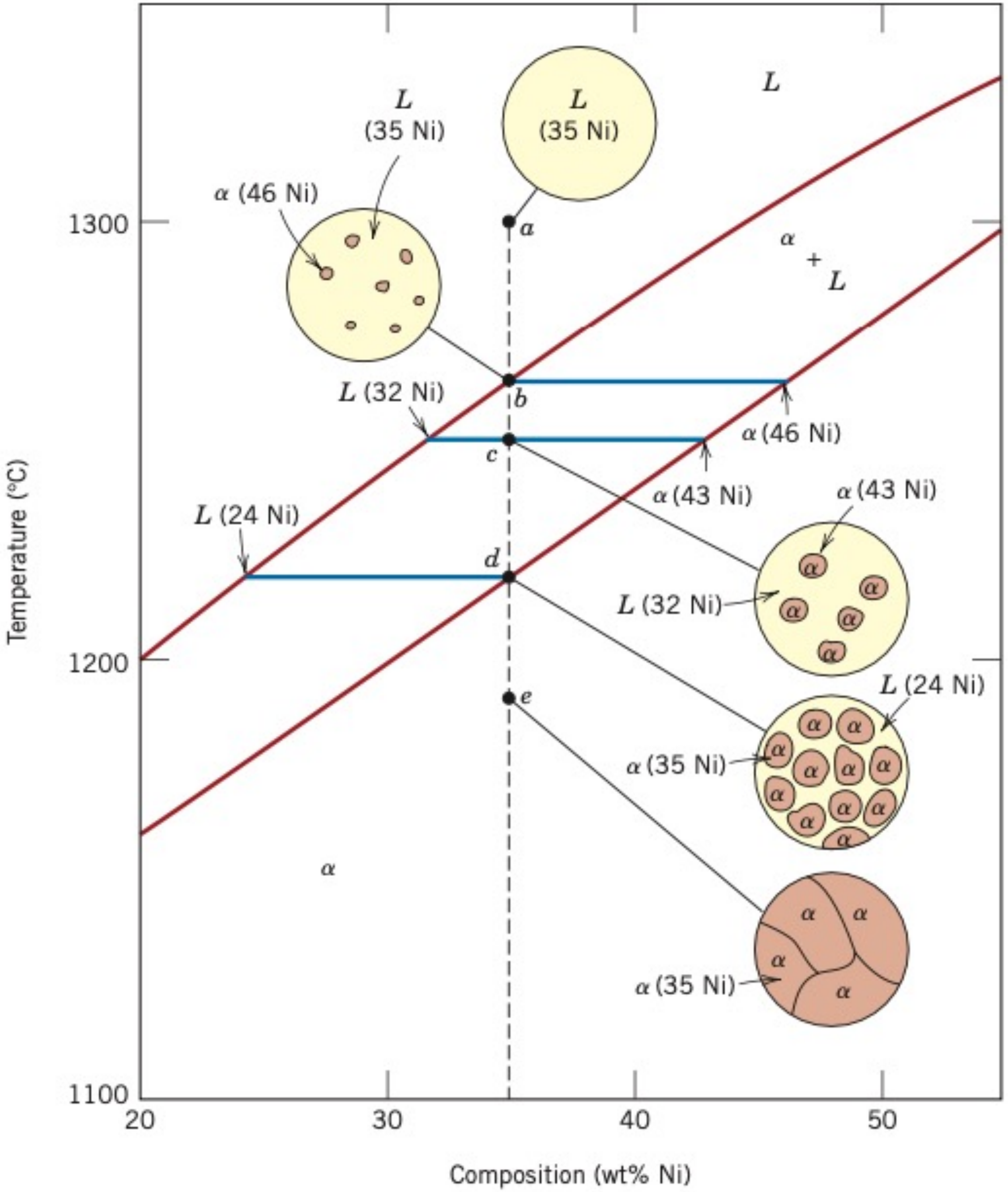
Point *b*: reach liquidus line → first solid begins to form

Using tie lines:

First solid with α phase is $Cu_{54}Ni_{46}$

Liquid is still ~ $Cu_{65}Ni_{35}$

Since overall composition of the alloy needs to stay as $Cu_{65}Ni_{35}$, this means that very little solid is formed!



Let's cool a $Cu_{65}Ni_{35}$ alloy very slowly from 1300˚C

Very slowly → Equilibrium maintained!

Point *c*: Within α + L region

Using tie lines:

Composition of α phase is $Cu_{57}Ni_{43}$

Composition of liquid phase is $Cu_{68}Ni_{32}$

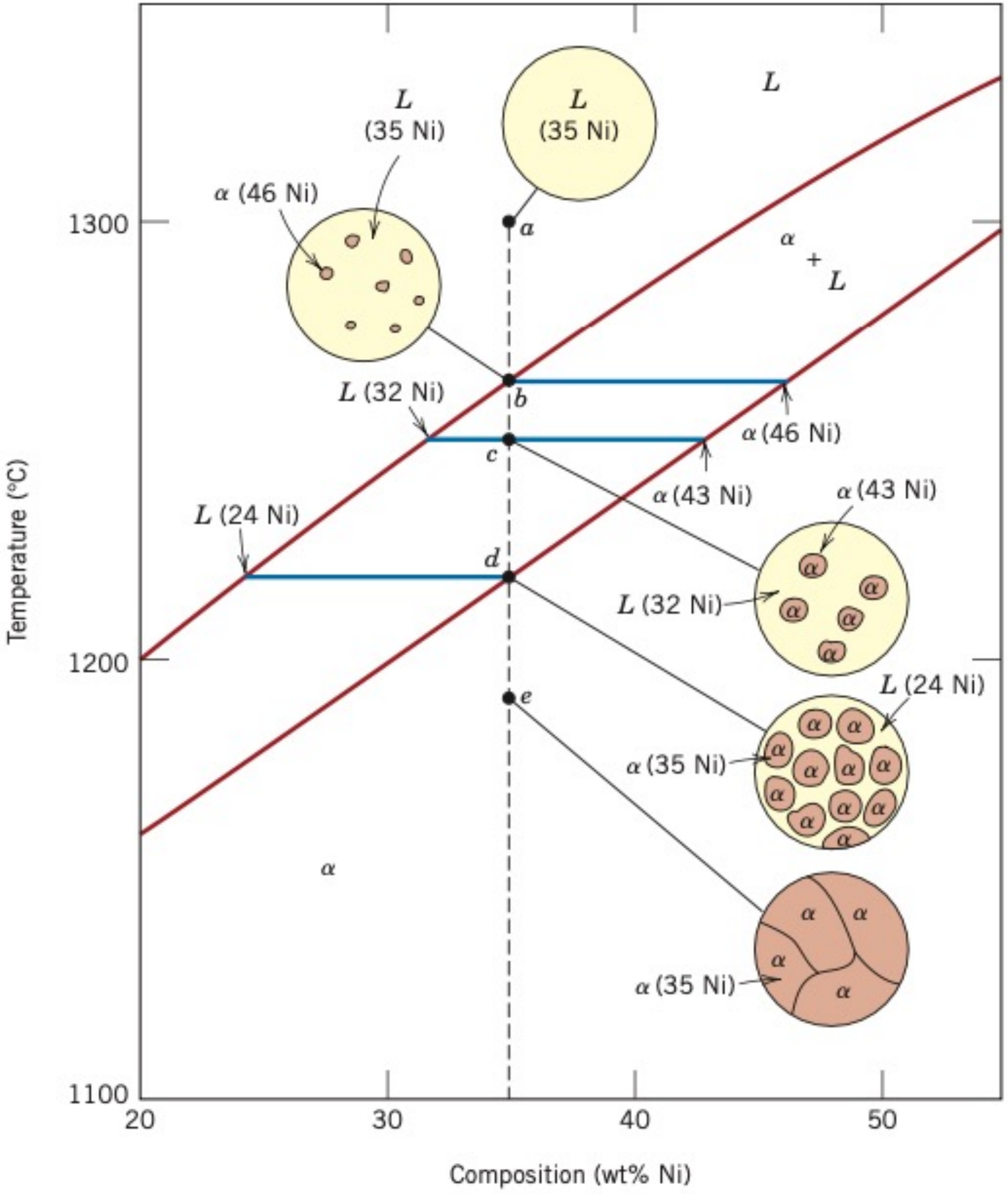
The composition and amount of liquid and α phase changes with temperature

Composition of liquid → Follow liquidus line

Composition of α phase → Follow solidus line

Slow cooling → Equilibrium → Diffusion can occur → The solids all have the same composition

Microstructure is solids + liquid



Let's cool a $Cu_{65}Ni_{35}$ alloy very slowly from 1300˚C

Very slowly → Equilibrium maintained!

Point *d*: Right above the solidus line

<u>Using tie lines:</u>

Composition of α phase is $Cu_{65}Ni_{35}$

Composition of liquid phase is $Cu_{76}Ni_{24}$

Solids have the same composition as the overall alloy

Remaining liquid is Ni poor

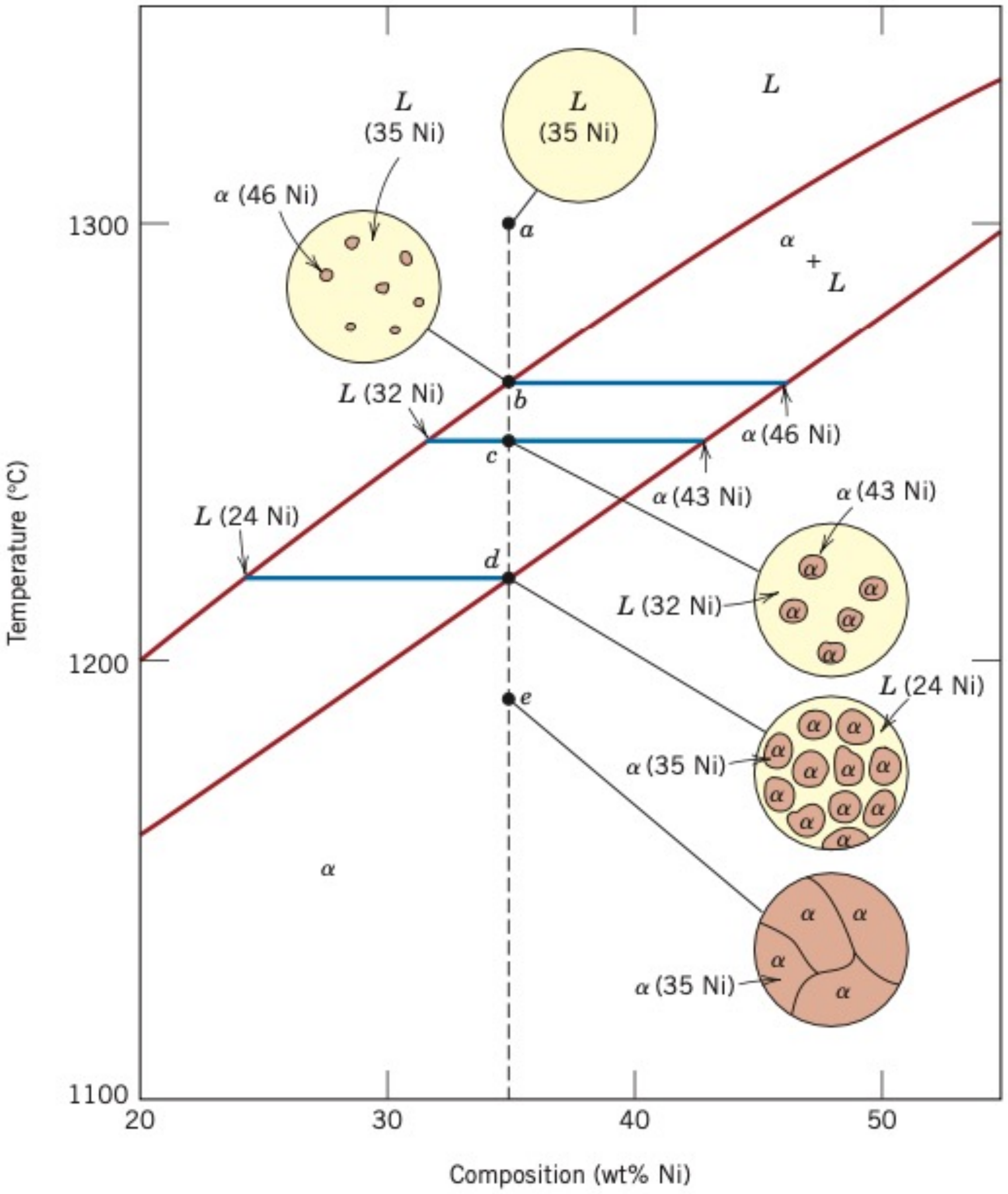
Microstructure is almost all solid. Little liquid left!

Point *e*: Within the α phase region

100% α phase solid solution with uniform $Cu_{65}Ni_{35}$

Microstructure is all solid.

No changes (composition or microstructure) with cooling



Let's cool a $Cu_{65}Ni_{35}$ alloy very slowly from 1300˚C

Very slowly → Equilibrium maintained!

Slow cooling → Equilibrium → Diffusion can occur
→ The solids all have the same composition

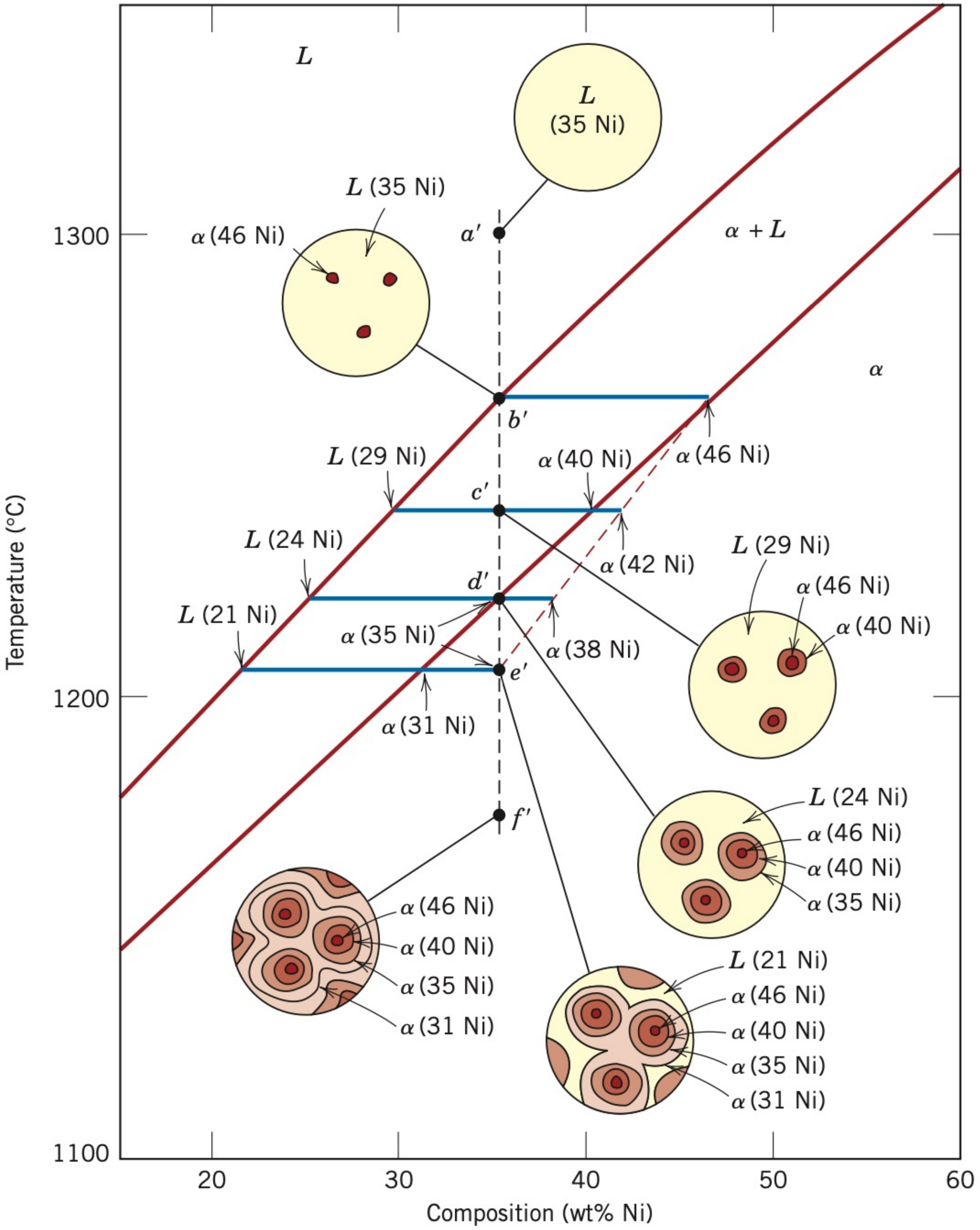
Is this a fair assumption?

Diffusion needs to occur in:

Liquid Phase	Solid Phase	Liquid-Solid Boundary
Fast	Slow	Slow

In addition, diffusion rates decreases with cooling

Equilibrium is almost never achieved in real life solidification processes!



Even in non-equilibrium conditions, the phase diagram can still provide insights about solidification

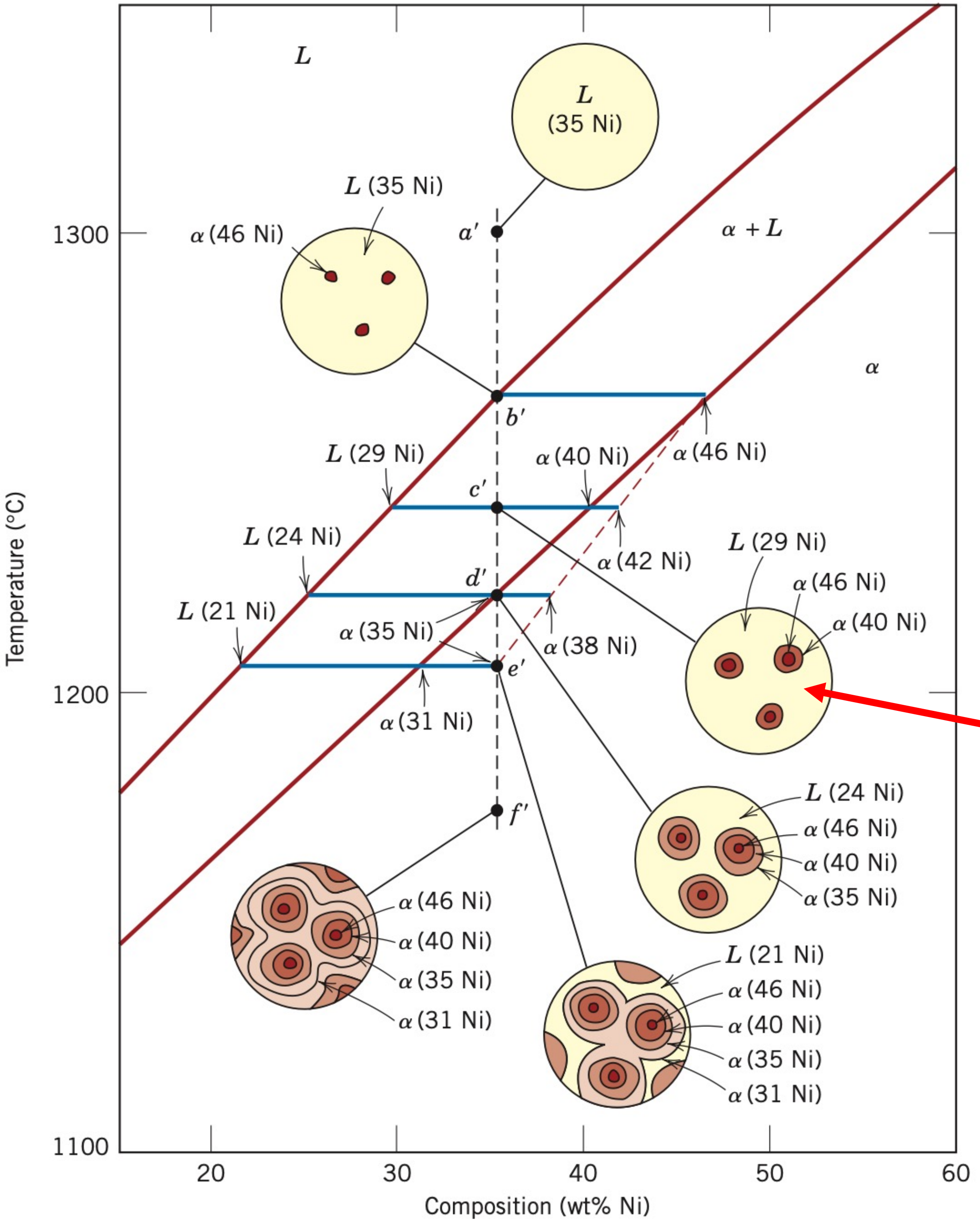
Point *a'*: Above liquidus line

All liquid of composition $Cu_{65}Ni_{35}$ (L(35 Ni))

Point *b'*: reach liquidus line → first solid begins to form

<u>Using tie lines:</u>
First solid with α phase is $Cu_{54}Ni_{46}$ (α(46 Ni))
Liquid is still ~ $Cu_{65}Ni_{35}$

Same as before. No difference yet



Even in non-equilibrium conditions, the phase diagram can still provide insights about solidification

Point *c'*: Within α + L region

Using tie lines:

α phase that forms is $Cu_{60}Ni_{40}$ (α(40 Ni))
Liquid composition is $Cu_{71}Ni_{29}$

But diffusion is slow!

The α phase that formed at Point b' cannot equilibrate

Solids have a gradient in composition

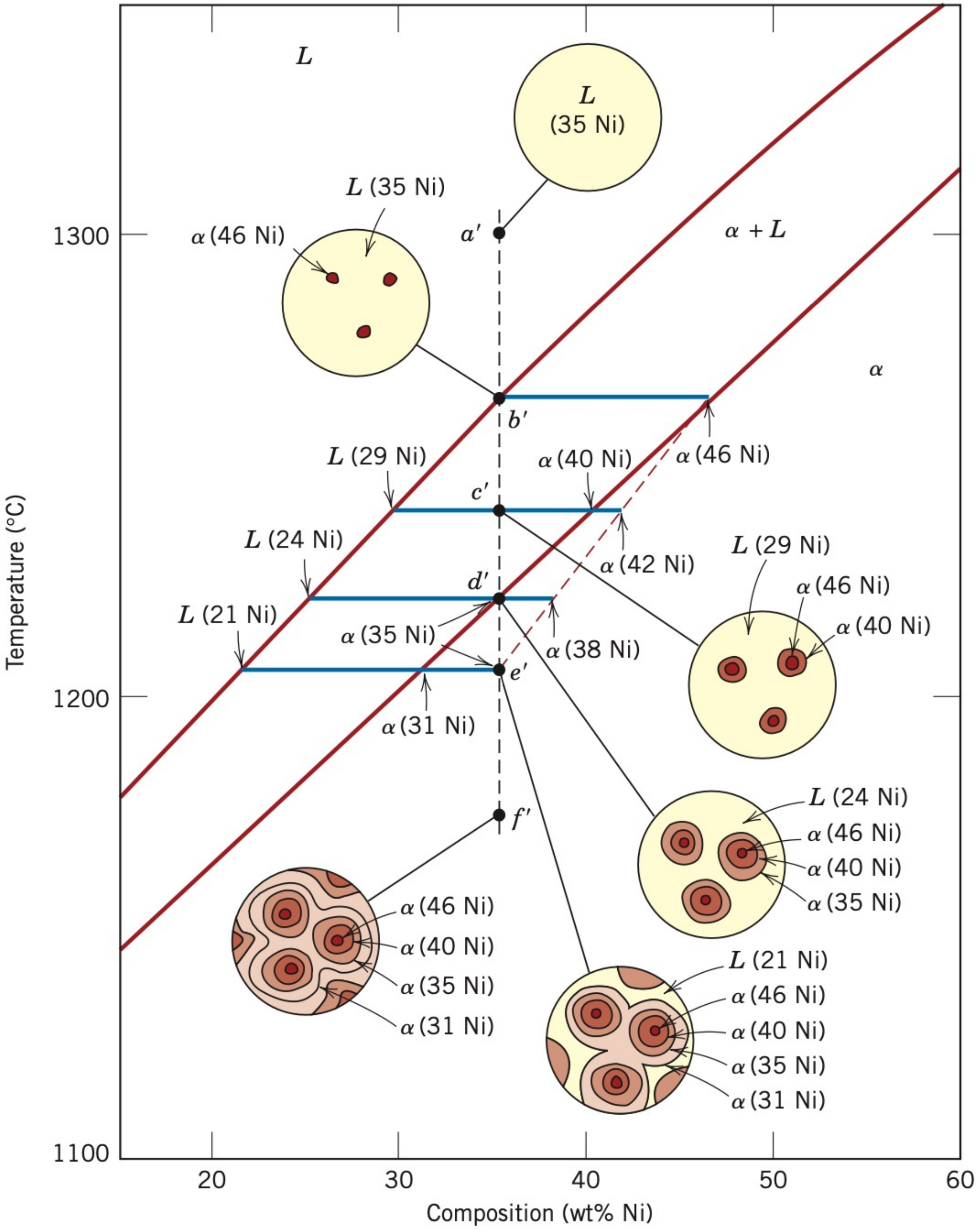
Core is α(46 Ni)

Surrounded by α(40 Ni

Average composition of the solid α phase is the volume-weighted average composition

$C_\alpha = \alpha(40\ \text{Ni}) - \alpha(46\ \text{Ni}) \longrightarrow C_\alpha = \alpha\ (42\ \text{Ni})$*

*For simplicity



Even in non-equilibrium conditions, the phase diagram can still provide insights about solidification

Point *c'*: Within α + L region

$C_\alpha = \alpha$ (42 Ni)*

Can draw a new solidus line (dashed line)

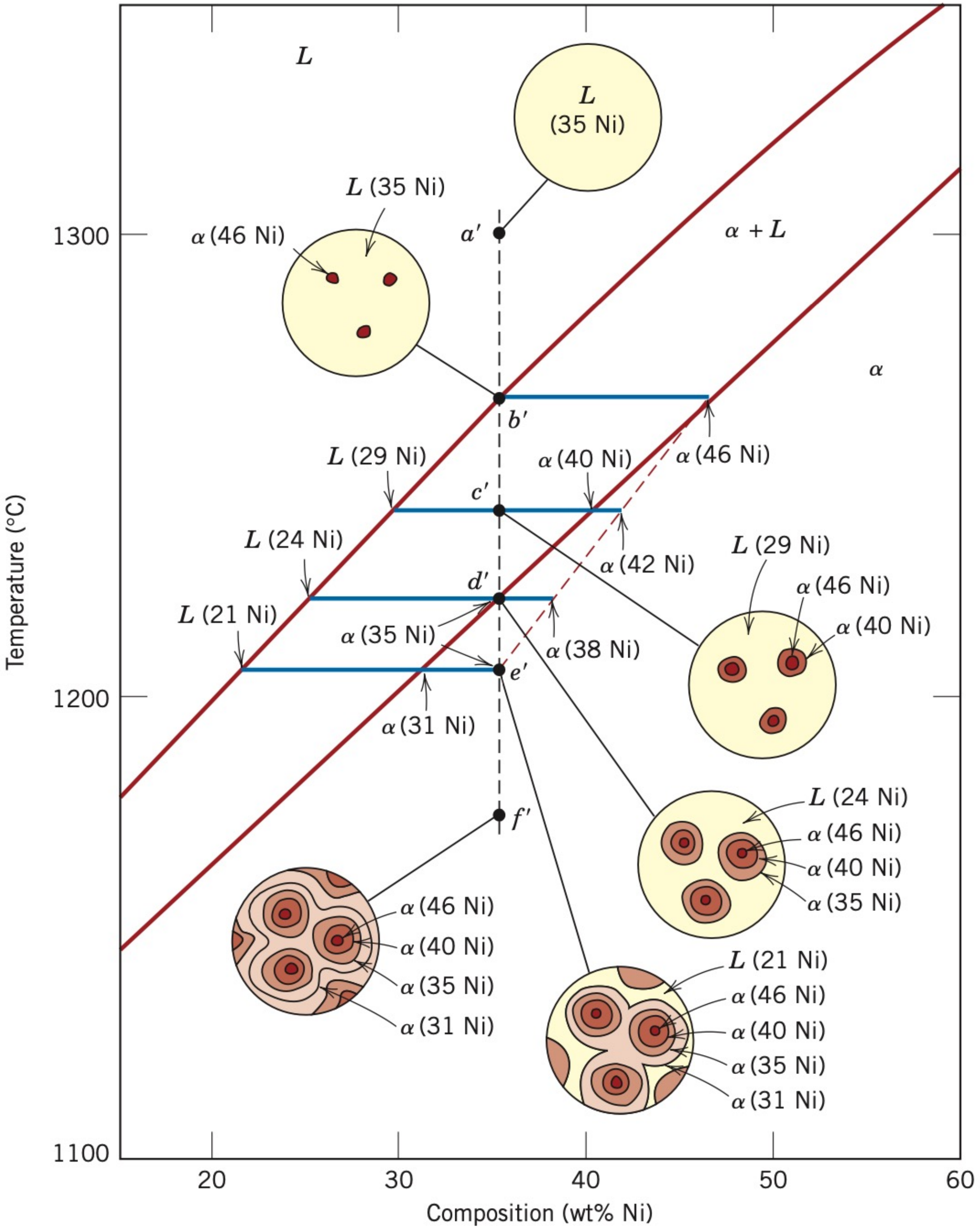
Implication 1: Tie line is extended

Implication 2: More liquid in the system (lever rule)

Assume: Rapid diffusion in liquid → No change to liquidus

The original solidus line (solid) tells you the composition of the α phase that forms at that temperature

The shifted solidus line (dashed) tells you the average composition of all the α phase at that temperature



Even in non-equilibrium conditions, the phase diagram can still provide insights about solidification

Point *d'*: Still within α + L region because solidus line has shifted.

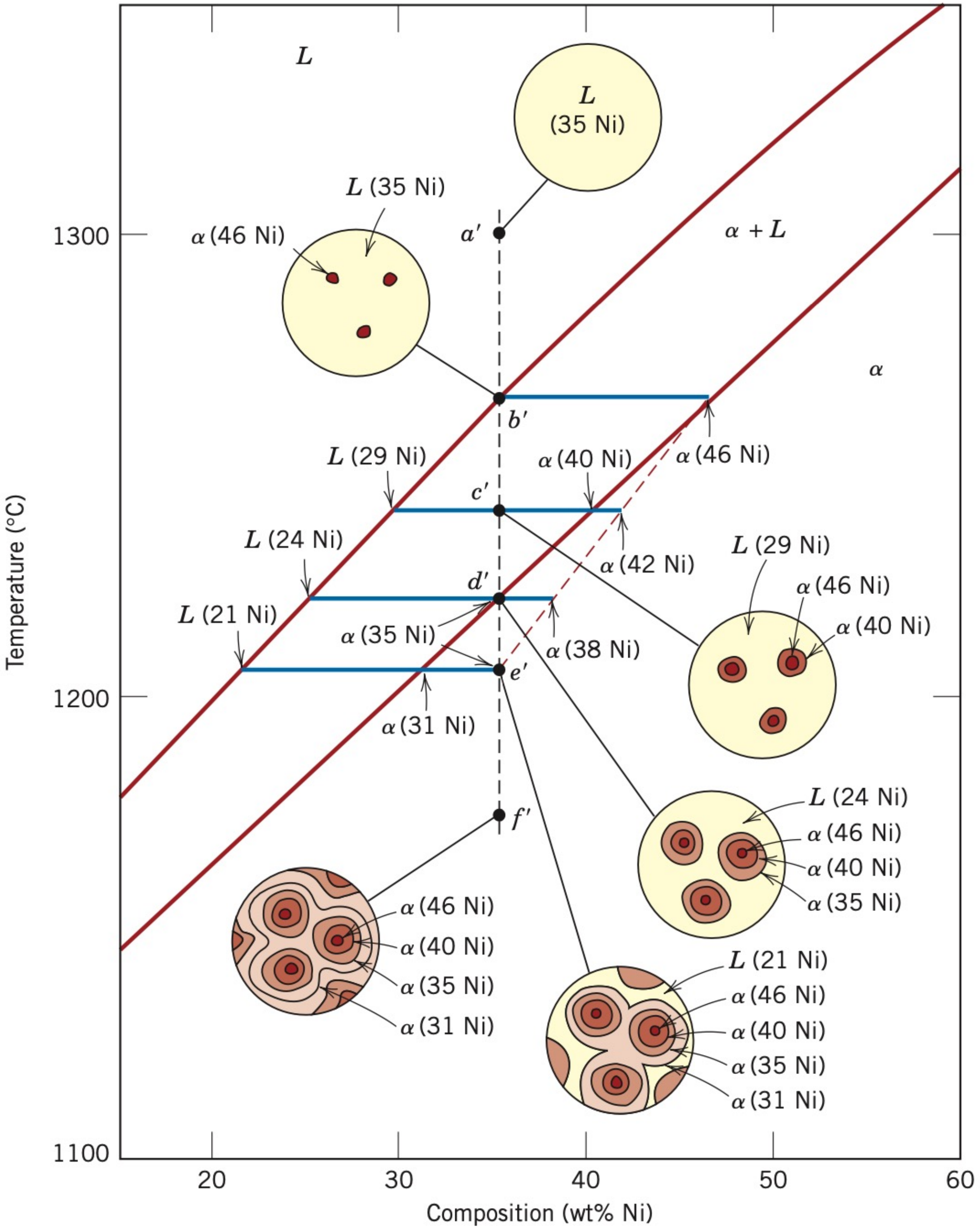
Still has liquid in the system!

The new α phase that forms is α(35 Ni) but the average α phase composition is α(38 Ni)

Point *e'*: Solidification just about complete

The new α phase that forms is α(31 Ni) but the average α phase composition is α(35 Ni)

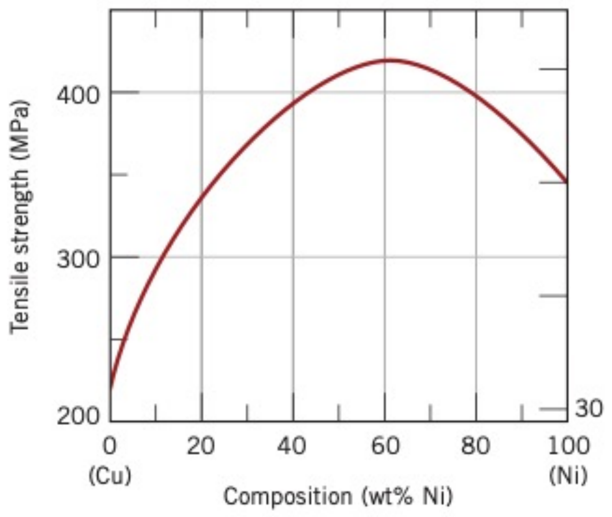
Last bit of liquid phase is α(21 Ni)

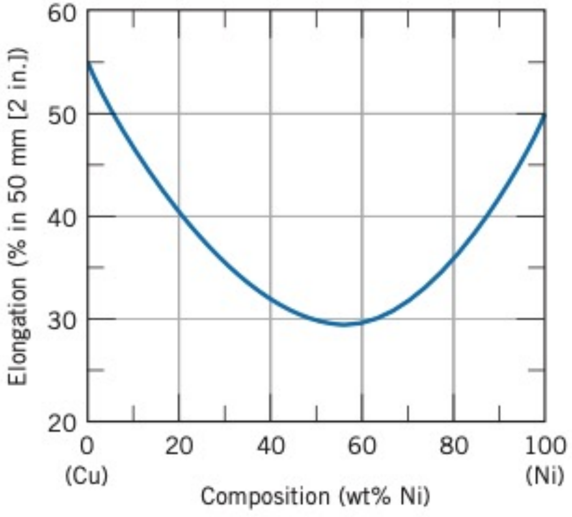


Outcome of rapid cooling = Inhomogeneous grains

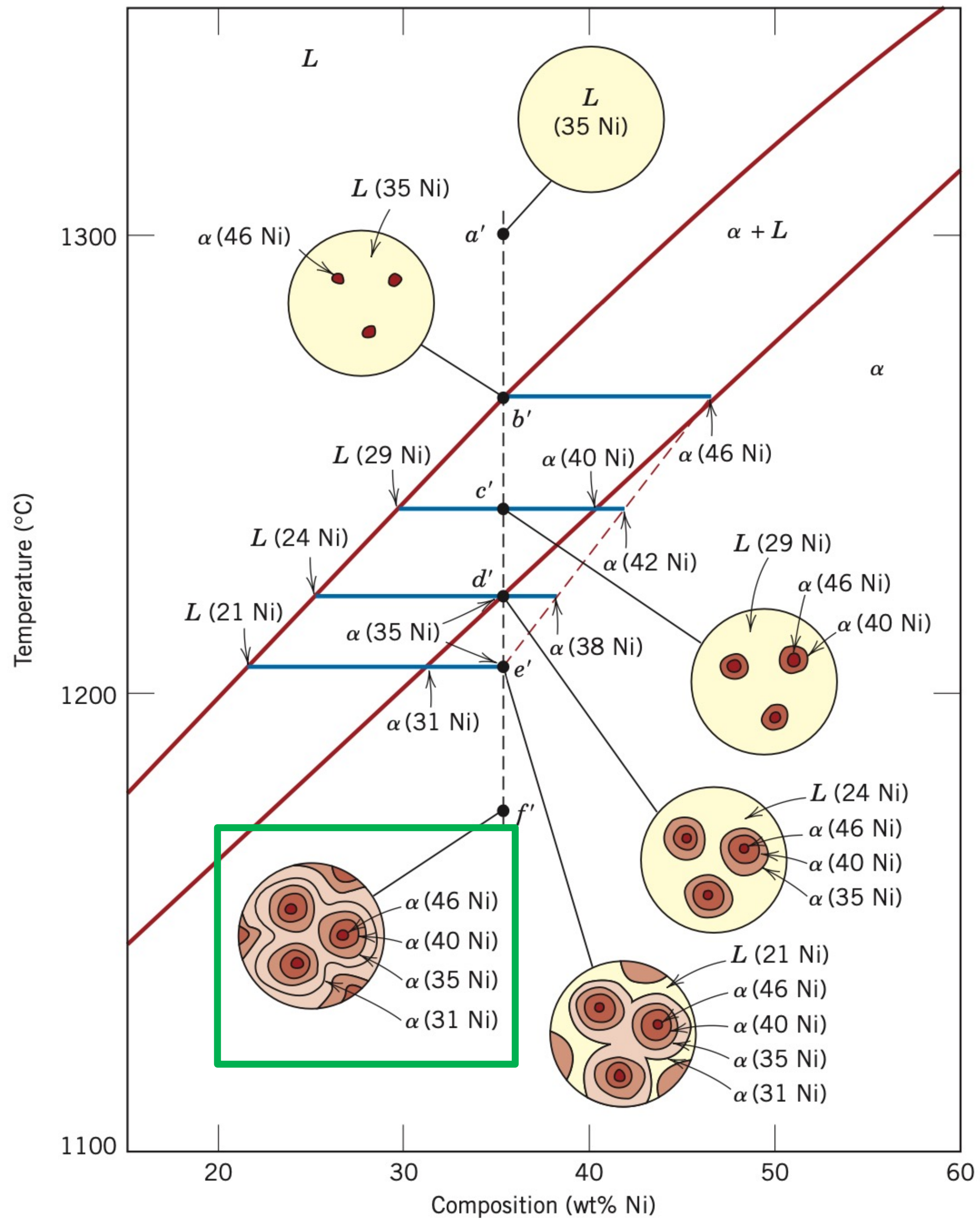
Cored structure

Implication 1: Changes to mechanical properties





Grain has spatially varying mechanical properties
Could lead to poor performance under load



Outcome of rapid cooling = Inhomogeneous grains

Cored structure

Implication 2: Reduced temperature stability

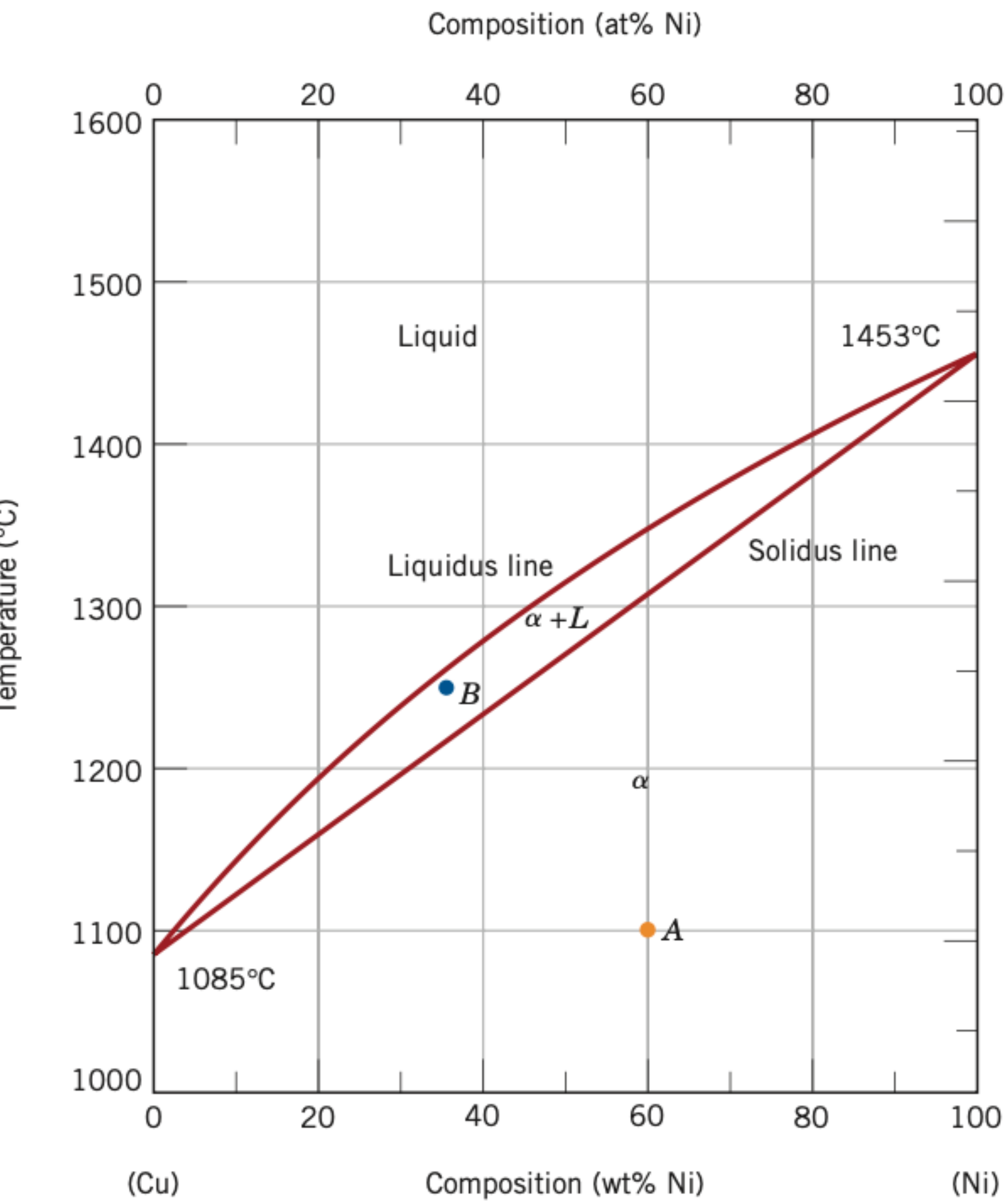
The grain boundaries are α(31 Ni)
The core of the grains are α(46 Ni)

Melting temperature of α(31 Ni) is ~ 1205˚C
Melting temperature of α(46 Ni) is ~ 1260˚C

Melting temperature of α(35 Ni) is ~ 1220˚C
This is what we expect if equilibrium

As temperature increases, α(31 Ni) melts first and forms a liquid film between the grains → Failure of metal

Binary phase diagrams — What we've learnt so far



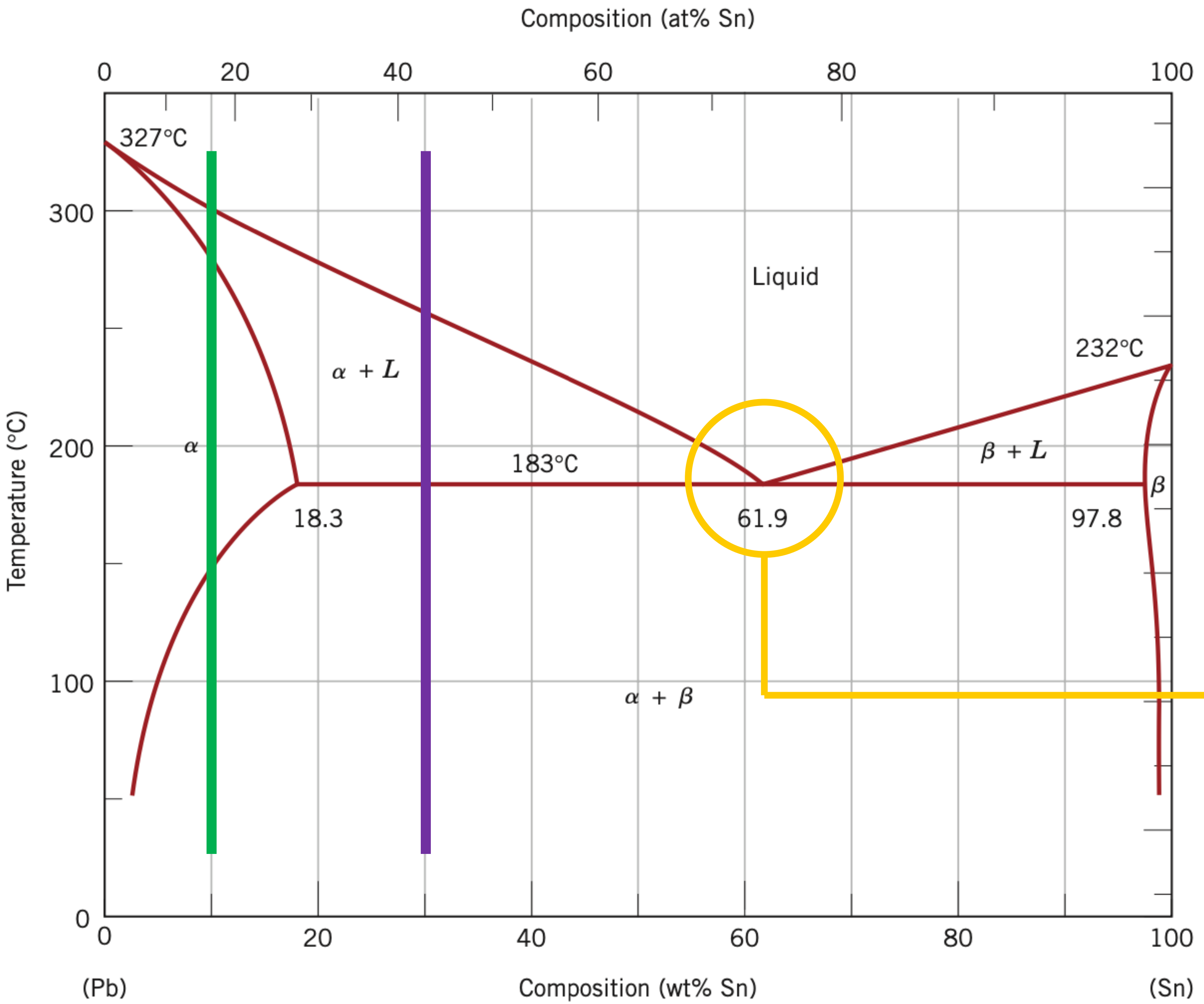
Information you can gain from a phase diagram

For a known composition and temperature:

1. The phases that are present
2. The composition of these phases (tie line)
3. Percentage of these phases (lever rule)

Although the phase diagram is meant for equilibrium situations, it can be used to estimate non-equilibrium situations

Ok let's go back to soldering and apply what we learnt

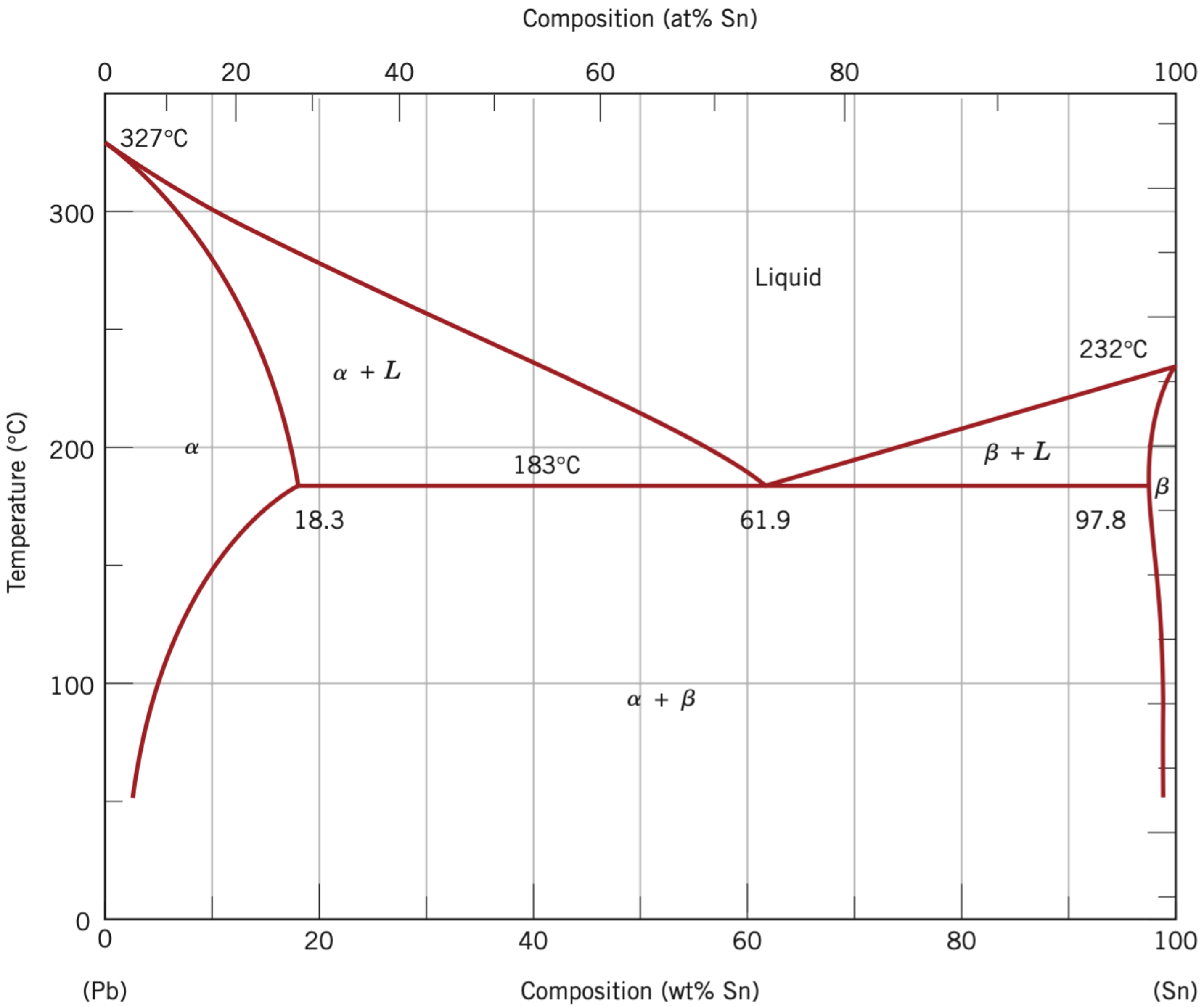


What happens when $Sn_{10}Pb_{90}$ is cooled slowly from 350˚C?

What happens when $Sn_{30}Pb_{70}$ is cooled slowly from 350˚C?

What is happening at this point/intersection?

Binary Eutectic System



Let's chracterize the phase diagram first

Three single phase regions:

α: Rich in Pb with up to 18.3 wt% of Sn
β: Rich in Sn with up to 2.2 wt% Pb
L: Contains any combination of Pb and Sn

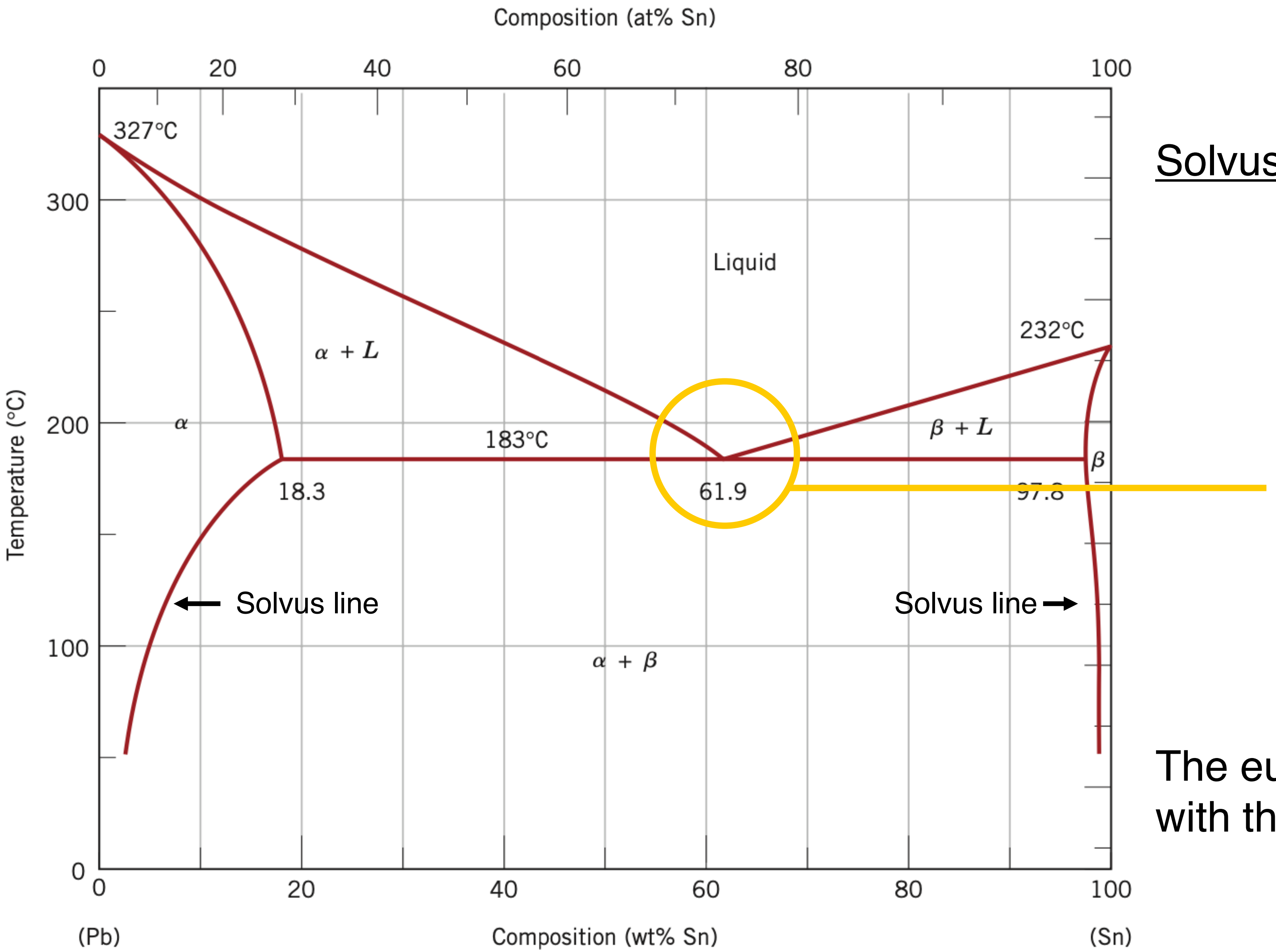
Three two phase regions:

α + L
β + L
$\alpha + \beta$

With Cu-Ni: 1 phase→2 phase→1 phase

Here: 1 phase→2 phase→2 phase
1 phase→2 phase→1 phase→2 phase
Are there more?

Binary Eutectic System



Some new terms:

Solvus line: line between solid phase regions

$$\alpha \leftrightarrow \alpha + \beta$$

$$\beta \leftrightarrow \alpha + \beta$$

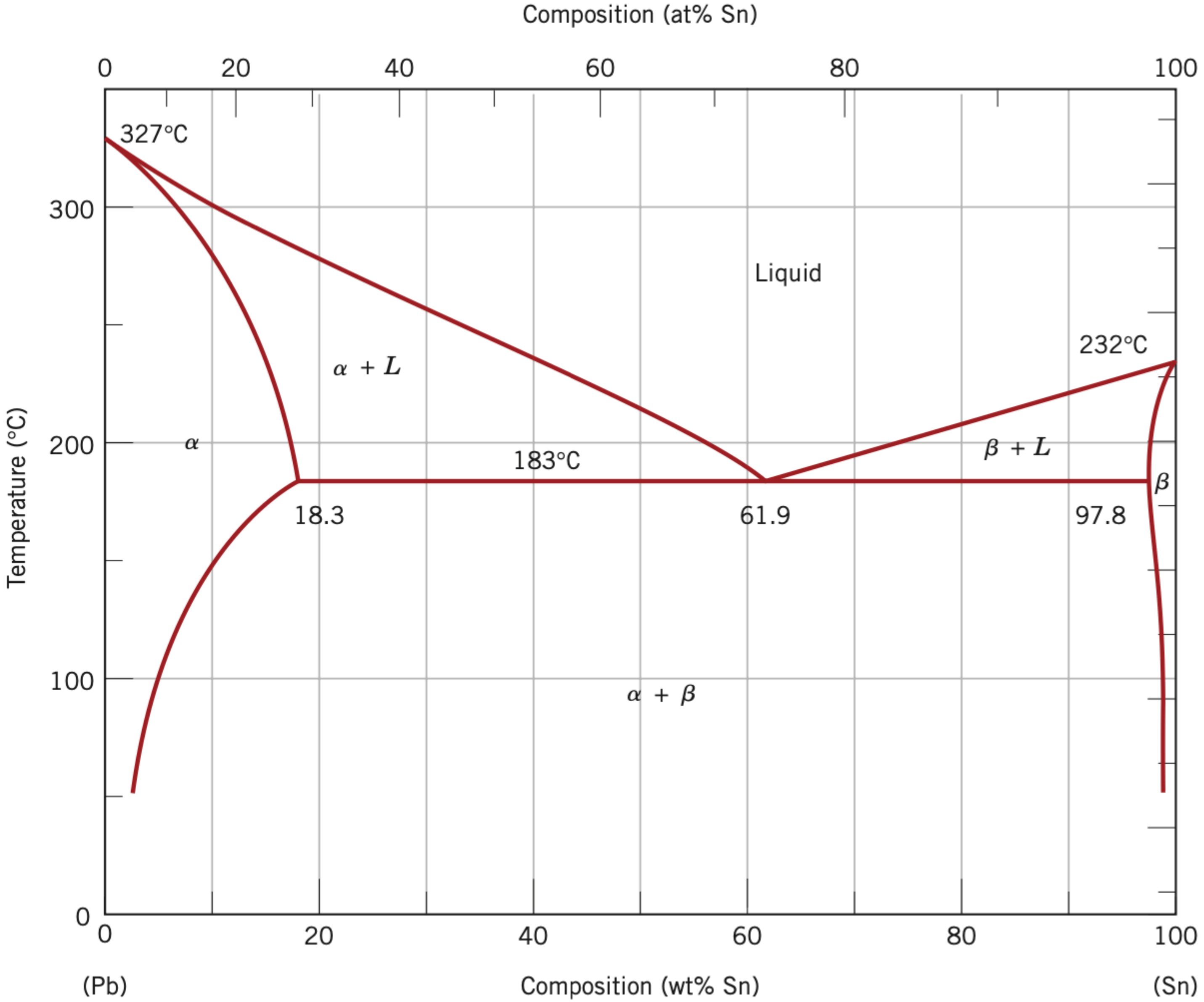
This is called the eutectic point

$$L \leftrightarrow \alpha + \beta$$

Liquid transformed into solid!

The eutectic composition is the composition with the lowest melting point

Let's look at solders again



With what we just learnt:

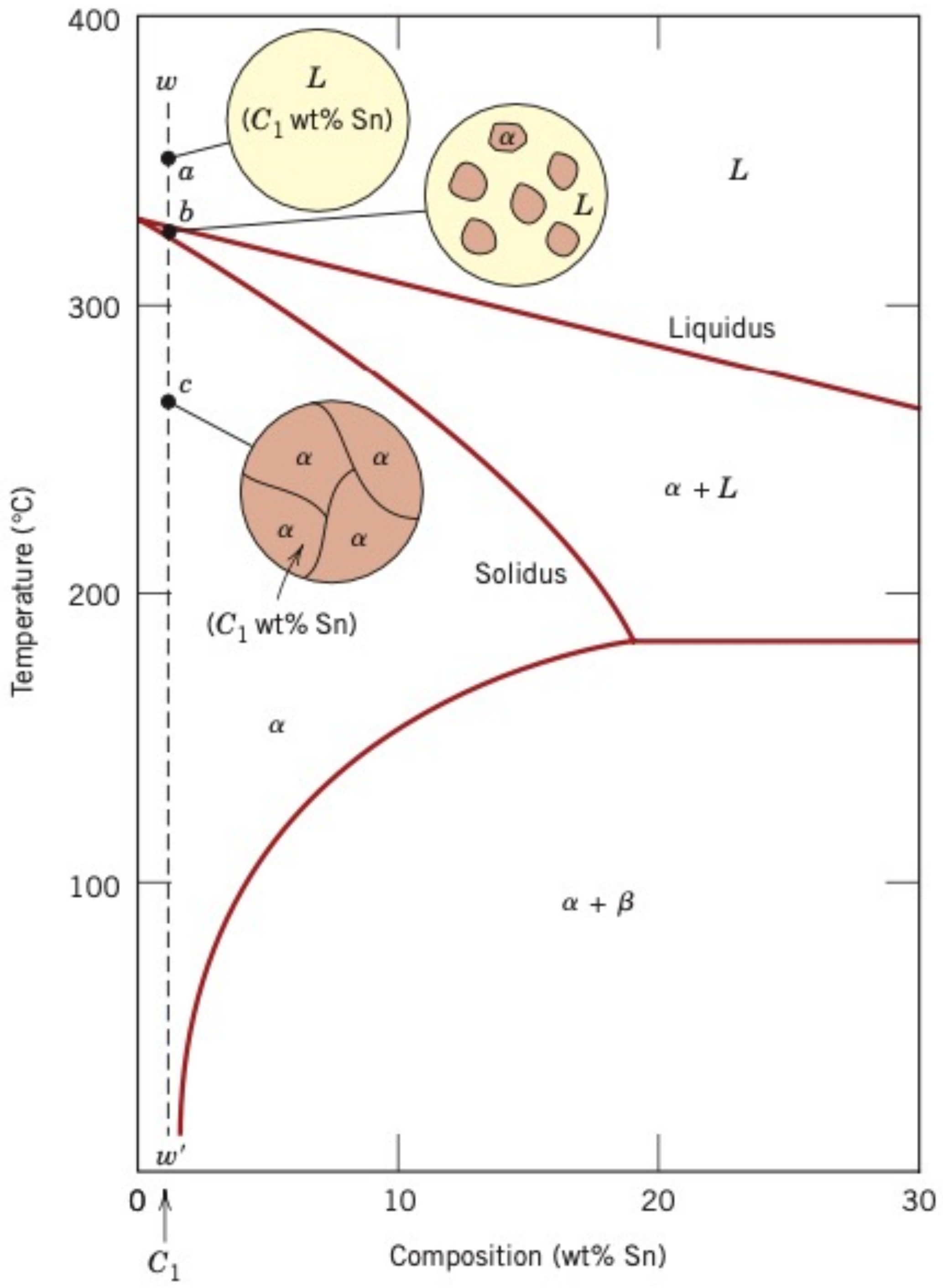
63% tin / 37% lead **(63/37)**	60% tin / 40% lead **(60/40)**
T_m = 183˚C	T_m = 183 – 191˚C
Less susceptible to cold soldering	Susceptible to cold soldering

60/40: Crosses the α + L

Has melting range + liquid present in the two phase region

63/37: Eutectic? → Excess tin added because tin oxidizes away

Liquid → Solid quickly



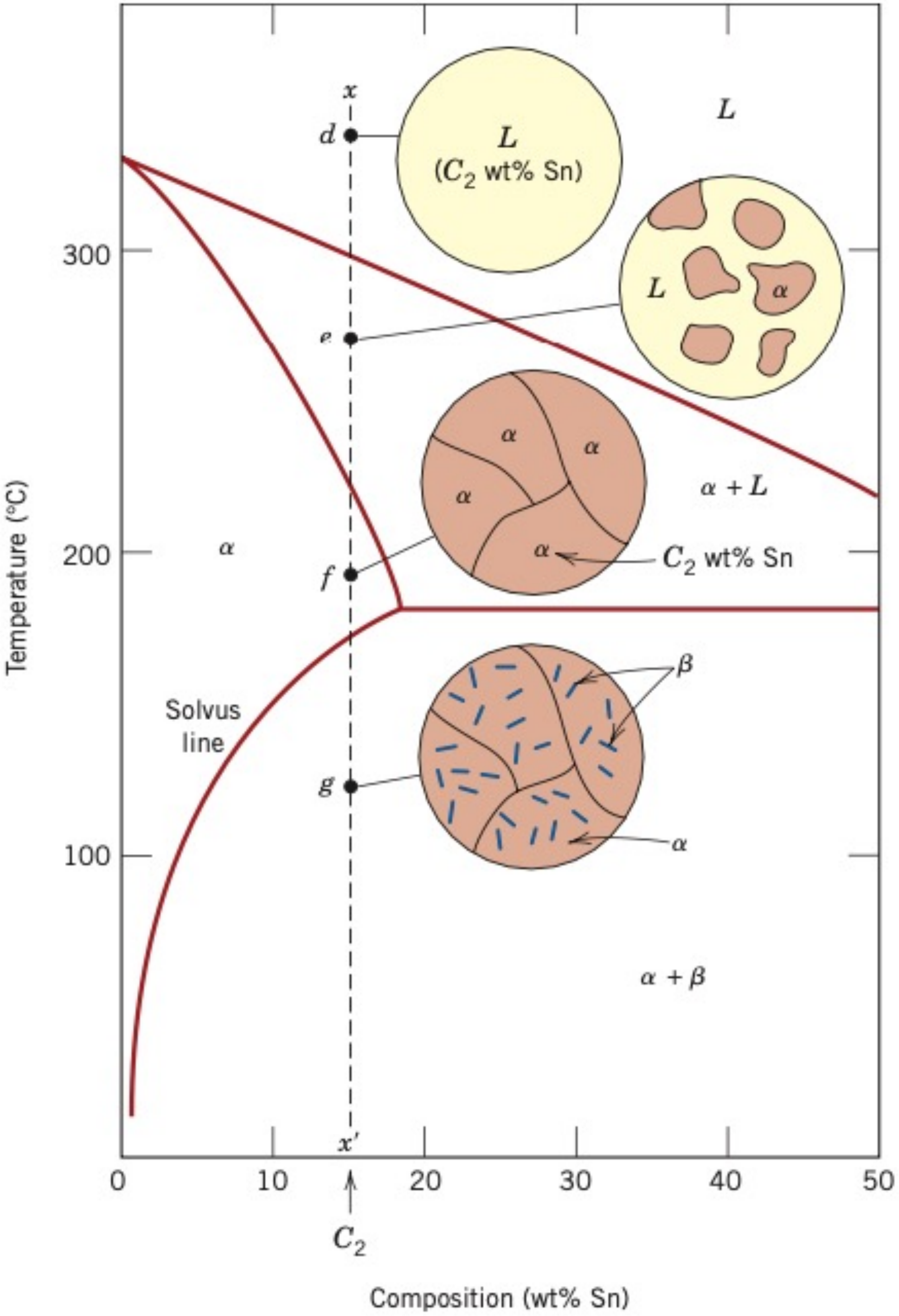
Let's look at Pb-Sn microstructure

At C_1, we have L → α + L → α

Almost identical conceptually to the Cu-Ni example presented earlier

Small α + L region → small temperature range for melting and solidification

Can use the tie lines and lever rule we learnt ealier to determine the amount and compositions of the α and L phases



Let's look at Pb-Sn microstructure

At C_2, we have L → α + L → α → $\alpha + \beta$

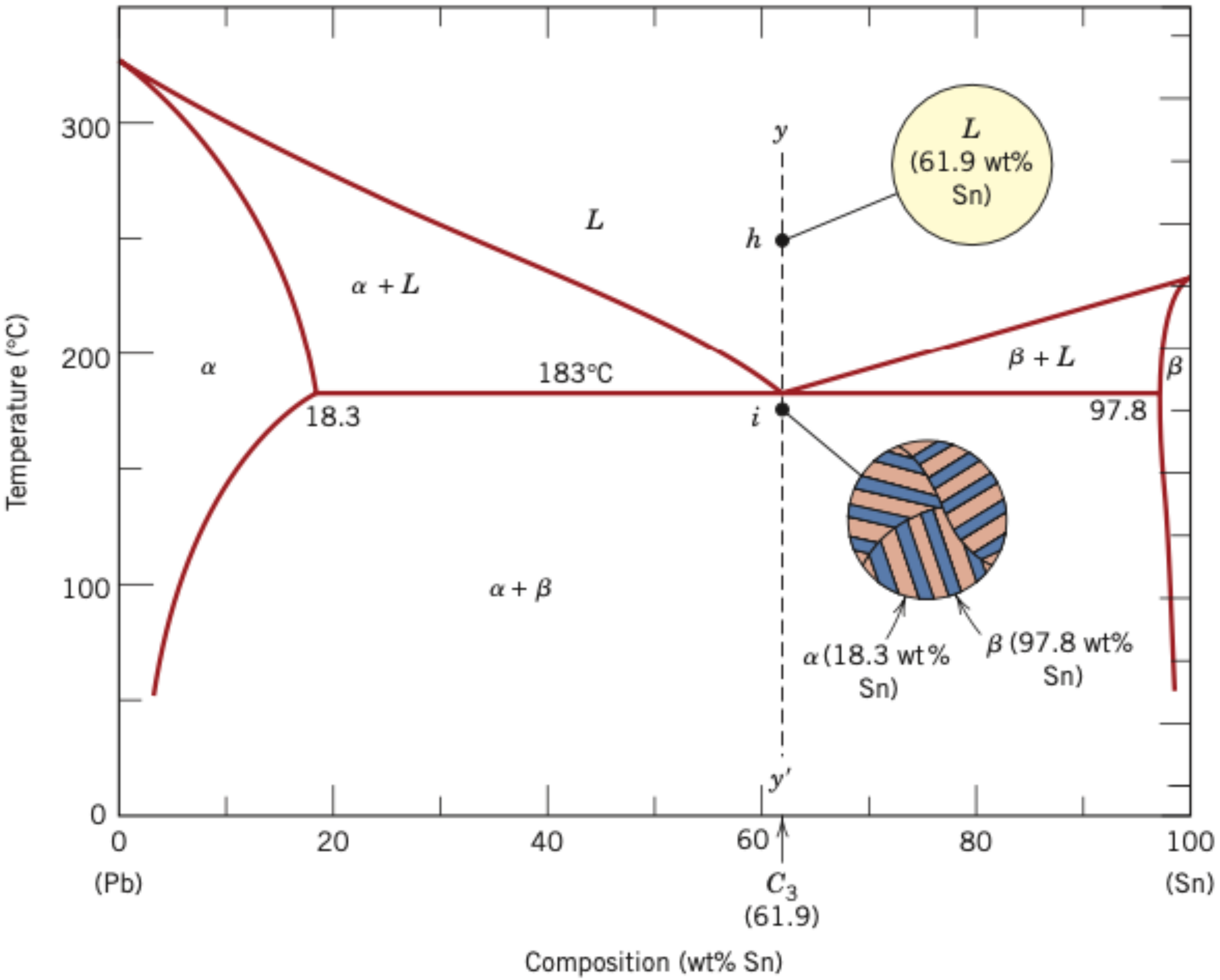
Point *d* to *f* is identical to the cases shown before

f → *g*: Crossing the solvus line, the solubility of Sn in α is exceeded which causes in the formation of β phases

As temperature decreases, the β phases grow in size since the mass fraction of β increases (see lever rule)

Can use the tie lines and lever rule we learnt ealier to determine the amount and compositions of the α and β phases

Now what happens at the eutectic?



At C_3, we have L → $\alpha + \beta$

<u>Important things about eutectics:</u>

Lowest melting temperature

No L + solid region

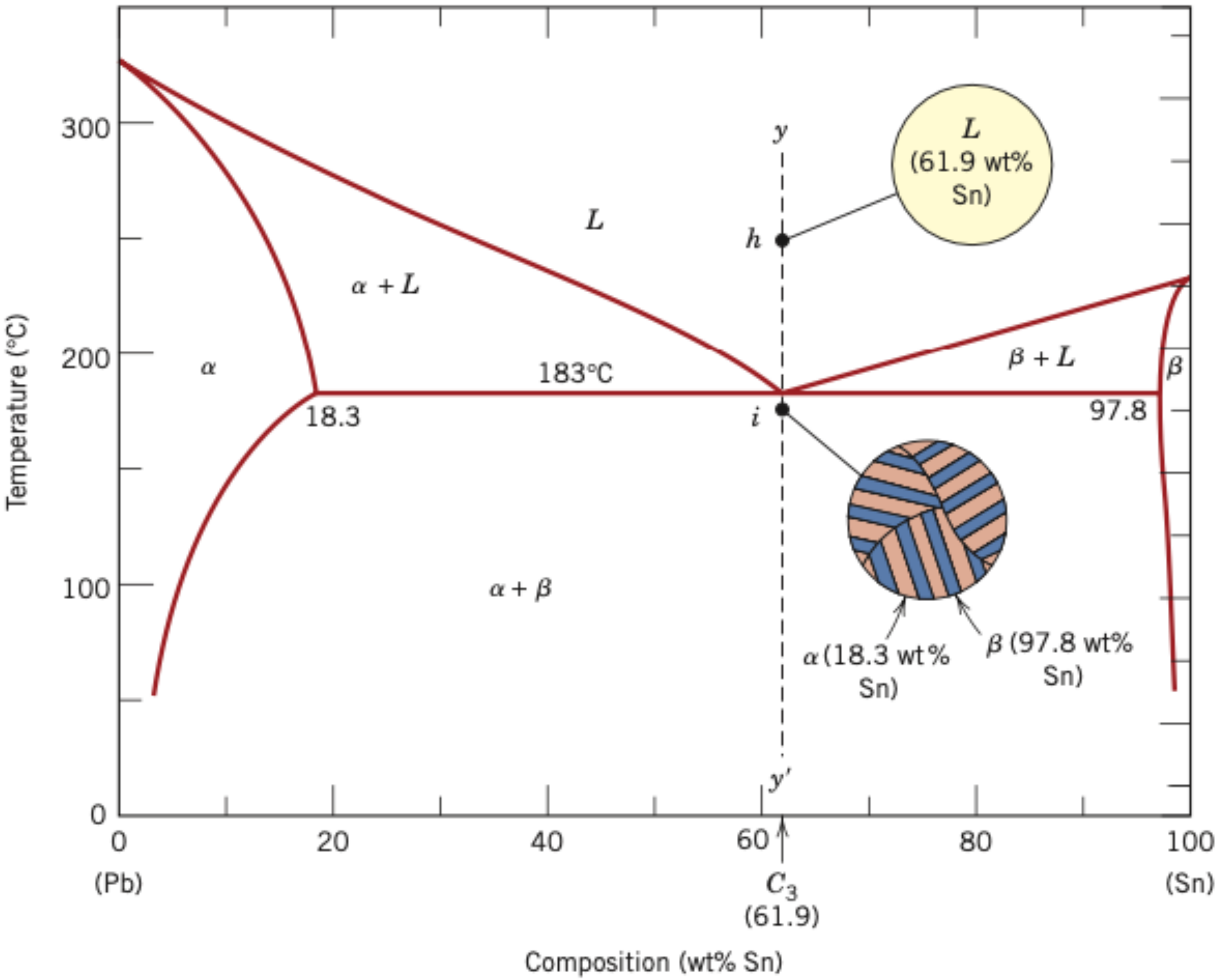
$$L(61.9\ \text{wt\% Sn}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(18.3\ \text{wt\% Sn}) + \beta(97.8\ \text{wt\% Sn})$$

Sn content for each phase is very different!

How can the atoms be redistributed quickly?

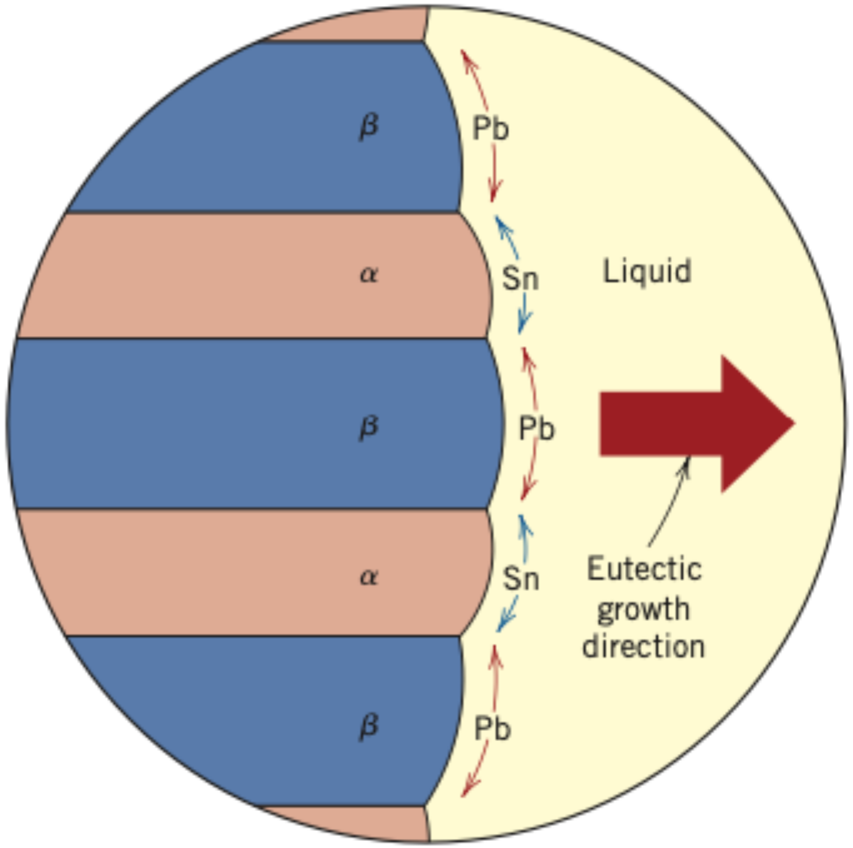
EPFL

Now what happens at the eutectic?

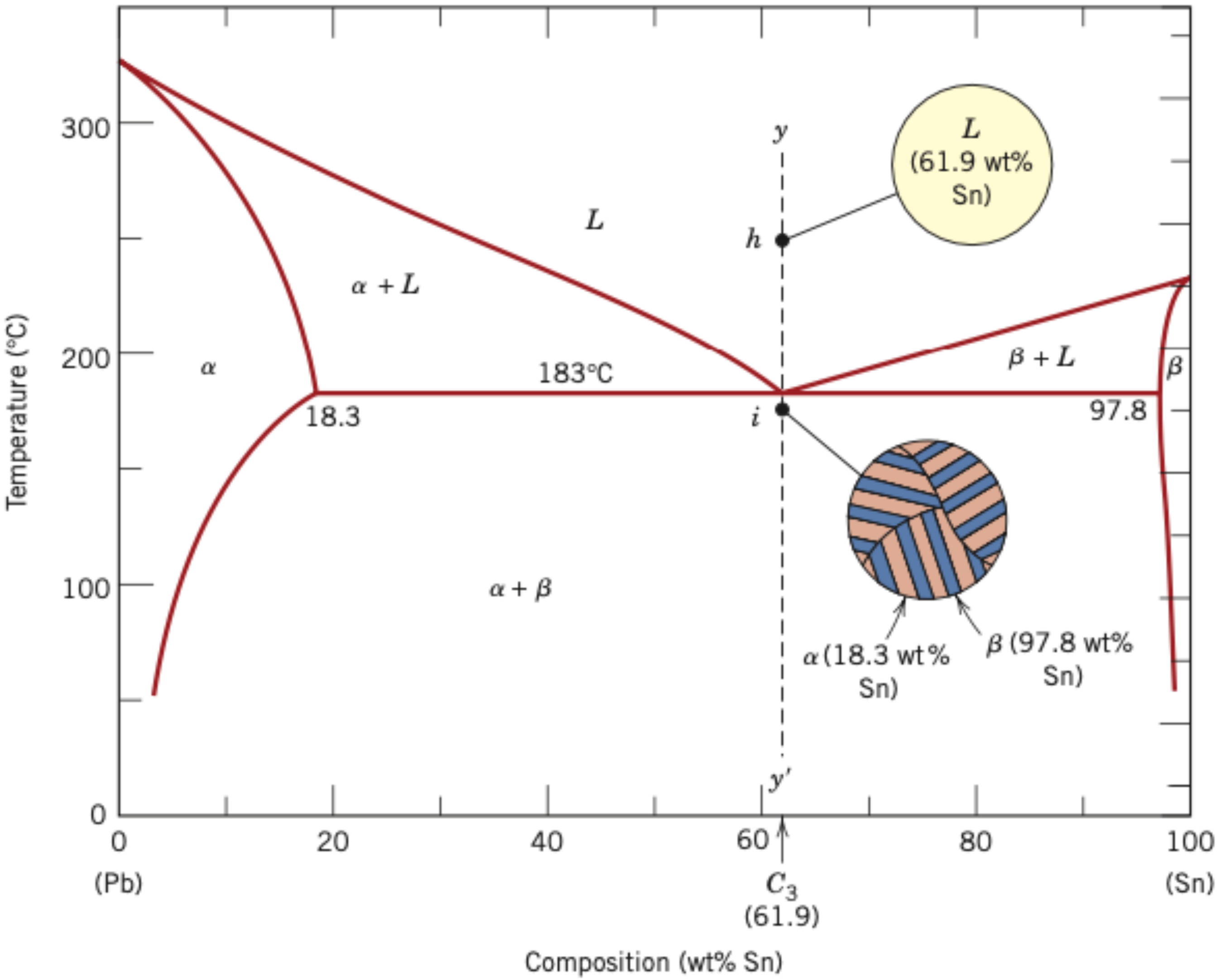


At C_3, we have L → $\alpha + \beta$

Alternating α and β layers are adopted to facilitate rapid atomic diffusion

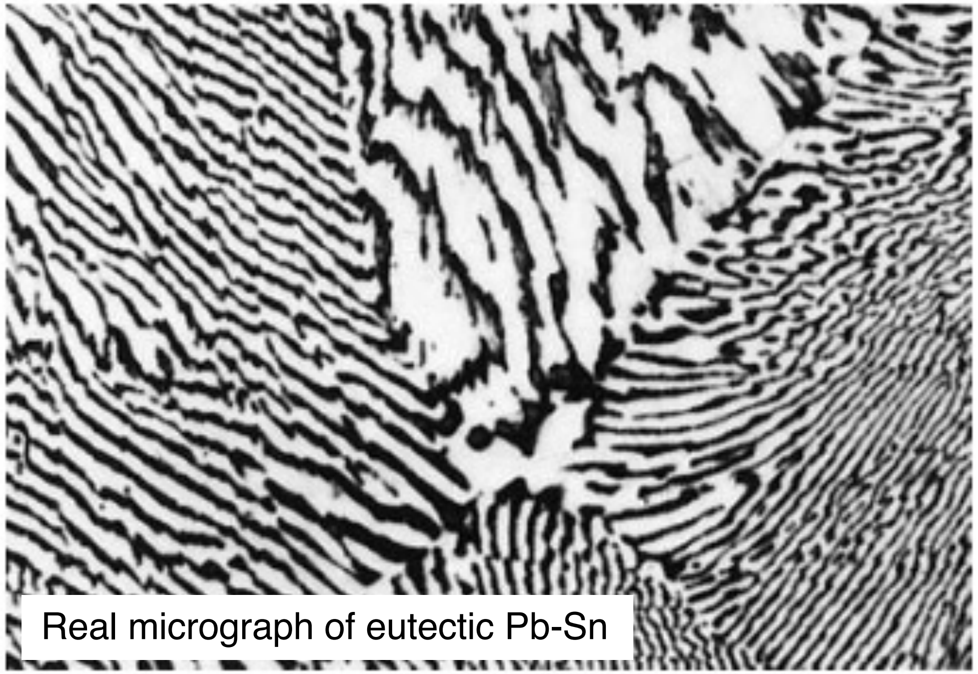


Now what happens at the eutectic?



At C_3, we have L → $\alpha + \beta$

Alternating α and β layers are adopted to facilitate rapid atomic diffusion



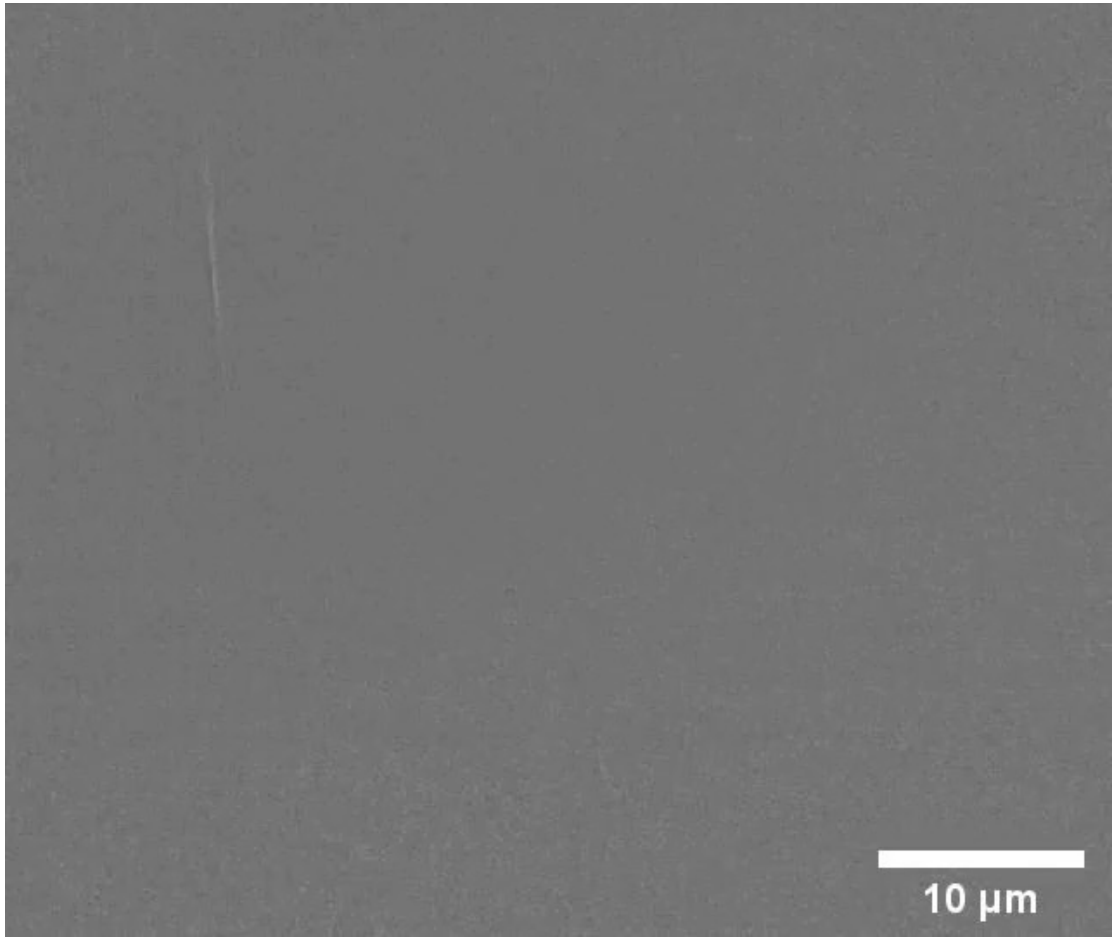
Real micrograph of eutectic Pb-Sn

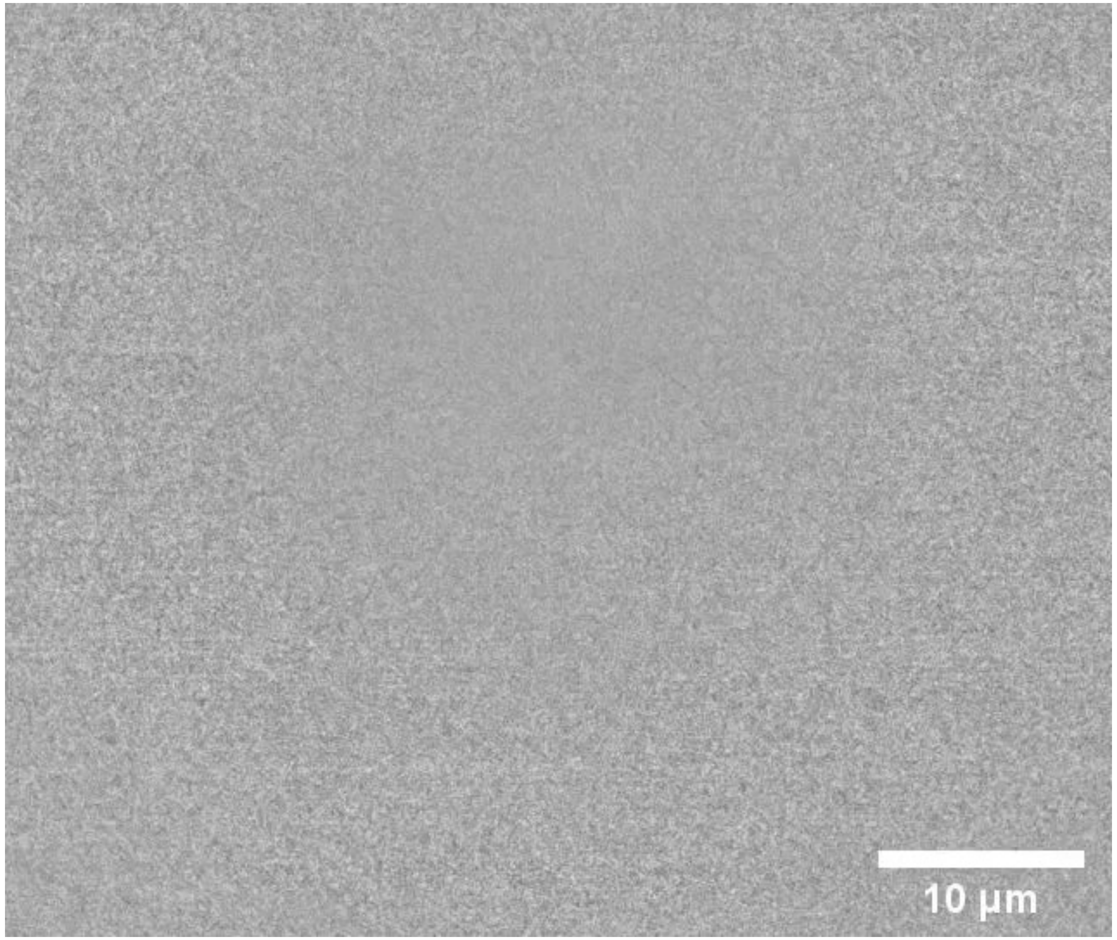
This is called a eutectic structure
Sometimes called a lamellae structure

EPFL

Now what happens at the eutectic?

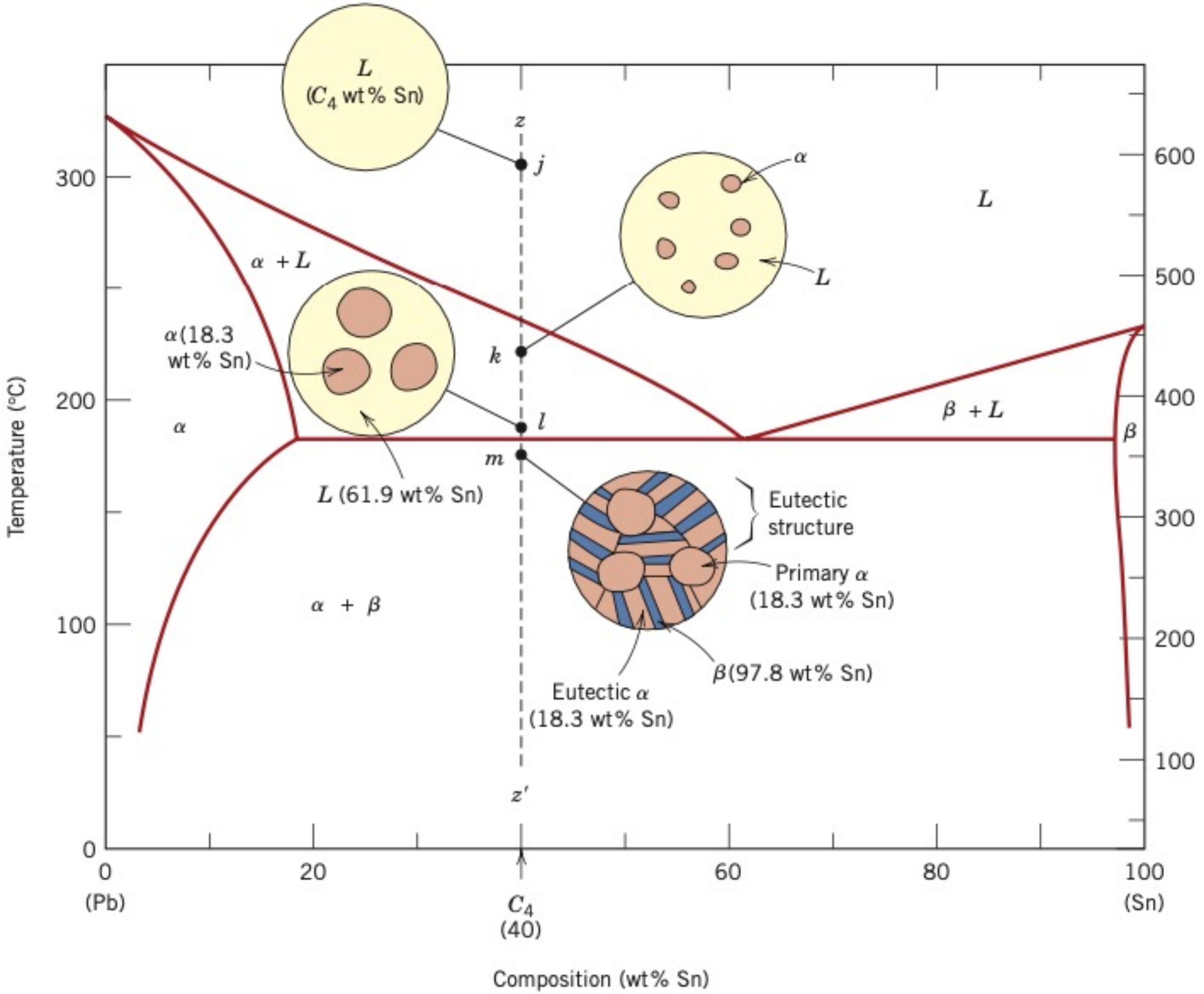
Real time imaging of eutectic formation using X-ray microscopy





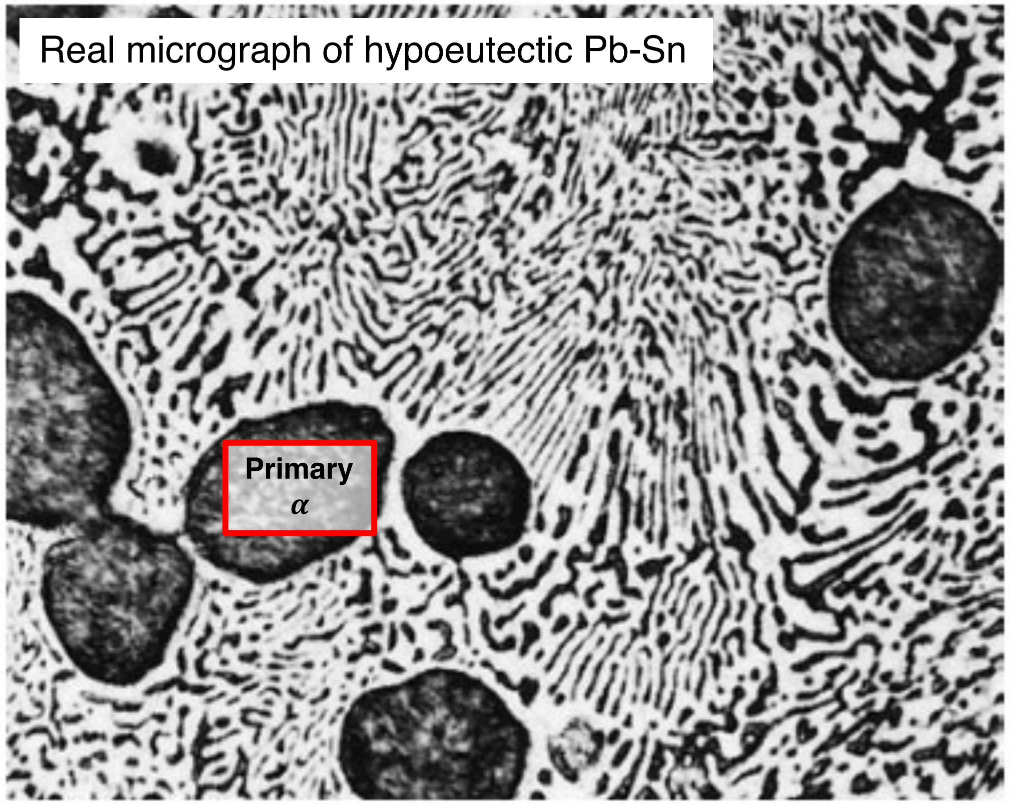
Chao, Paul, et al. *Acta Materialia* 280 (2024): 120314.

Last possible scenario: 1 phase → 2 phase → 2 phase



Point *j* → *l* is the same as before

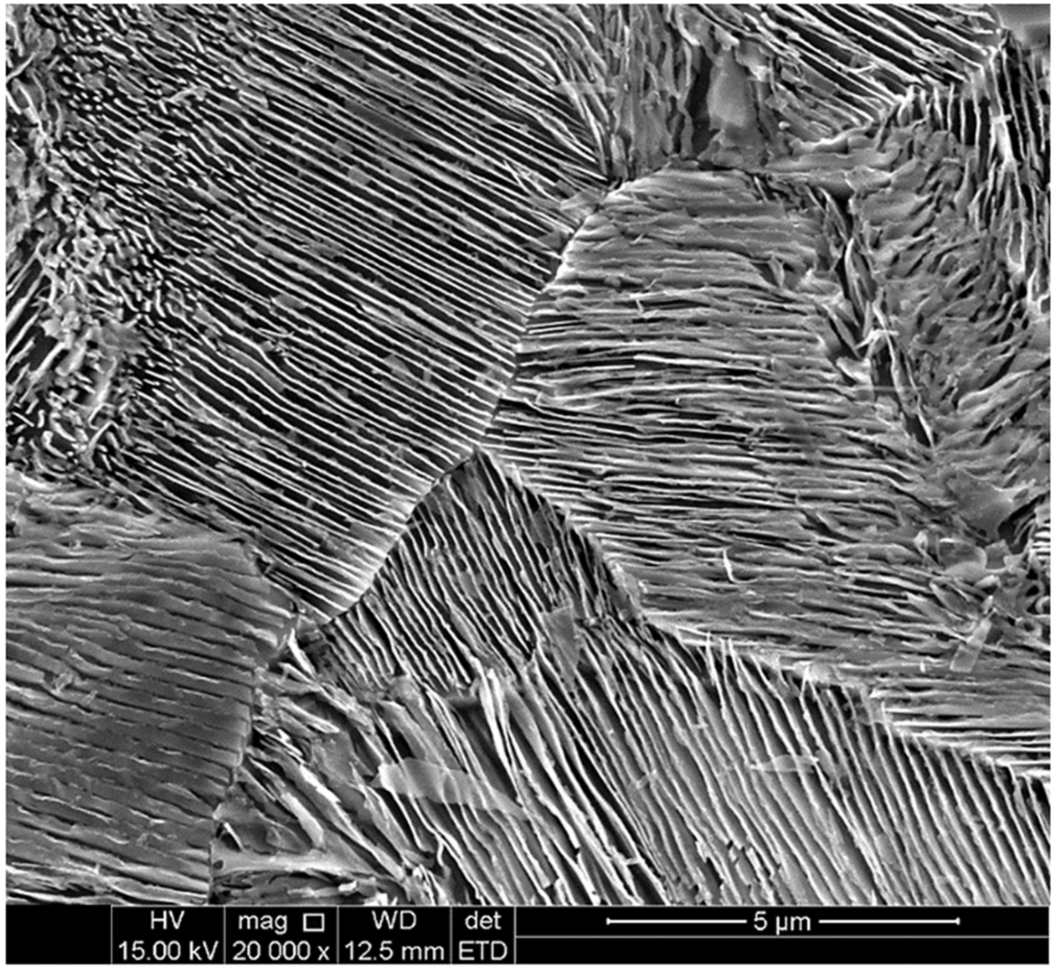
Going from Point *l* → *m*, all the liquid in the system transforms into the eutectic solid

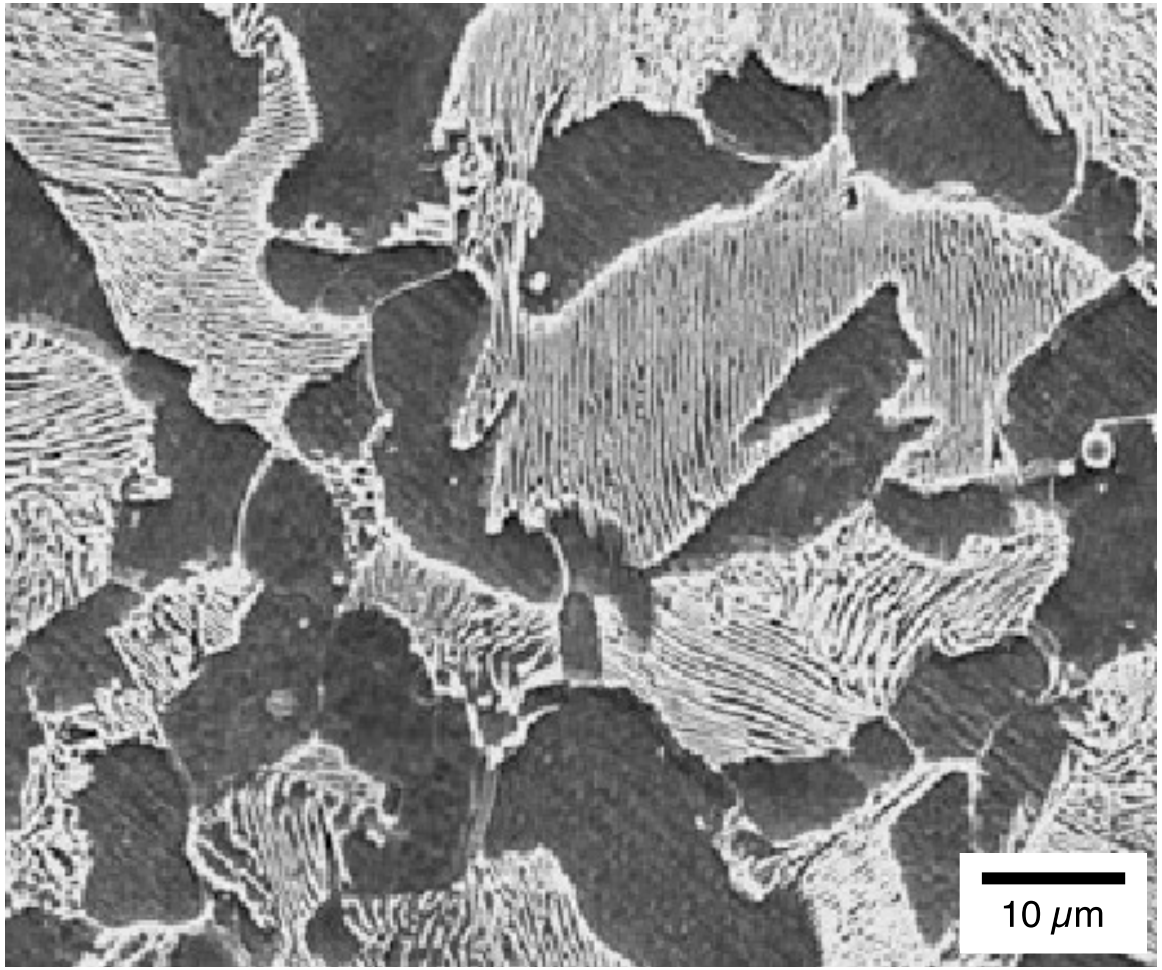


Let's bring it back to MT. Why do we need to look at microstructure?

You deposited some metal onto your device. The metal is supposed to be a eutectic.

What microstructure should you expect? → Qualitative check





Week 8 Learning Objectives

- Understand why alloying strengthens a metal
- Understand what a phase diagram is
- Understand how to read a binary phase diagram for:
  - Isomorphous systems
  - Eutectic systems
- Be able to predict alloy microstructure from the phase diagram
- Be able to use tie lines and the lever rule to calculate the amount and composition of the phases formed in a two-phase region.