Lecture 6: Phase Diagrams and Microstructures

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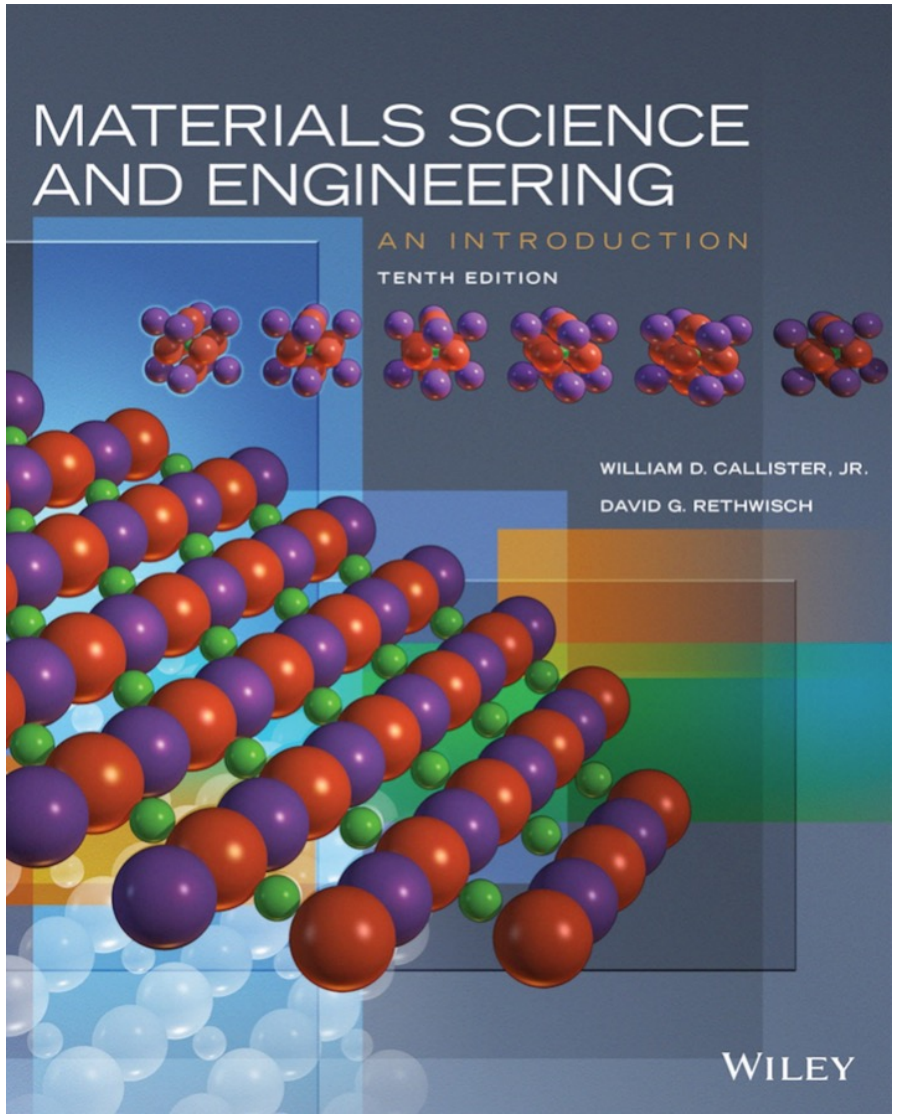
Reading for this subject



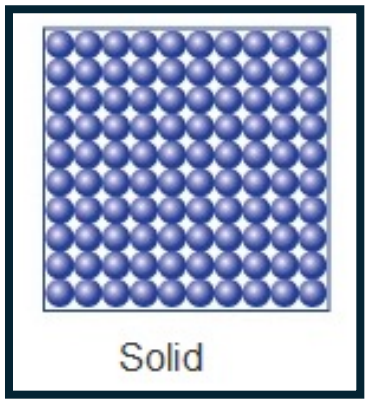
Chapter 9 Phase Diagrams

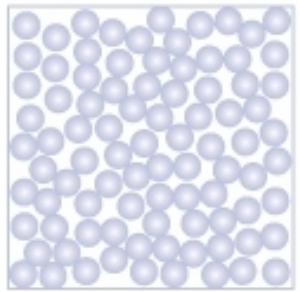
This discussion will closely follow **Chapter 9** of Callister, **pages 252-298** of the 10th edition.

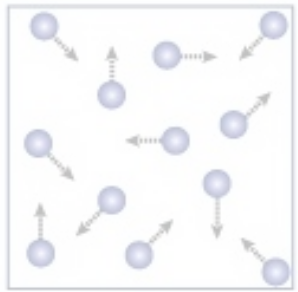
Very important chapter, please read!

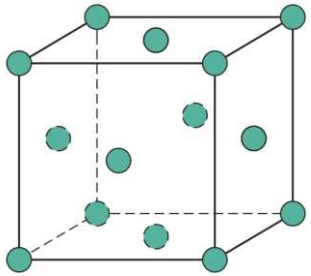
Review of some key concepts

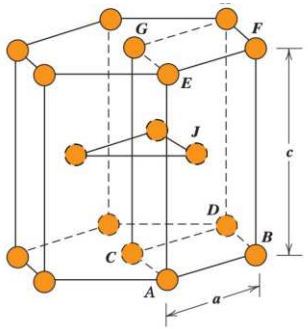
Given some **fixed composition**, atoms can rearrange themselves in various ways

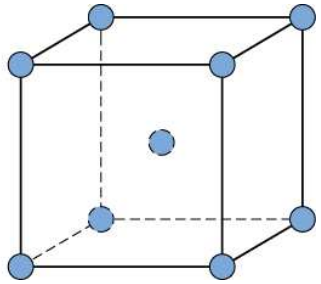






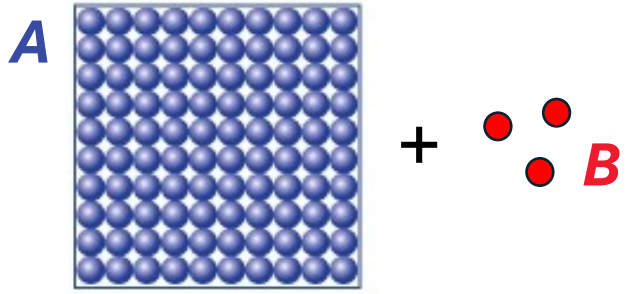


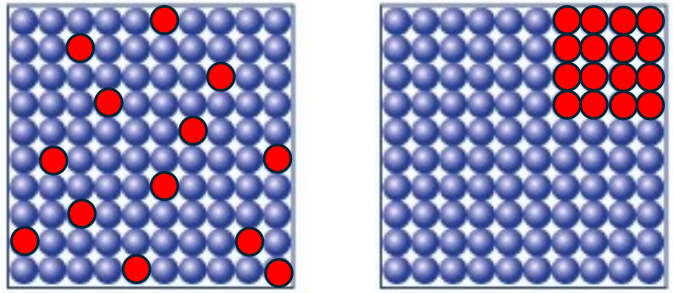




Which arrangement is most stable will **depend on the conditions** (temperature, pressure, *etc.*)

We can also **vary the composition** by adding new atoms from a different element



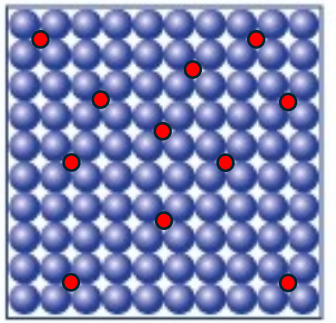


…conditions *and* concentration

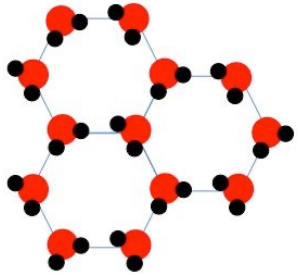
Definitions: *Components* and *Phases*

Components (*C*) = chemical species (elements *or* molecules) in a system

Example 1: simple alloys of steel have two components (**Fe** and **C**)

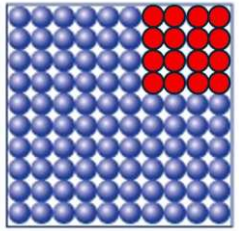


Example 2: water has one component (H_2O)

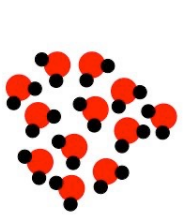


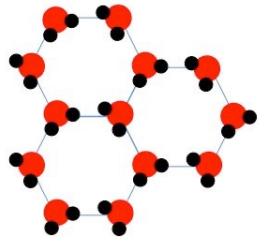
Phases (*P*) = parts of the system with chemically/physically distinct properties

Example 1: If Fe + C form a uniform solution → one phase
But if C separates from Fe → two phases

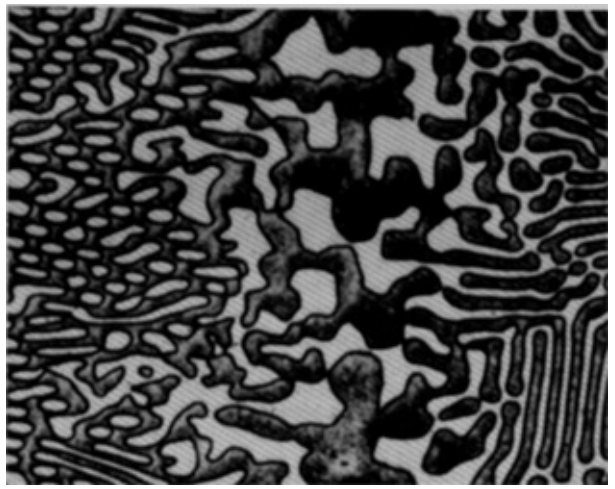


Example 2: Water and ice would be considered two separate phases





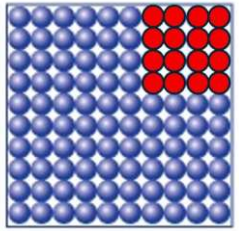
Definitions: *Components* and *Phases*



A real example:
Two Al-Cu alloys with different structures
→ Clearly distinguishable in a microscope!

Phases (*P*) = parts of the system with chemically/physically distinct properties

Example 1: If Fe + C form a uniform solution → one phase
But if C separates from Fe → two phases



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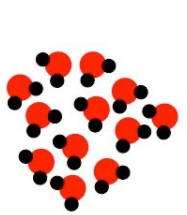
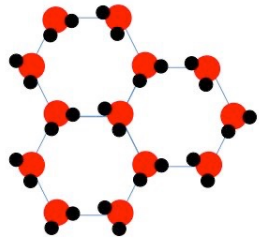
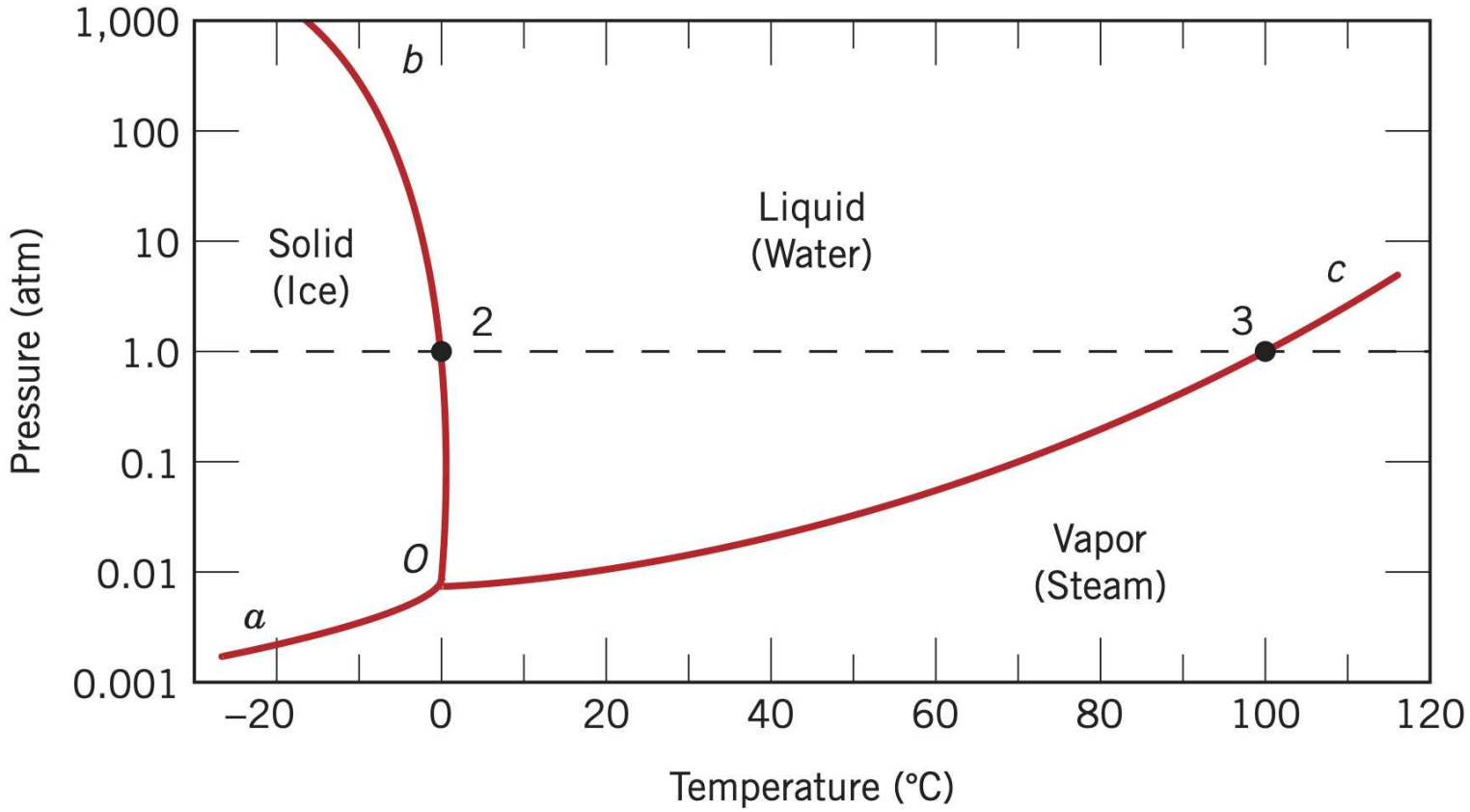


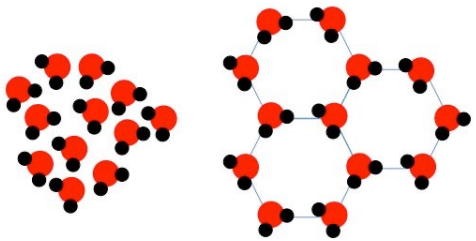


Single-component (unary) phase diagrams



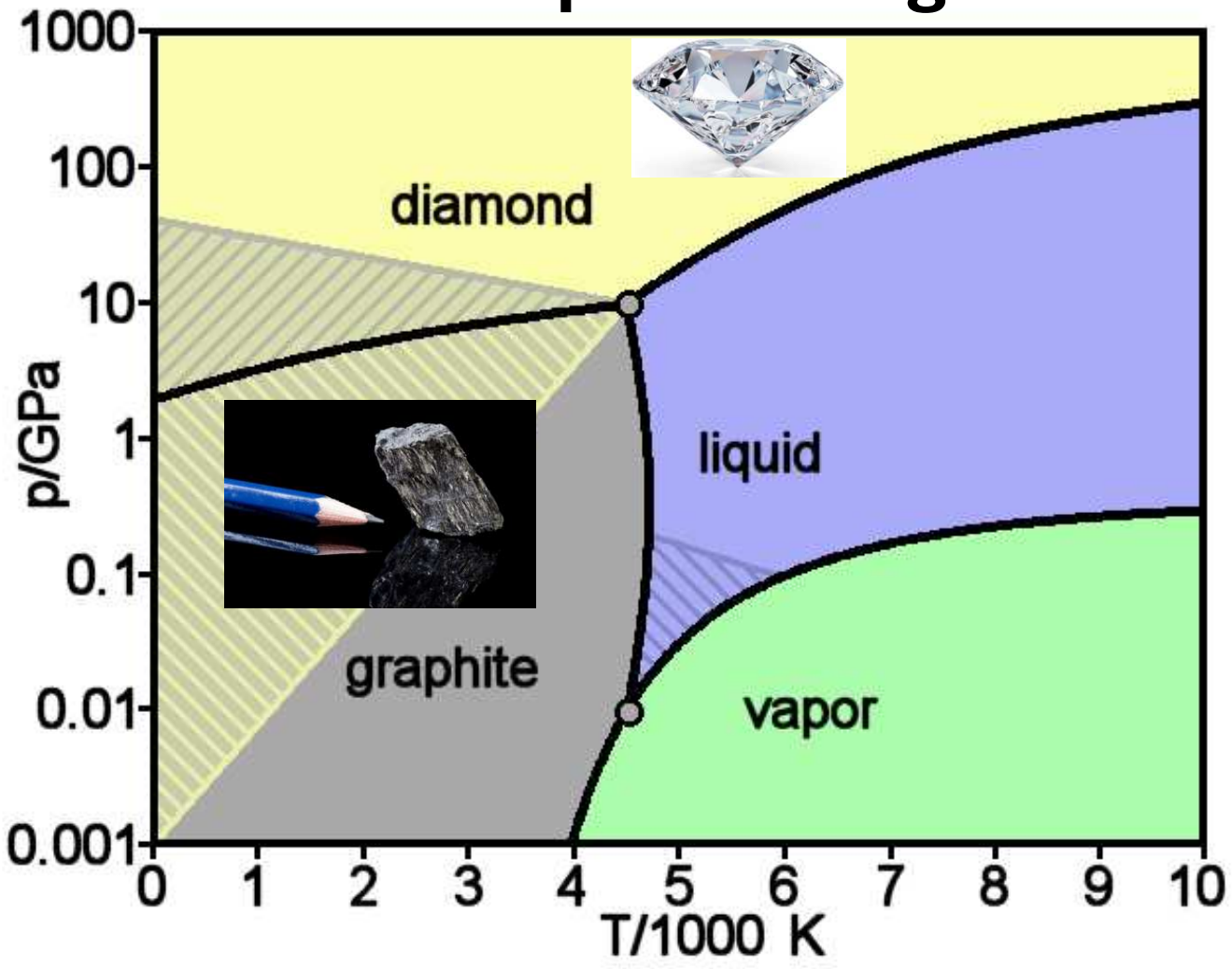
- **Phase diagrams** tell us what phase is most stable under a given set of conditions
- **Unary = single-component**, no change in composition
- **Temperature and pressure** are common axes

Example 2: Water and ice would be considered two separate phases



Single-component (unary) phase diagrams

Carbon phase diagram



Diamond is only stable at very high pressures, but (luckily) is metastable under ambient conditions

Graphite is the ground state under ambient conditions

Phase diagrams tell us what should form ***at equilibrium***

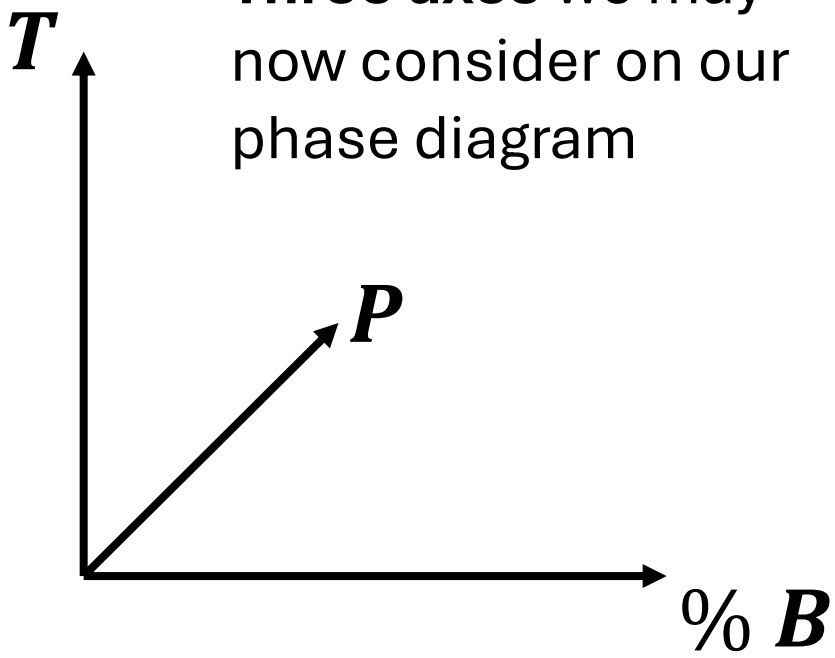
Two-component (binary) phase diagrams

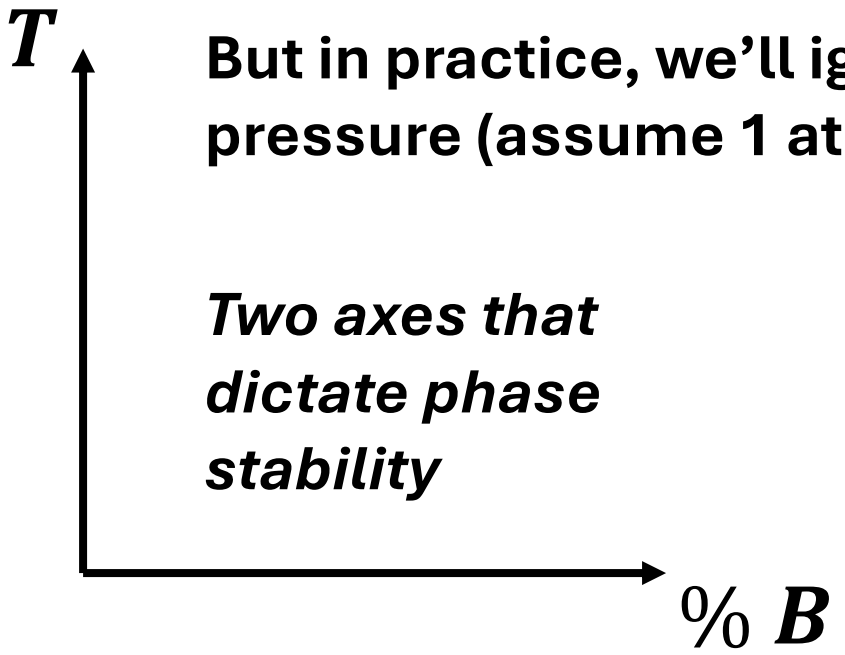
Most useful materials have > 1 component.
Let's look at the **2-component (binary)** case next.

Consider an *A*-*B* mixture whose composition we can specify using **one variable: % *B***

→ % A is simply given by (100 - % *B*)

Three axes we may now consider on our phase diagram



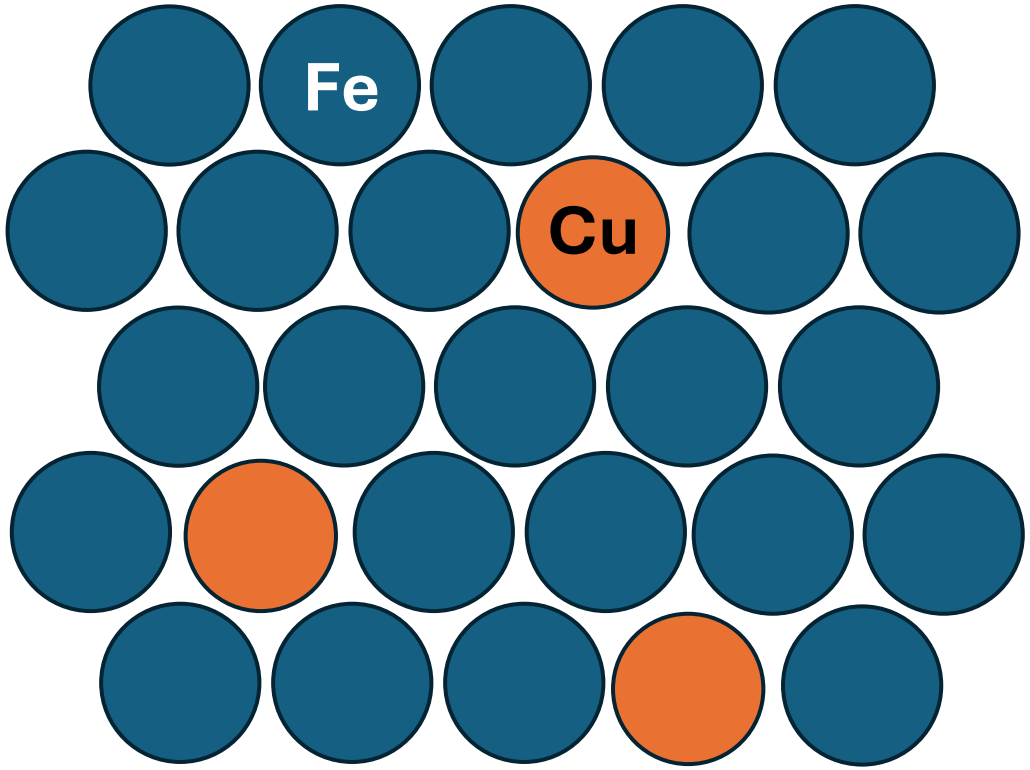


But in practice, we'll ignore pressure (assume 1 atm)

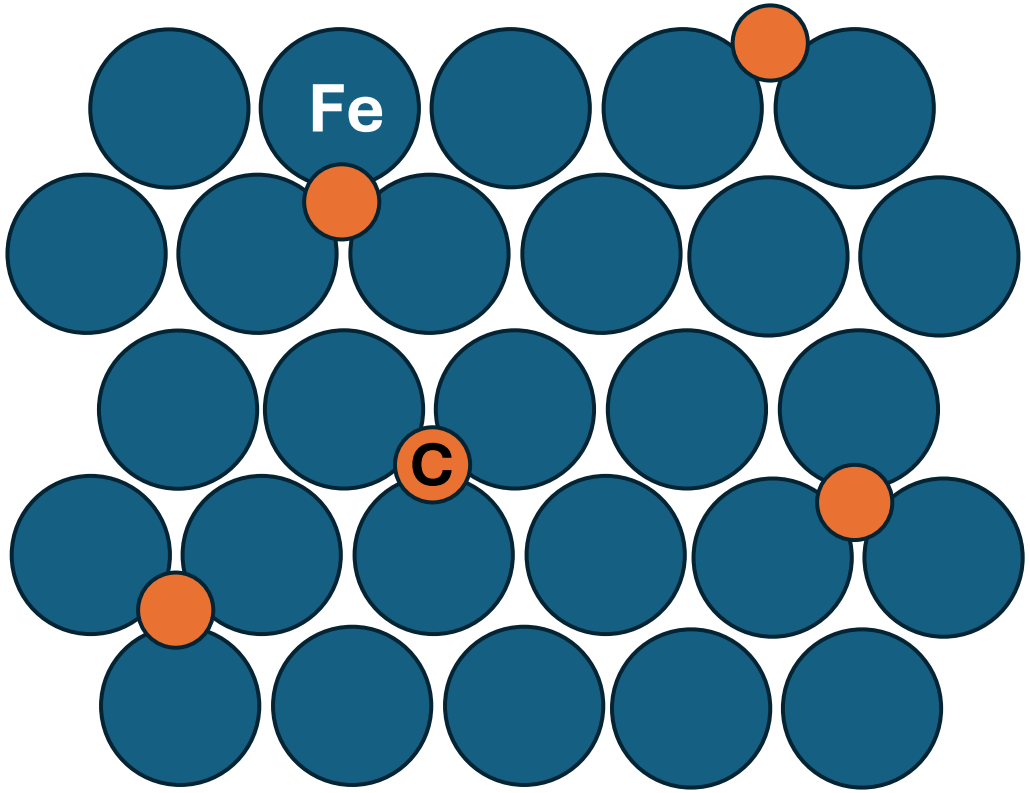
Two axes that dictate phase stability

Recall: what happens when a small amount of *B* is added to a host lattice of material *A*

Option 1: Substitution
(if *A* and *B* are comparable in size)



Option 2: Interstitial formation
(if they are not comparable in size)



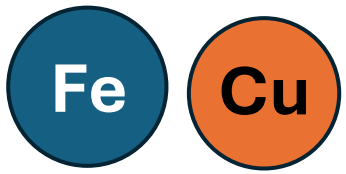
These are **solid solutions**

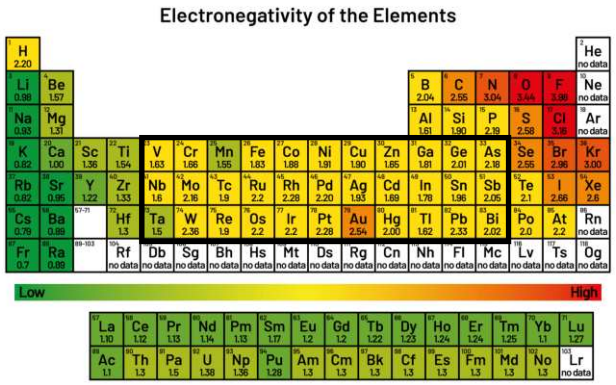
Recall: conditions for substitution

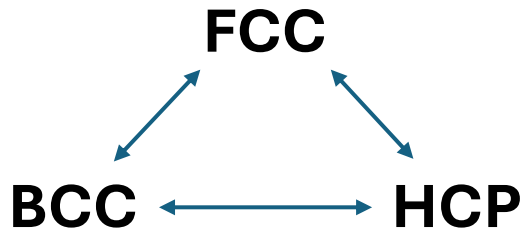
Hume-Rothery rules tell us (roughly) when substitution can be expected:

A substitutional solid solution between *A* and *B* is likely when:

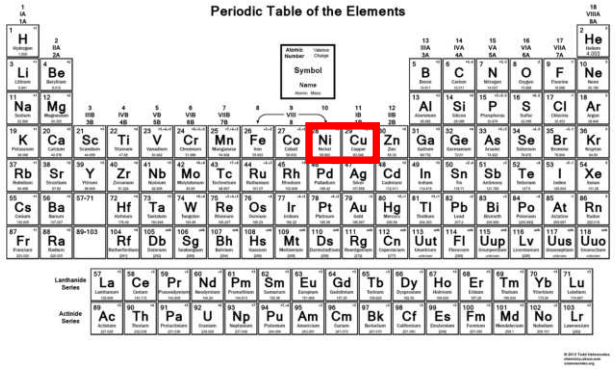
1) Their **atomic radius differs by < 15%**
2) They have **similar electronegativity** (are close on periodic table)
3) They have **the same crystal structures** as pure elements

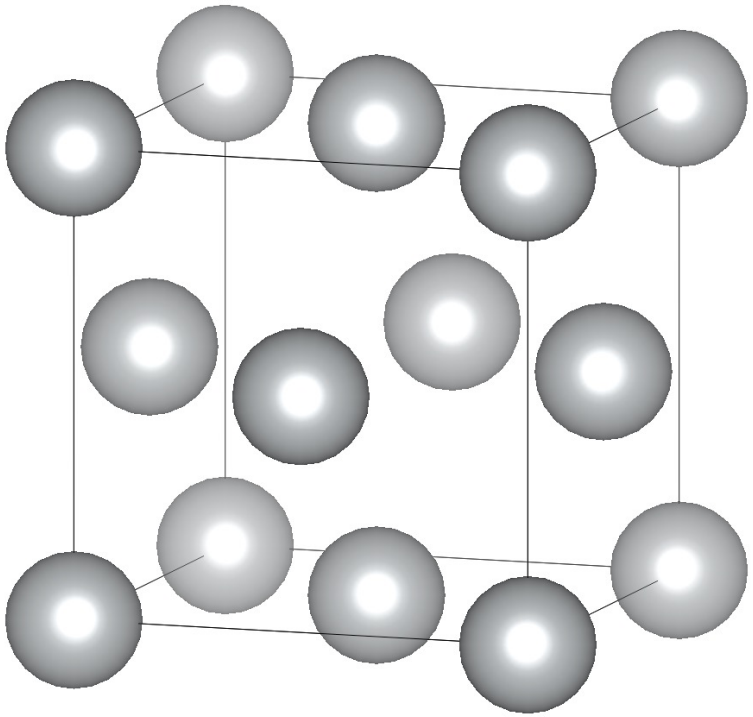






Example: Cu-Ni phase diagram (isomorphous)

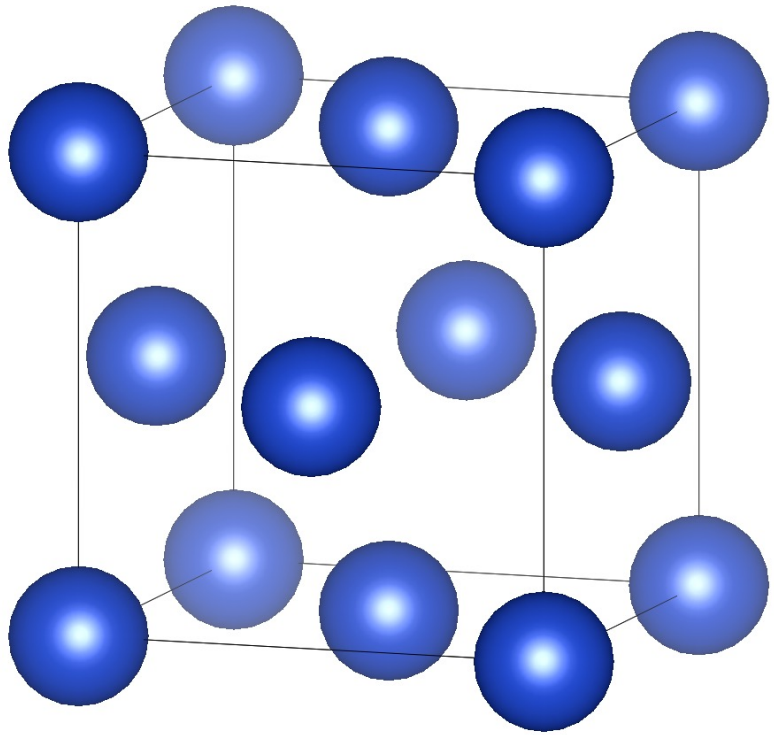




Copper

Cu and Ni are next to each other on the periodic table, and both adopt the FCC structure

A substitutional solid solution is expected

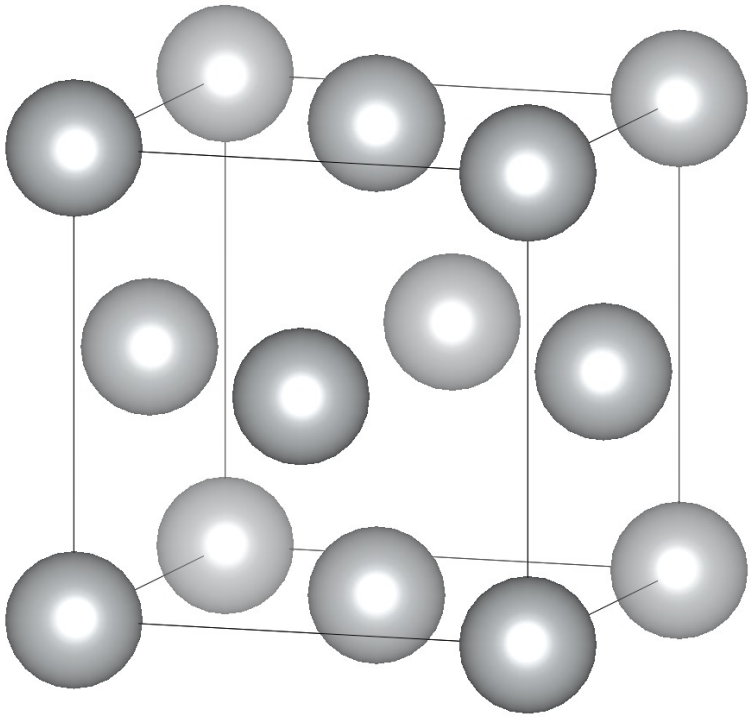


Nickel

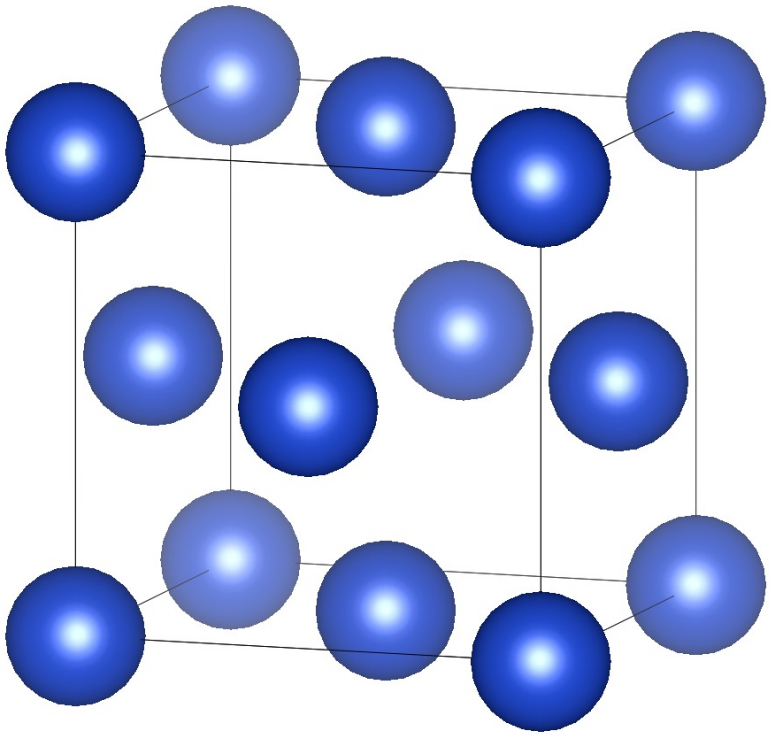
Example: Cu-Ni phase diagram (isomorphous)

$T_M \sim 1,085\ °C$ ⟷ $T_M \sim 1,455\ °C$

Melting of intermediate compositions should occur somewhere in between the pure solids



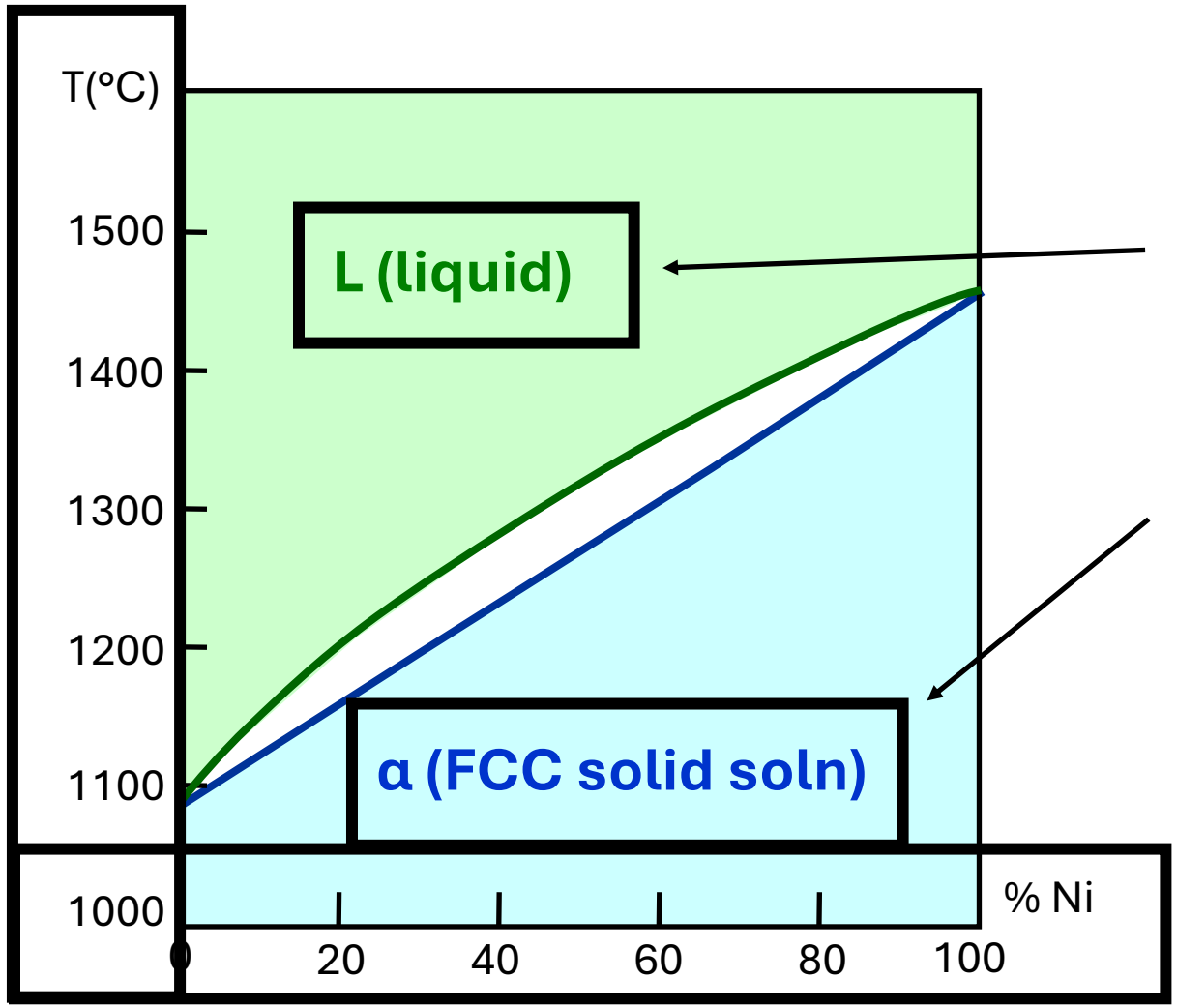
Copper



Nickel

Example: Cu-Ni phase diagram (isomorphous)

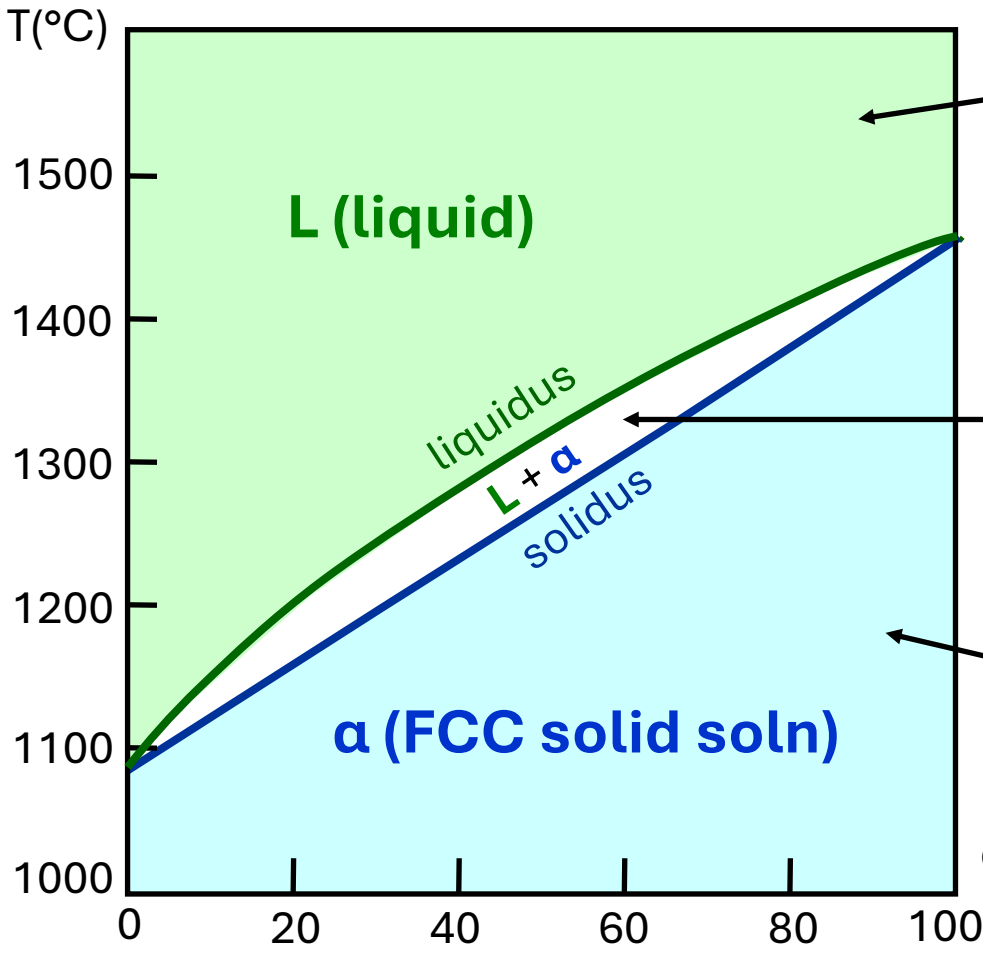
y-axis tells us what temperature we are at



Labels tell us what phase is stable under those conditions

x-axis tells us what composition we are at

Example: Cu-Ni phase diagram (isomorphous)



Single-phase region:
All of the material will be melted

Two-phase region:
Some material will be liquid, *some* solid

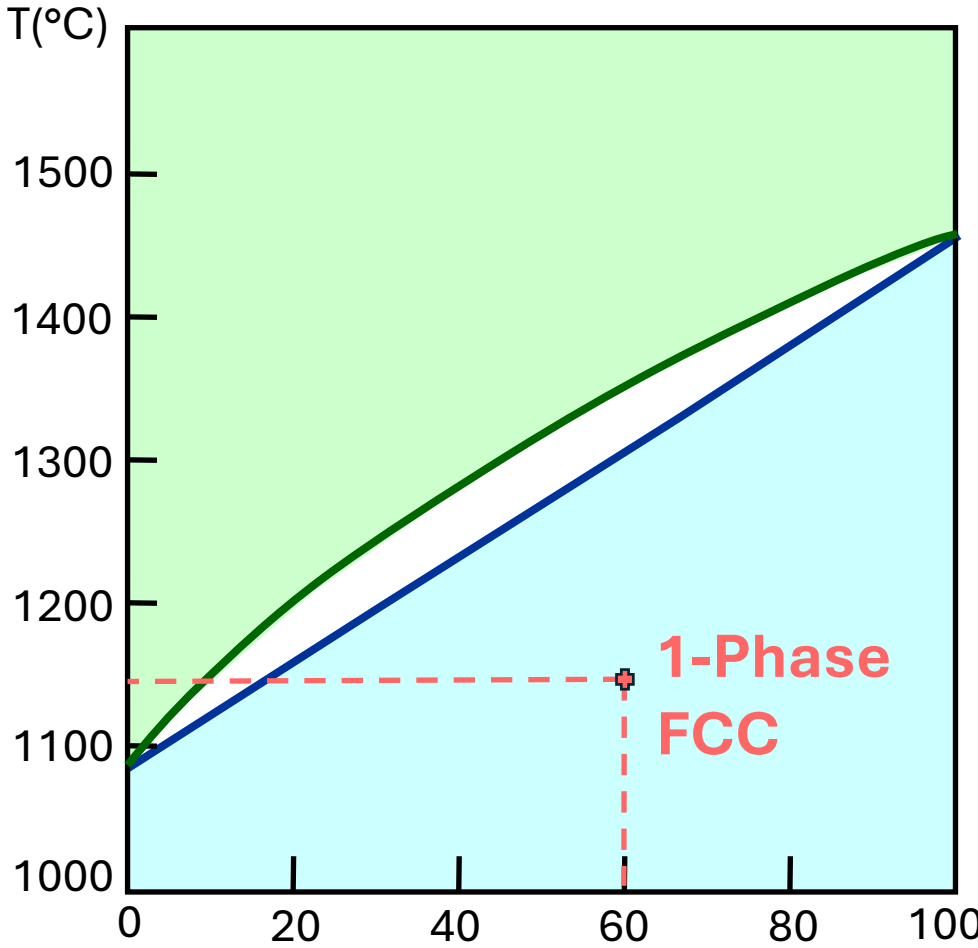
Single-phase region:
All of the material will be solid

Interpretation: what phases are present?

If we know T **and** x, we can determine **what phase(s)** are most stable

For example:

1150°C, 60% Ni





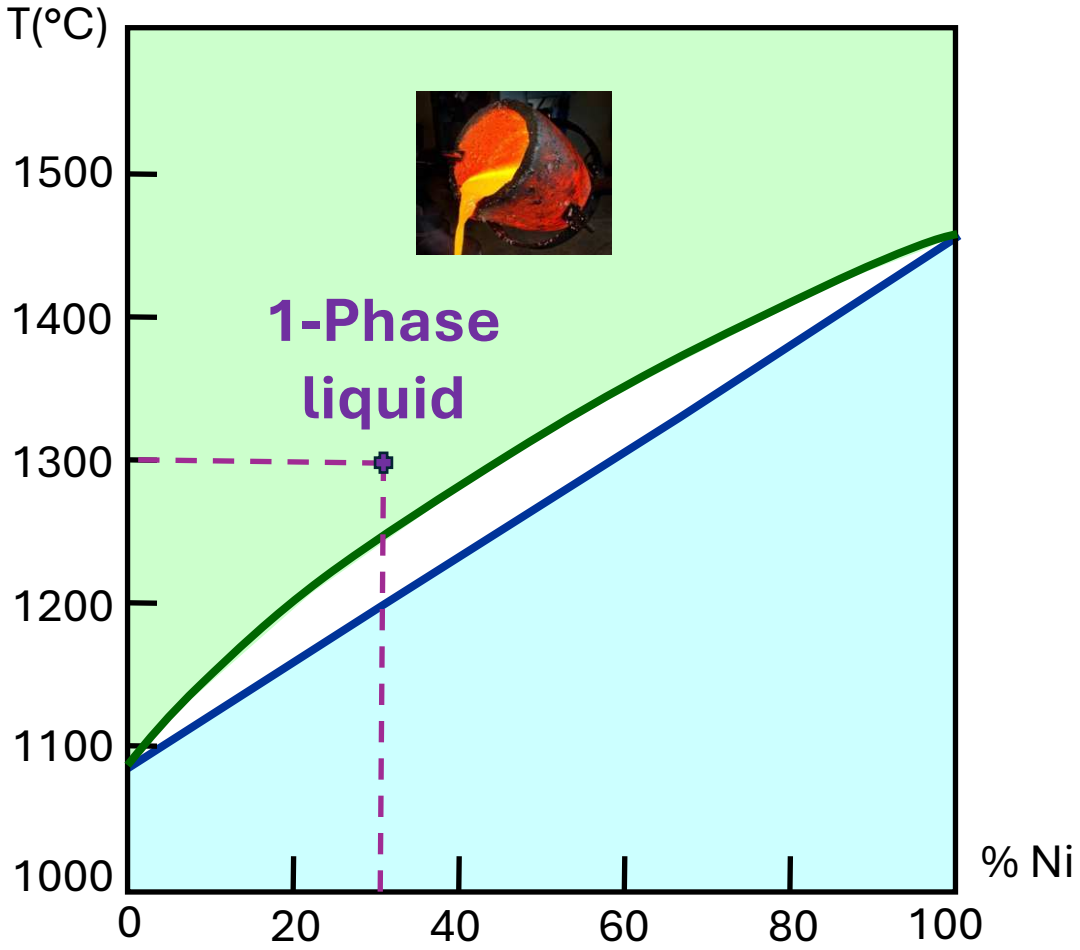
Interpretation: what phases are present?

If we know T **and** x, we can determine **what phase(s)** are most stable

For example:

1150°C, 60% Ni

1300°C, 30% Ni



Interpretation: what phases are present?

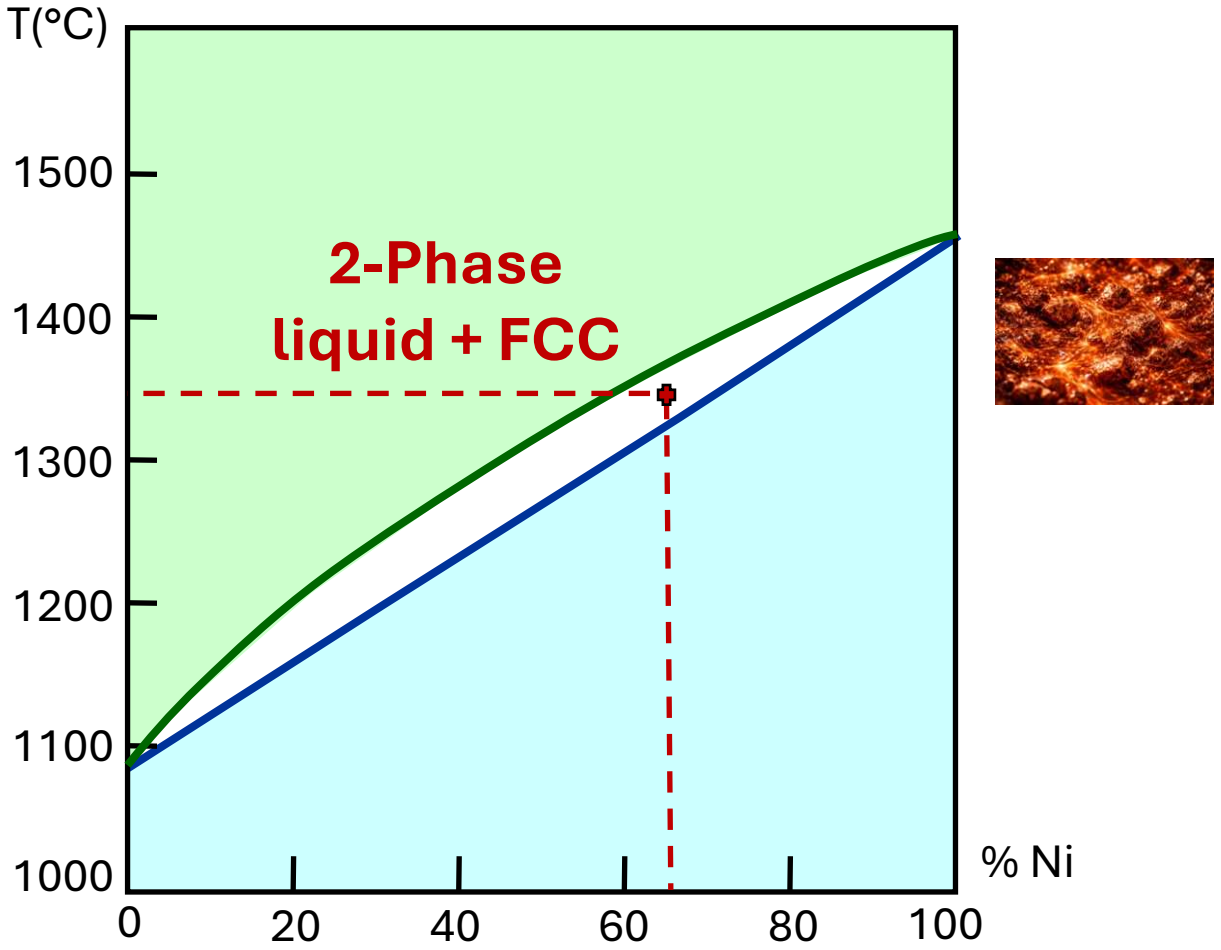
If we know T **and** x, we can determine **what phase(s)** are most stable

For example:

1150°C, 60% Ni

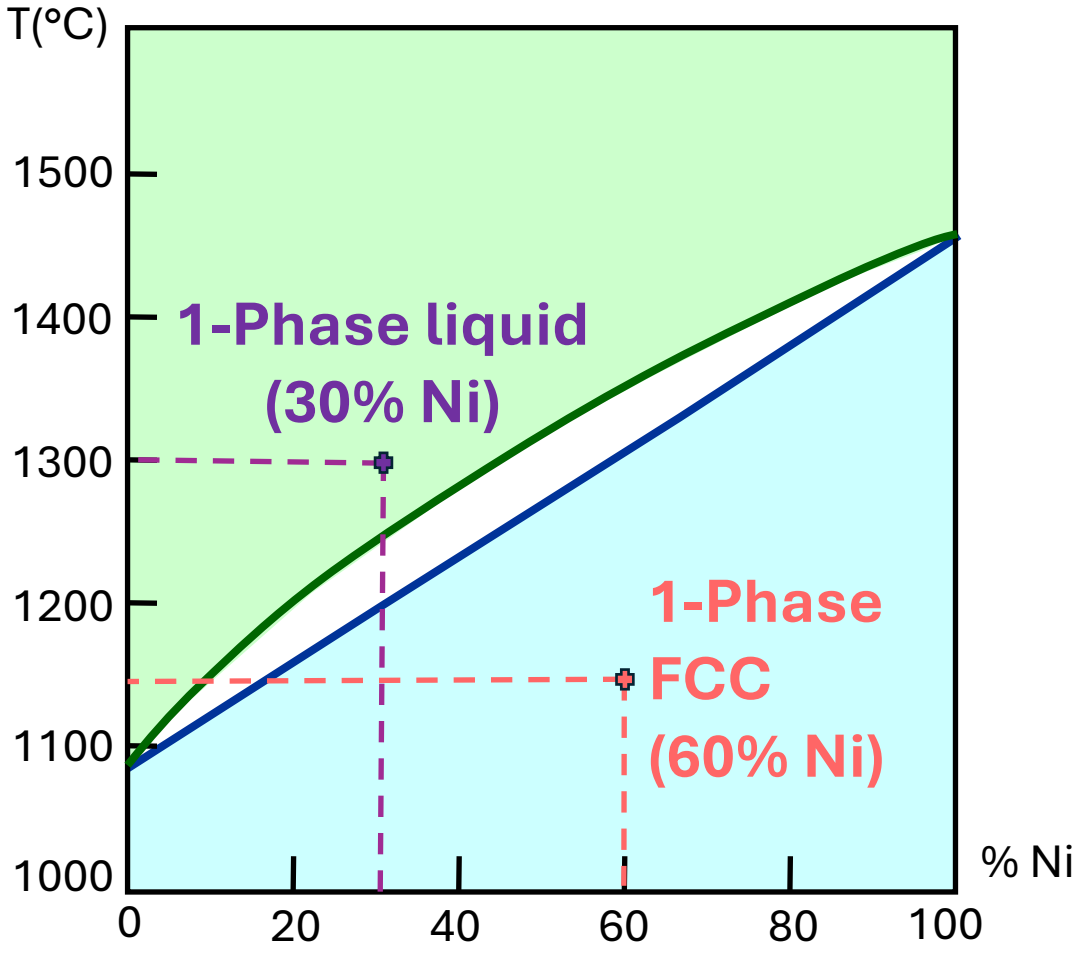
1300°C, 30% Ni

1350°C, 65% Ni



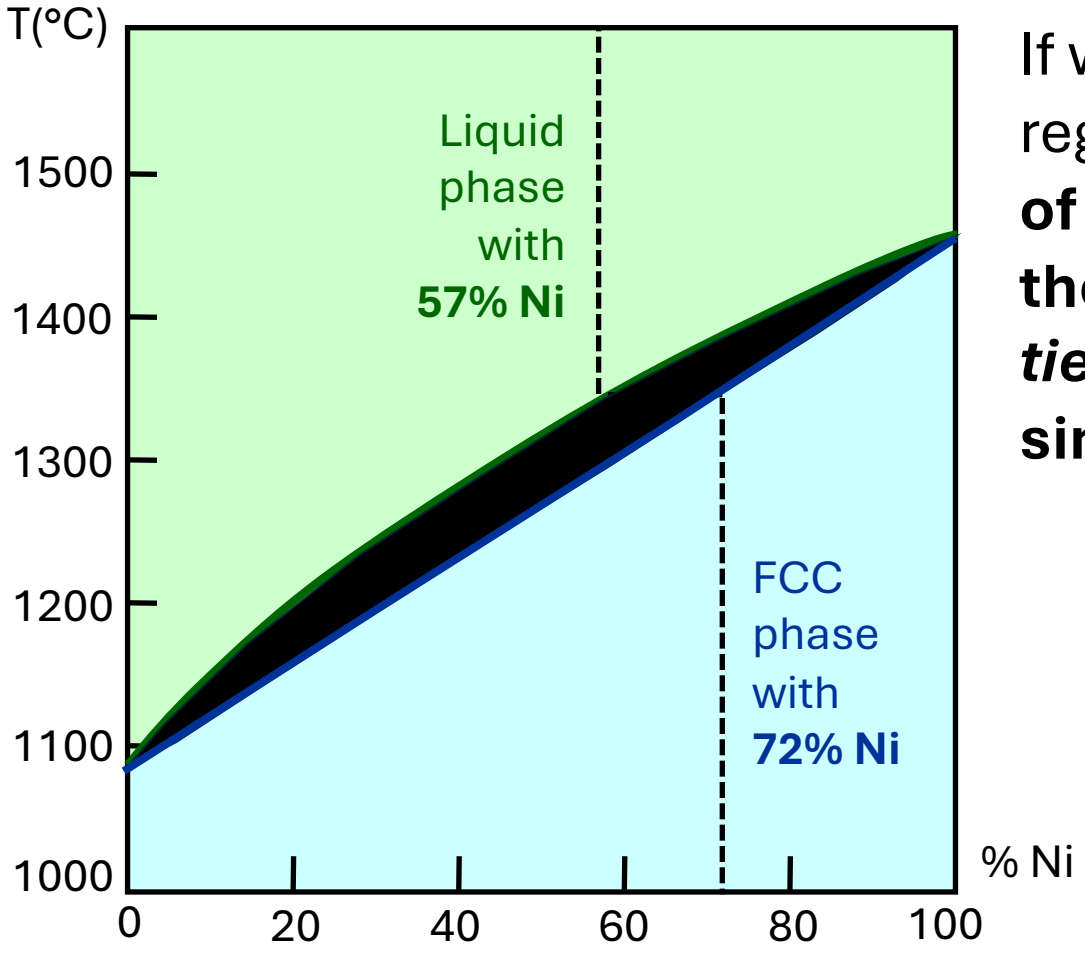
What are the *compositions* of these phases?

If we are in a **single-phase** region, the **composition of that phase is given by its position on the *x*-axis**



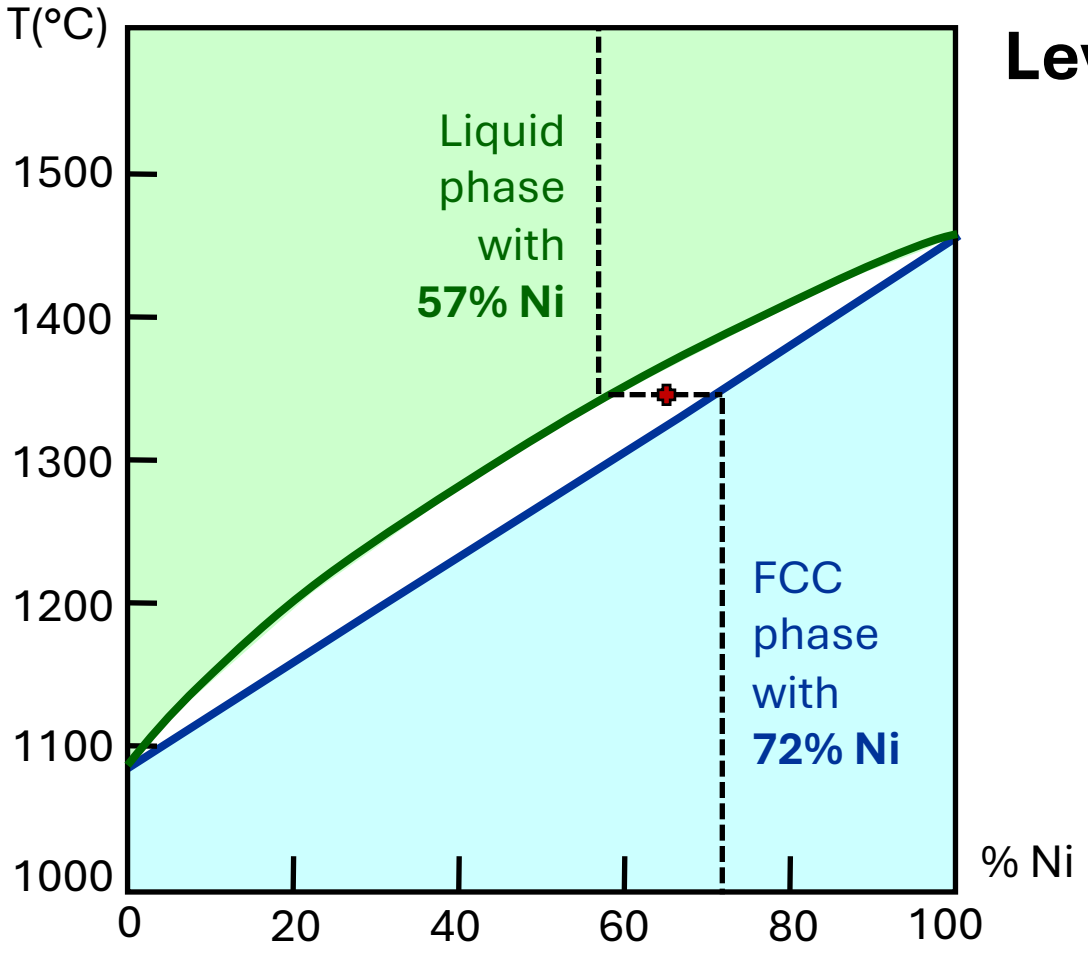
What are the *compositions* of these phases?

The two-phase region is like a **“hole”** in the diagram. We can *never* have a phase with a stable composition in that region.



If we are in a **two-phase** region, the **composition of each phase is given by the *x*-values where the *tieline* touches each single-phase region**

How much of each phase is present?

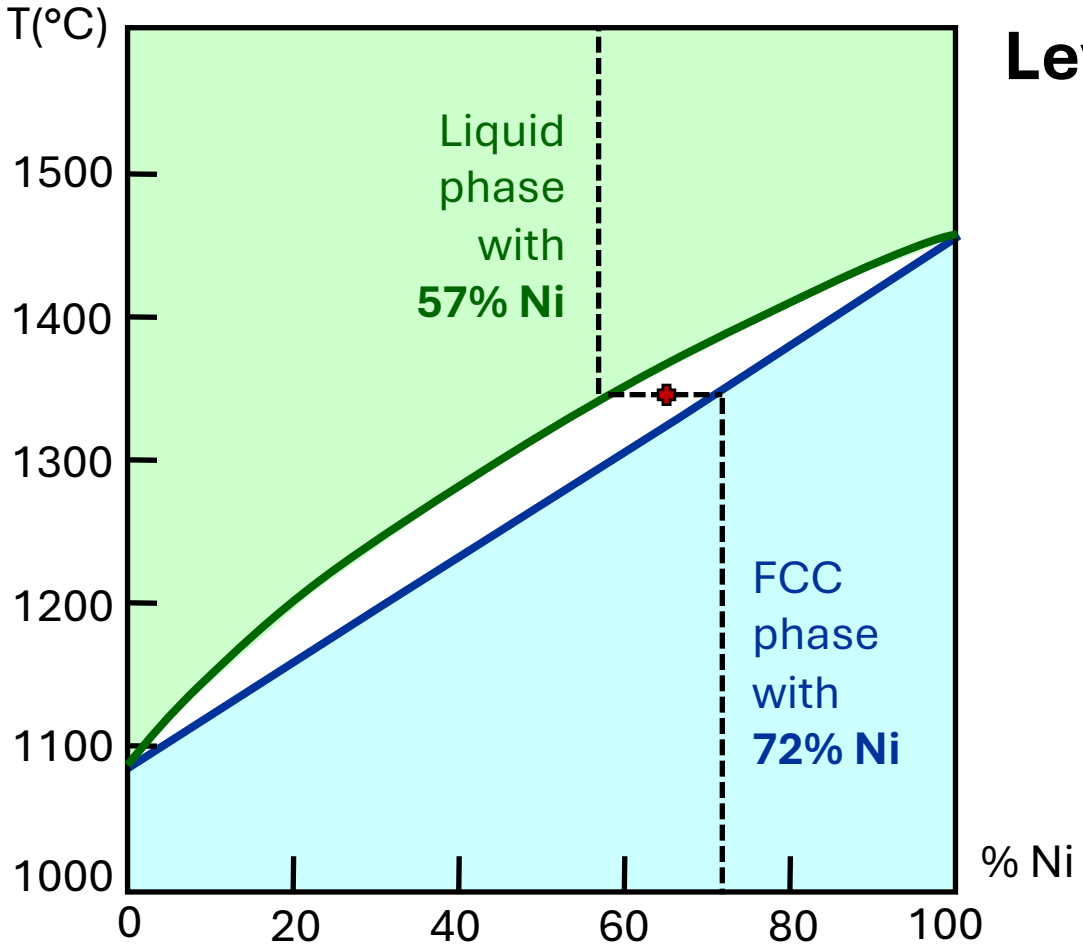


Lever rule:

$$W_L = \frac{C_\alpha - C_0}{C_\alpha - C_L}$$

The weight fraction of the liquid

How much of each phase is present?



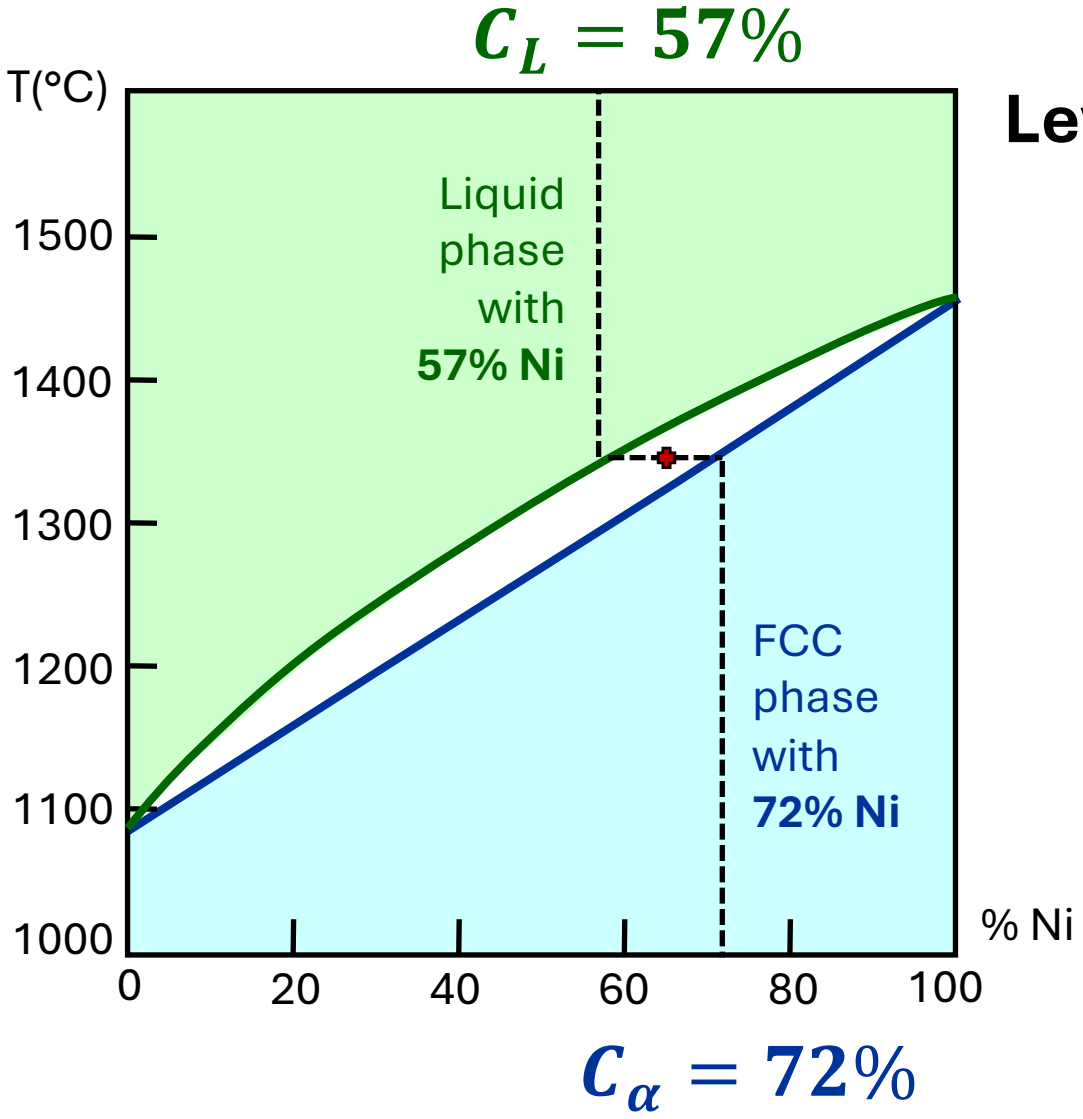
$C_\alpha = 72\%$

Lever rule:

$$W_L = \frac{C_\alpha - C_0}{C_\alpha - C_L}$$

Composition of the solid

How much of each phase is present?



Lever rule:

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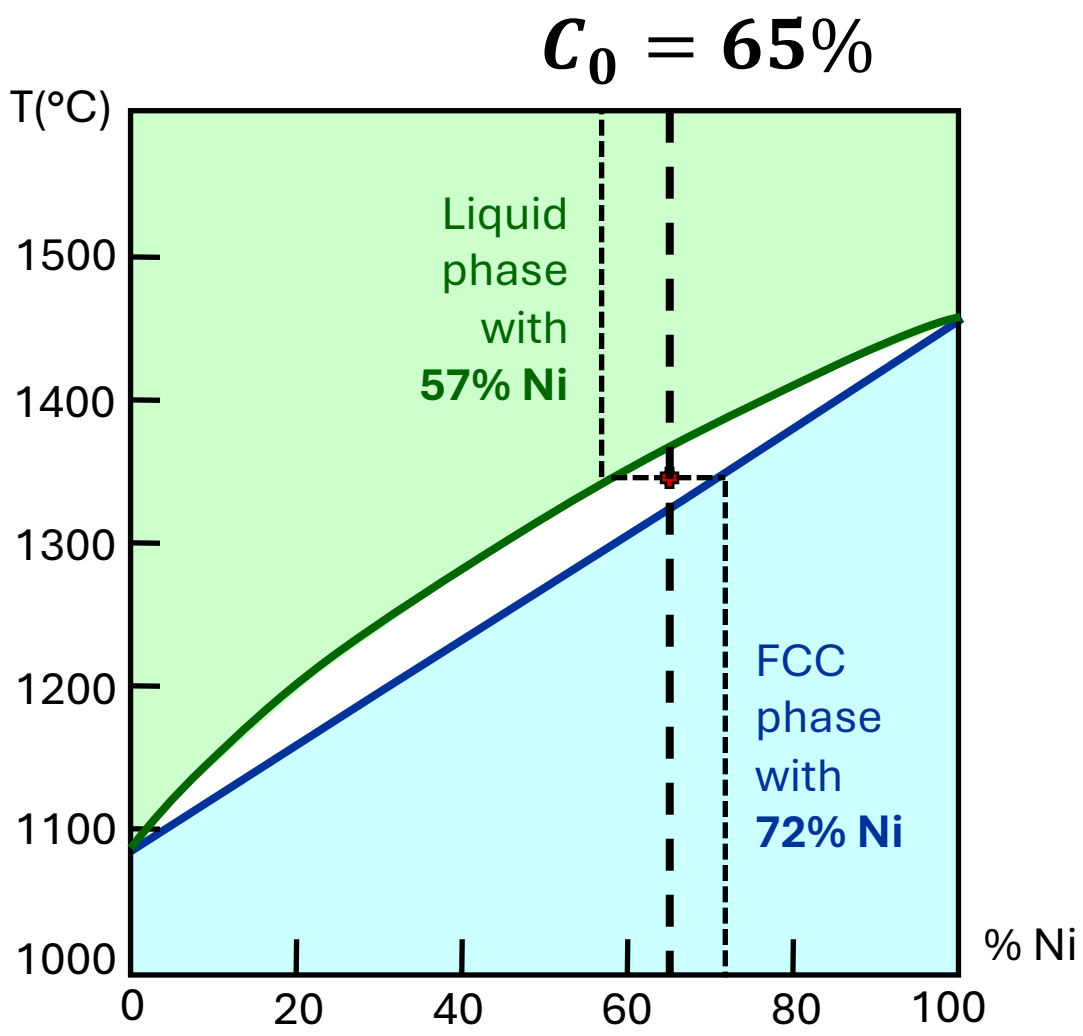
Composition of the liquid

How much of each phase is present?



Average composition of the mixture

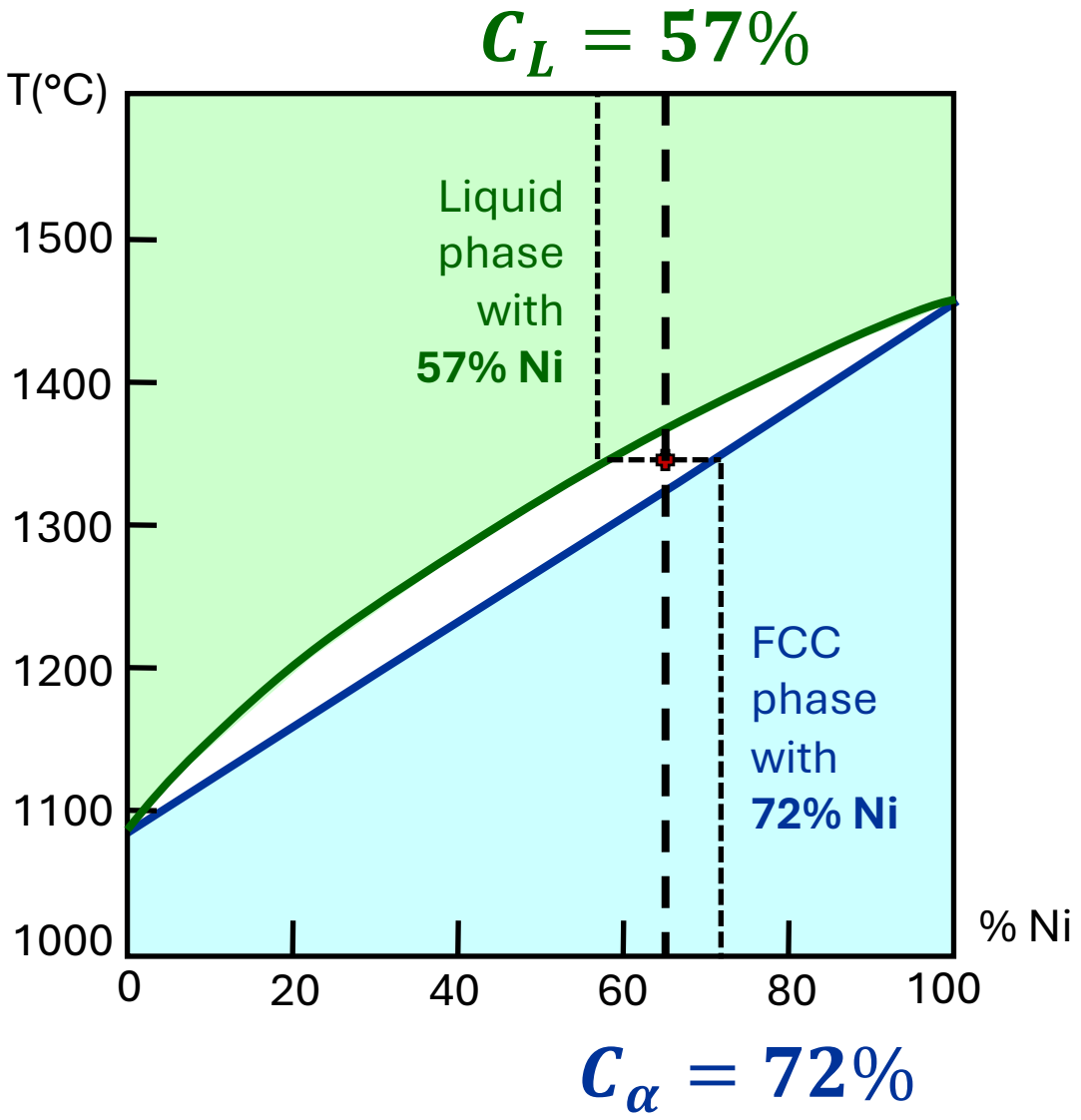
$$W_L = \frac{C_\alpha - C_0}{C_\alpha - C_L}$$

How much of each phase is present?

Weight fraction of the **solid** is then just:

$$W_\alpha = 1 - W_L$$

$$= 0.533$$



$$W_L = \frac{C_\alpha - C_0}{C_\alpha - C_L}$$

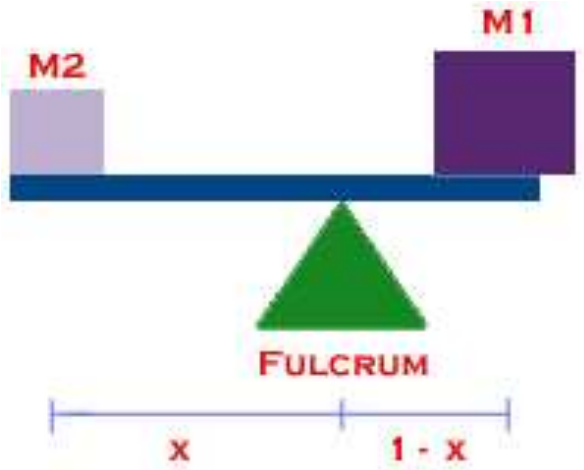
$$W_L = \frac{72 - 65}{72 - 57}$$

$$= 0.467$$

$$W_L = \frac{C_\alpha - C_0}{C_\alpha - C_L}$$

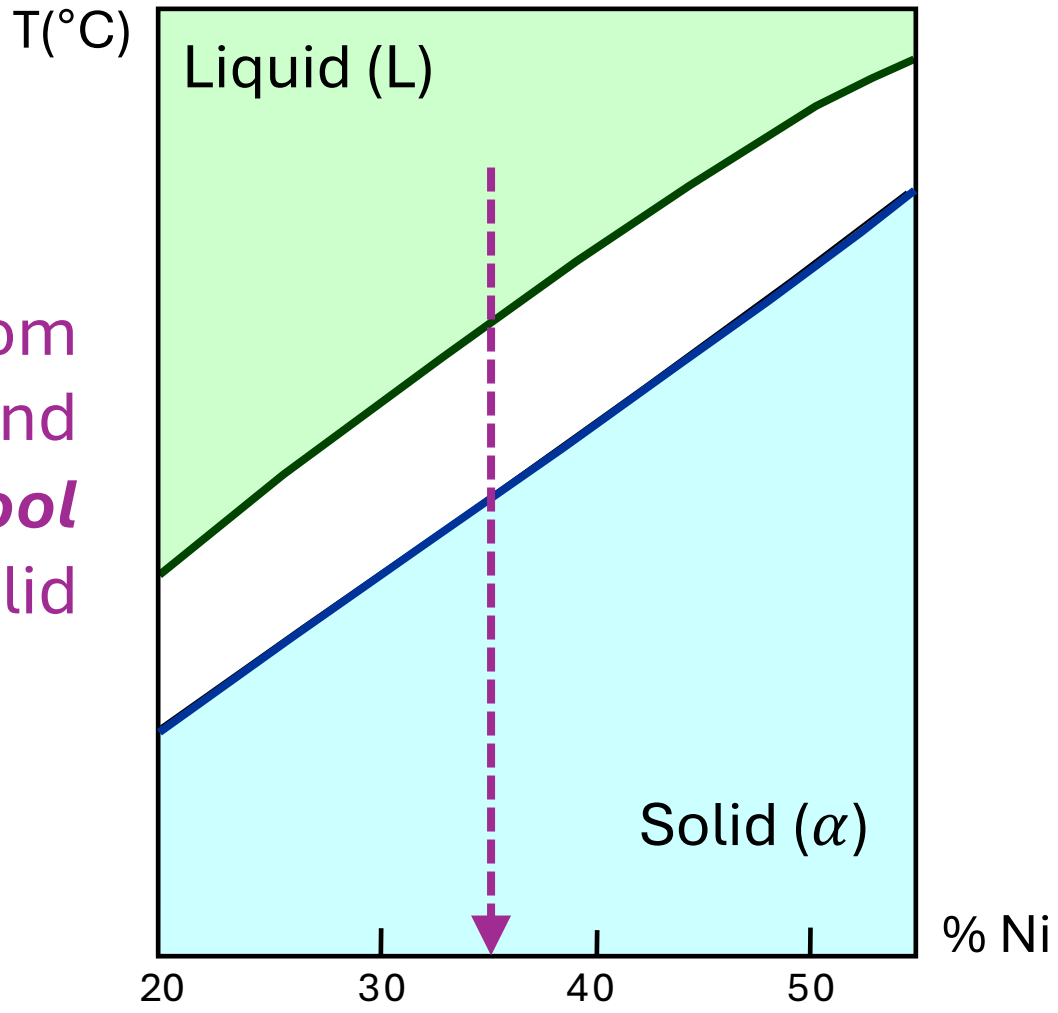
Questions on the lever rule?

Know how to use it!



What if we cool through the two-phase region?

Start from liquid and ***slowly cool*** down into solid



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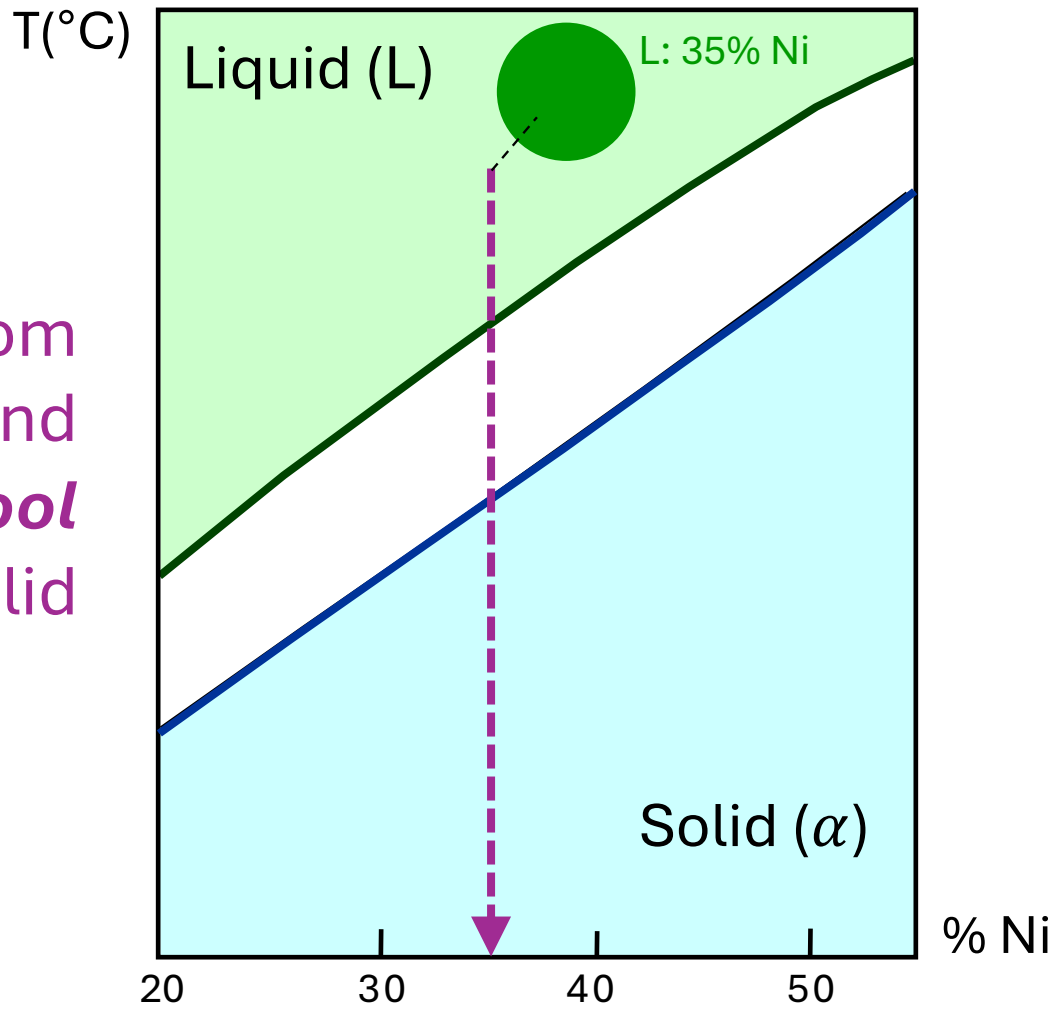

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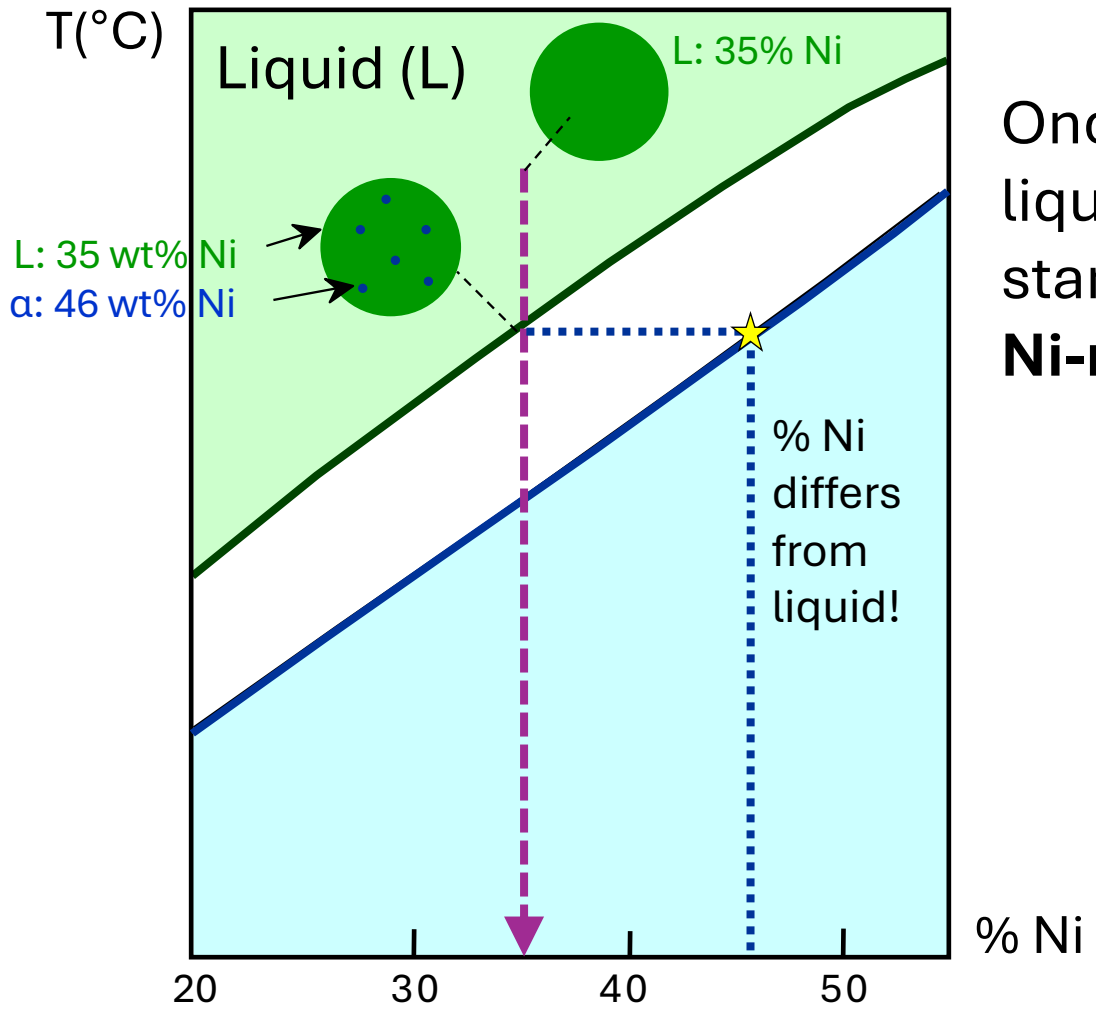
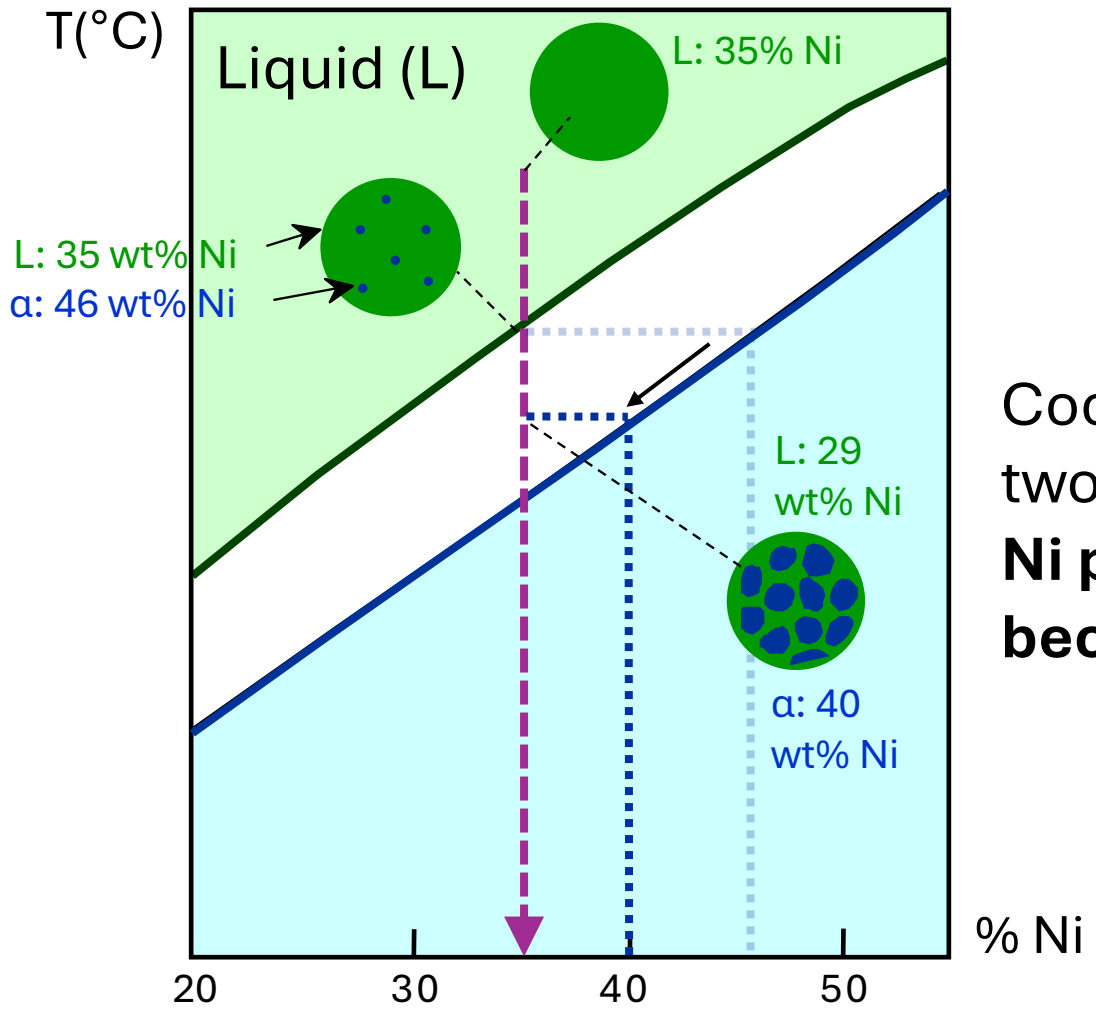


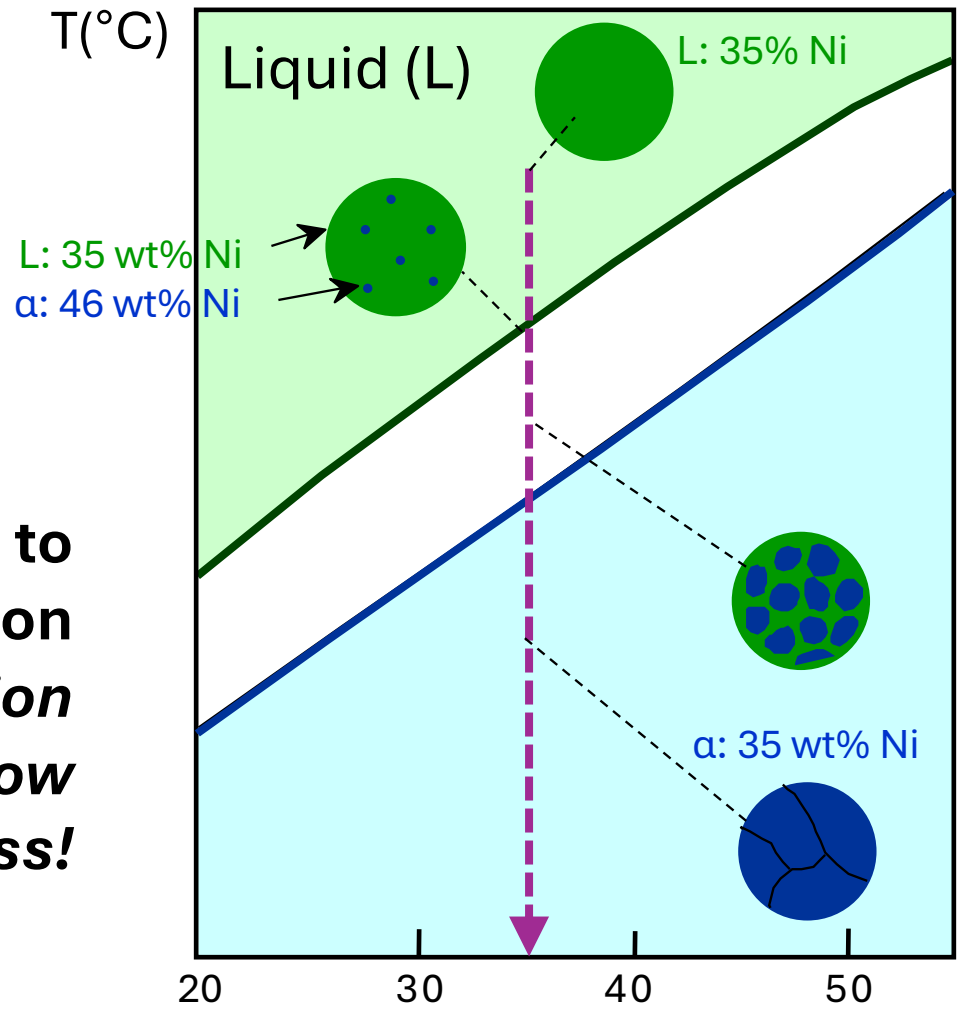
Once we hit the liquidus curve, we start to nucleate small **Ni-rich solid particles**

What if we cool through the two-phase region?



Cooling through the two-phase region, the **Ni particles grow and become Ni-deficient**

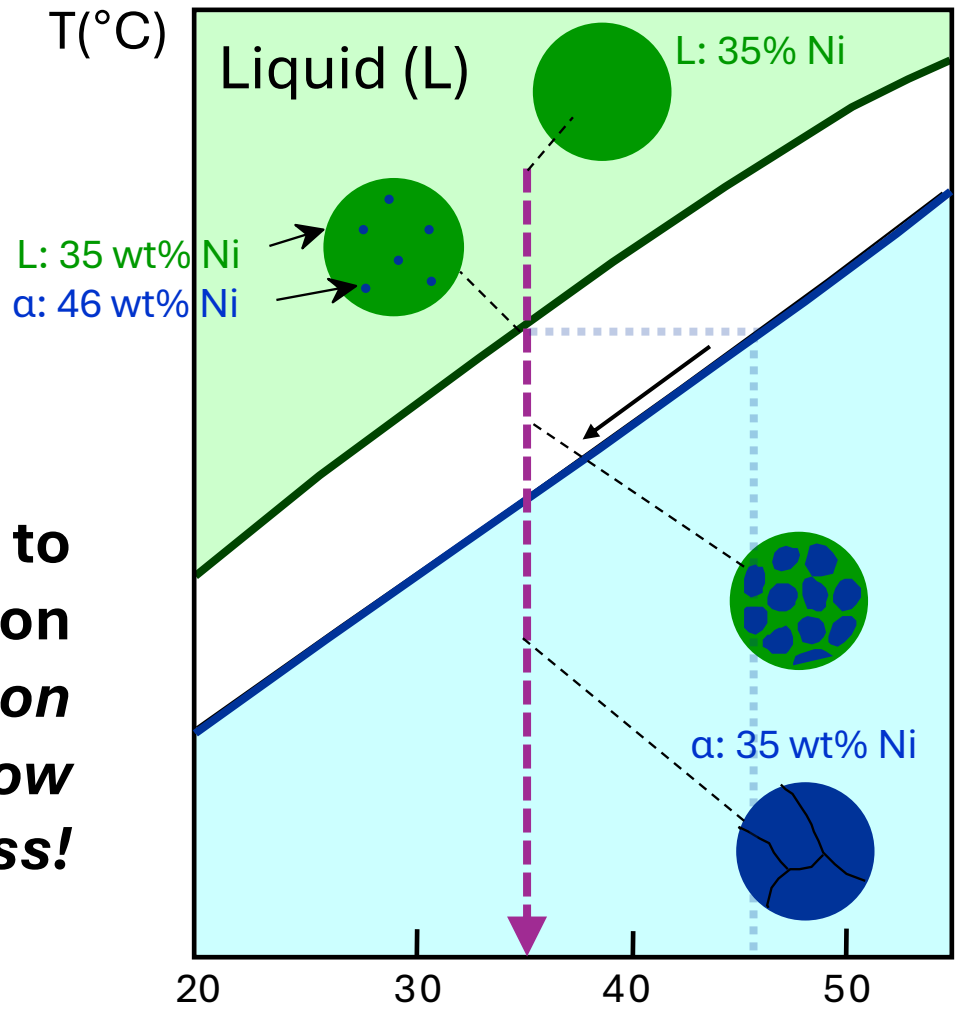
What if we cool through the two-phase region?



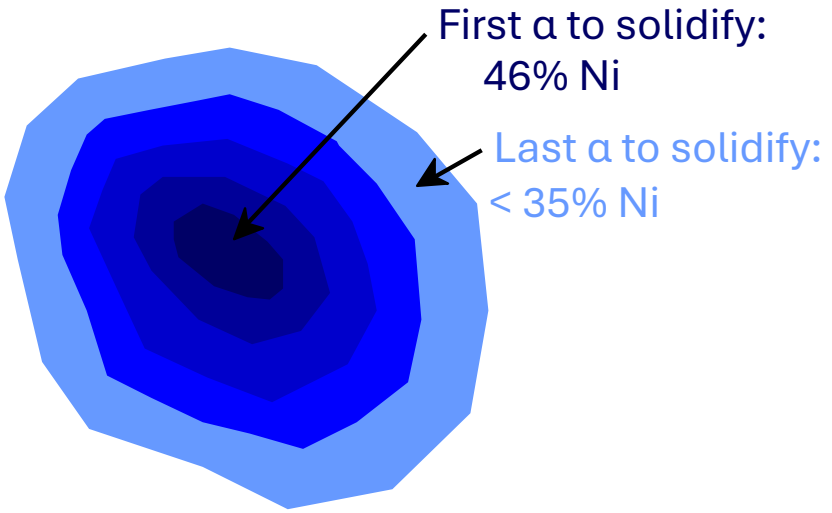
Note that changes to the solid composition require *diffusion* → *often a slow process!*

Eventually, all of the material solidifies and reaches the average composition

What if we cool *quickly* through the two-phase region?



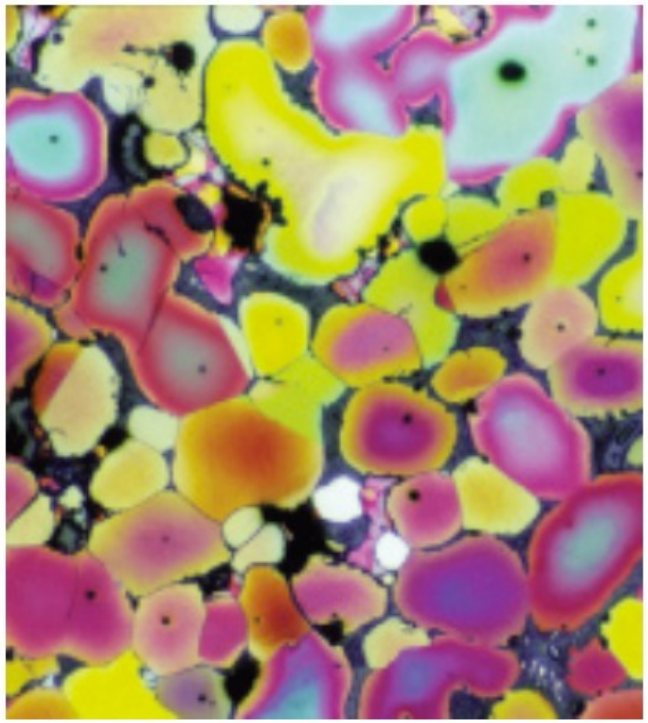
First α to solidify has C_α = 46% Ni
Last α to solidify has C_α = 35% Ni

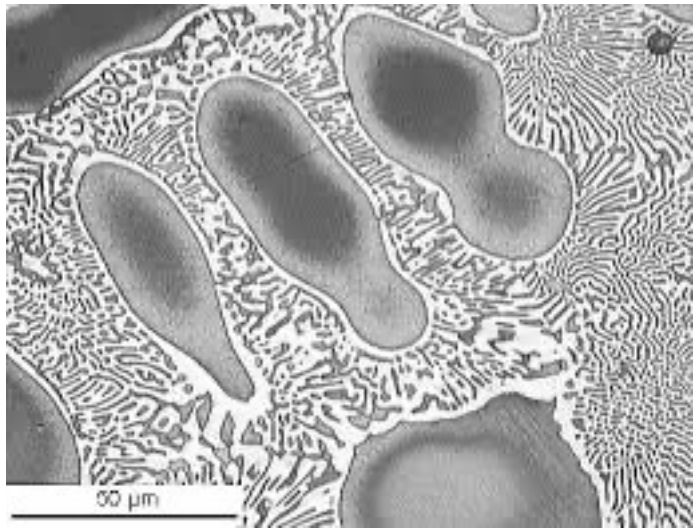


Note that changes to the solid composition require *diffusion* → *often a slow process!*

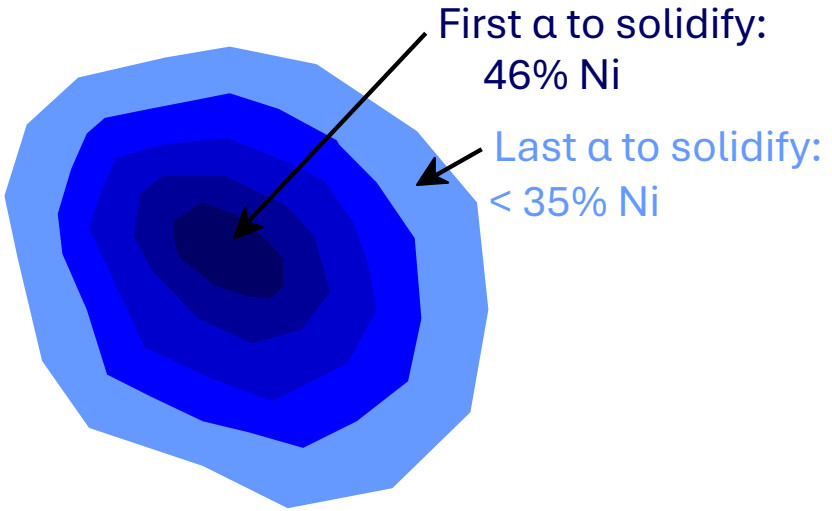
What if we cool *quickly* through the two-phase region?

This is known as ***coring***

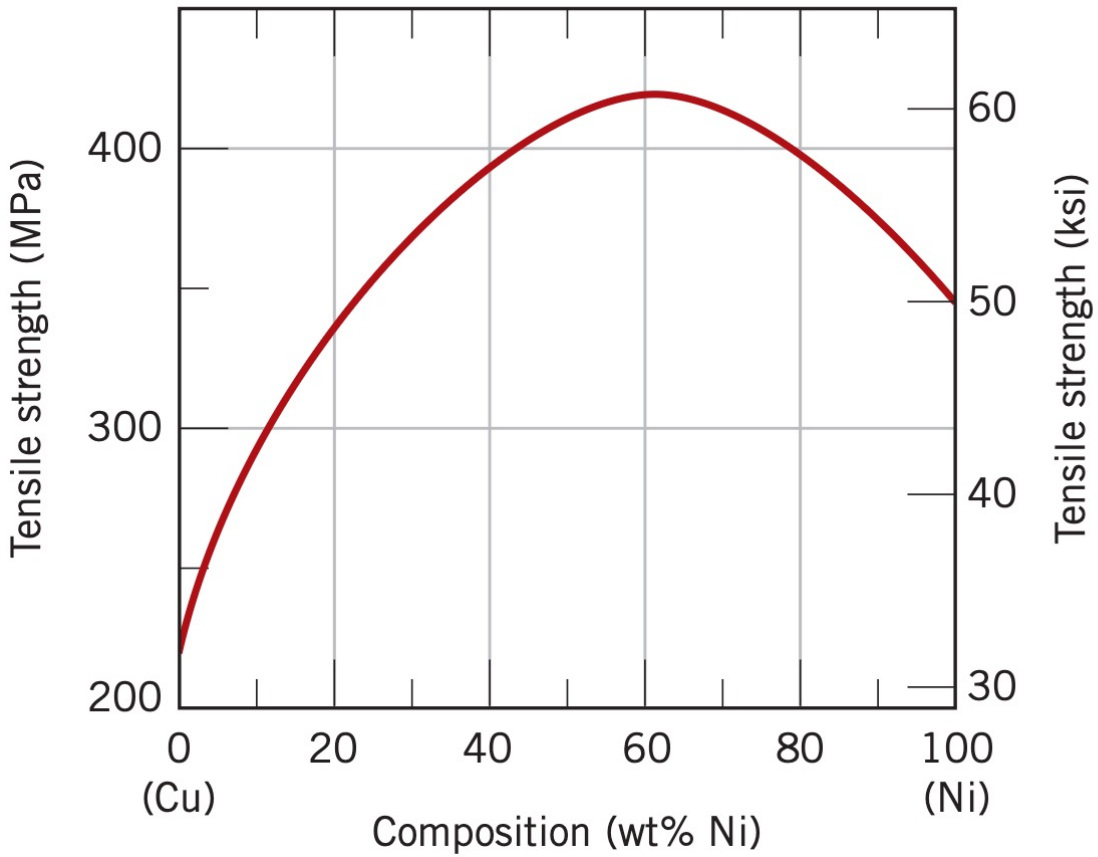




Often observed in experiment!

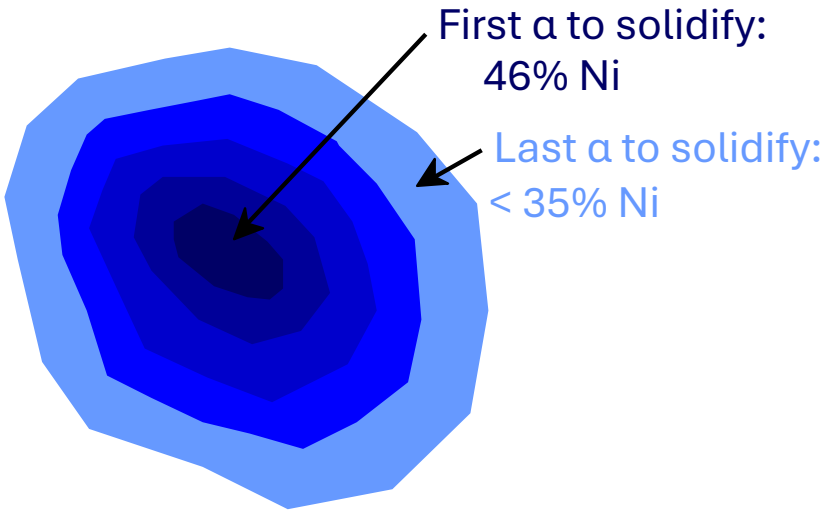


Coring has a big impact on performance



We can avoid this by **slow cooling** or **re-annealing** once cooled



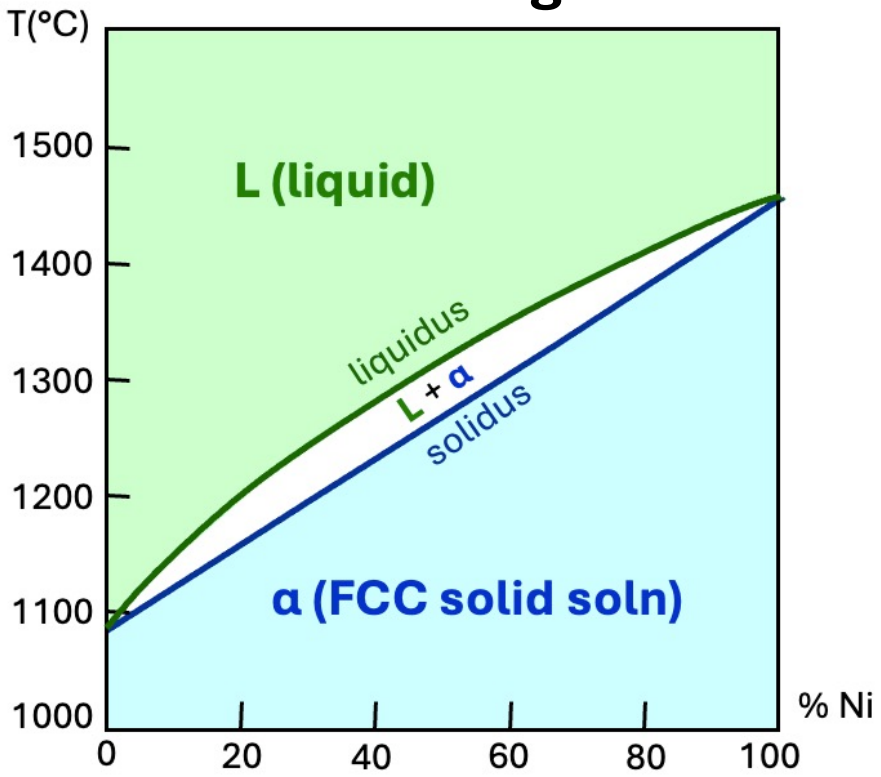


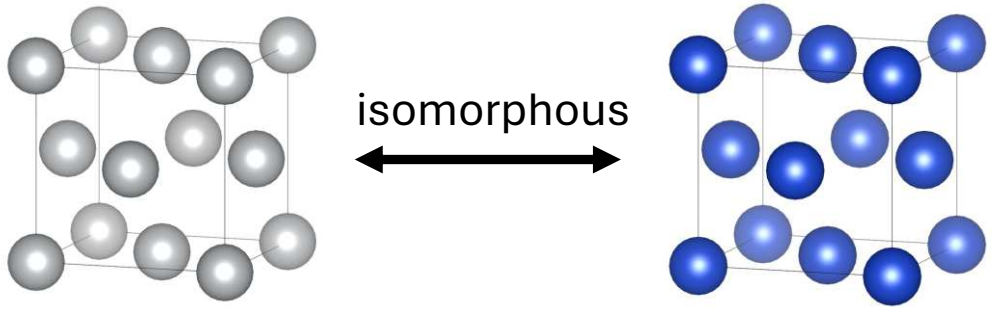
Remember that properties like tensile strength vary strongly with composition. Therefore, coring leads to **non-uniform properties.**

Questions on the microstructure that results from slow versus fast cooling?

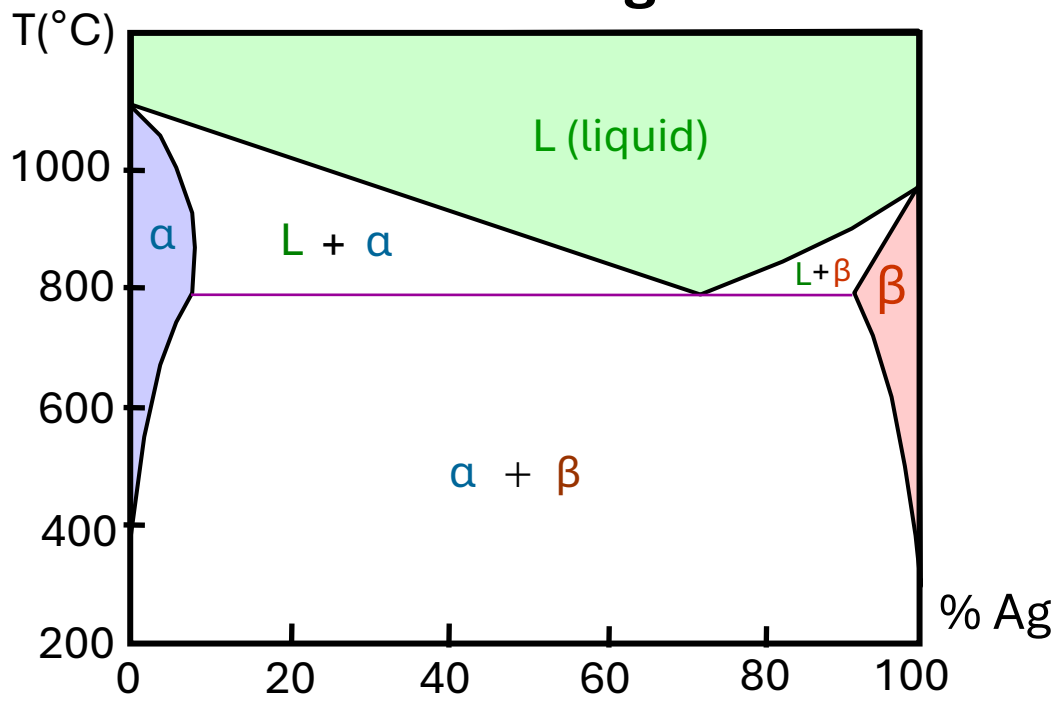
Different types of binary phase diagrams

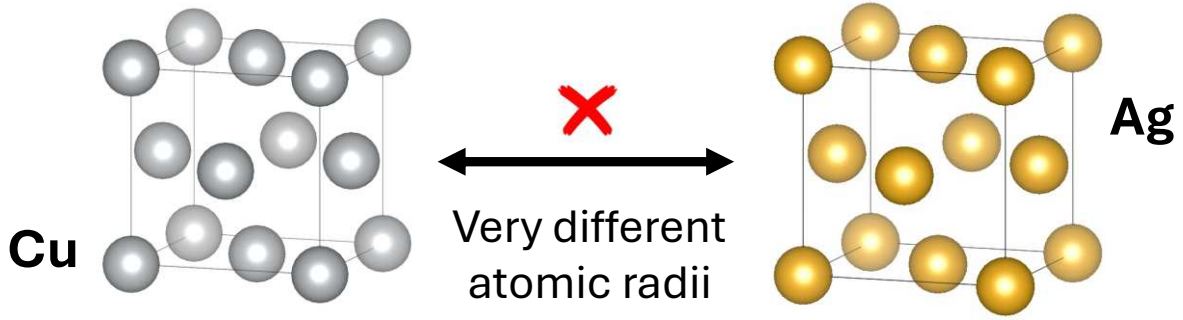
"Lens" diagram





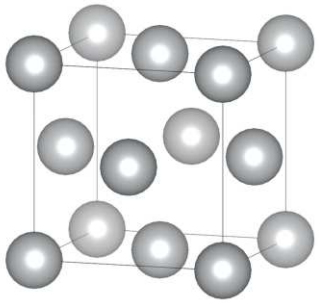
Eutectic diagram

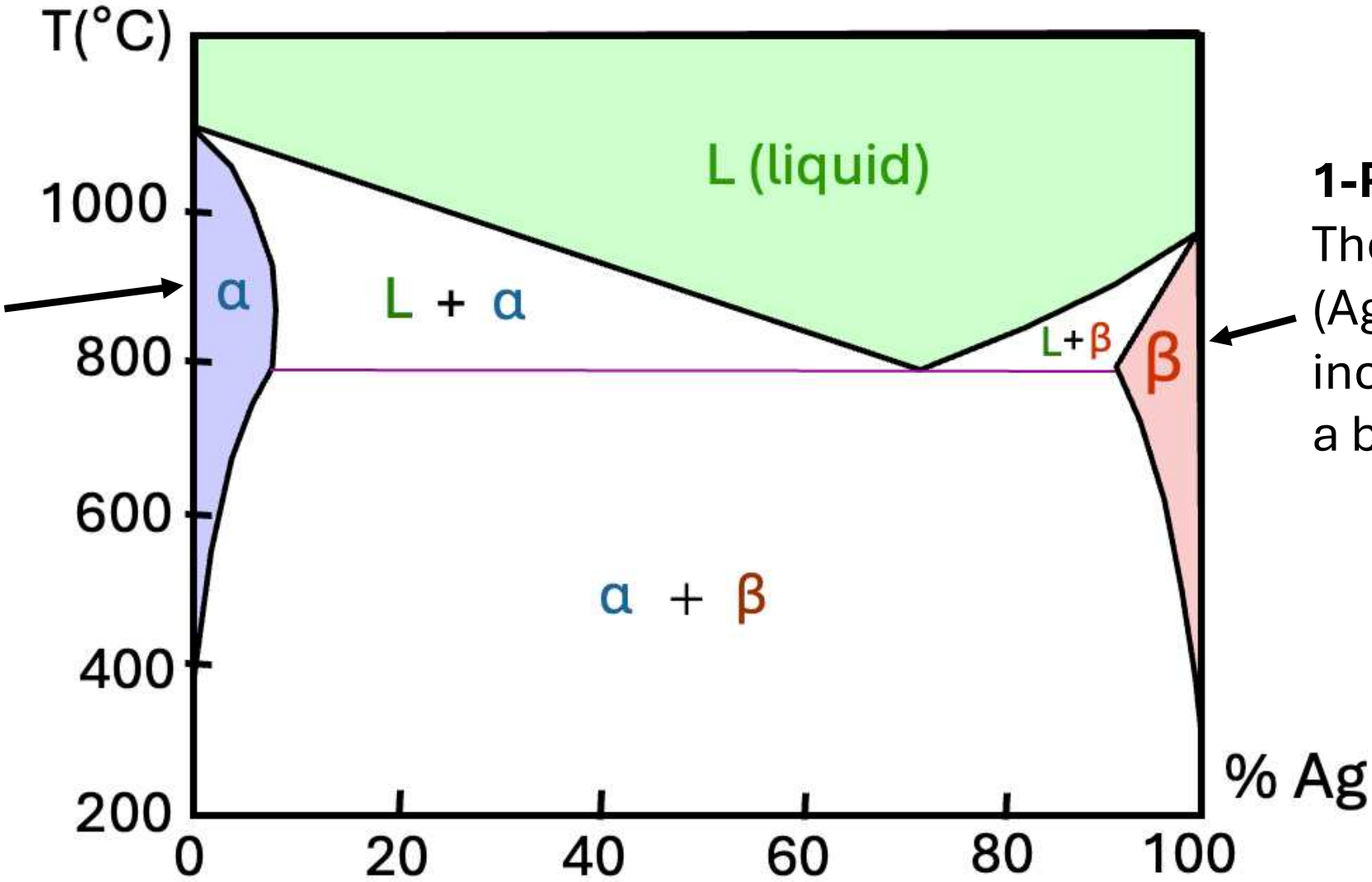




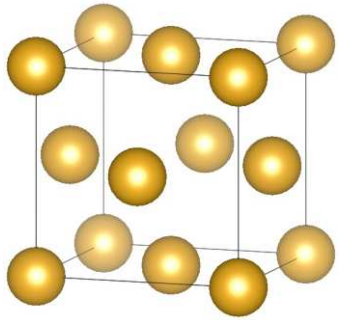
Binary eutectic phase diagram

1-Phase:
The α phase (Cu) can incorporate a bit of Ag

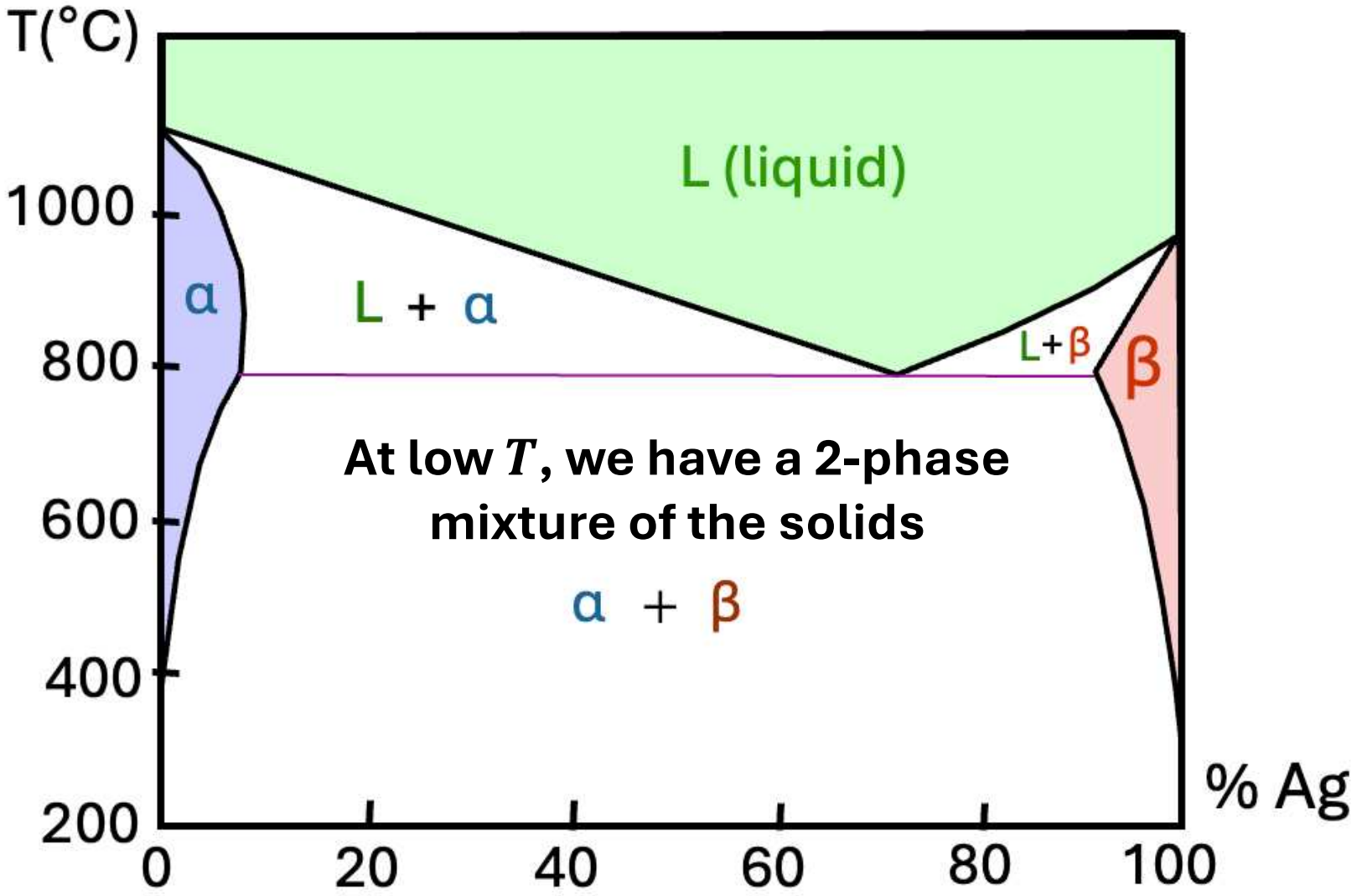




1-Phase:
The β phase (Ag) can incorporate a bit of Cu

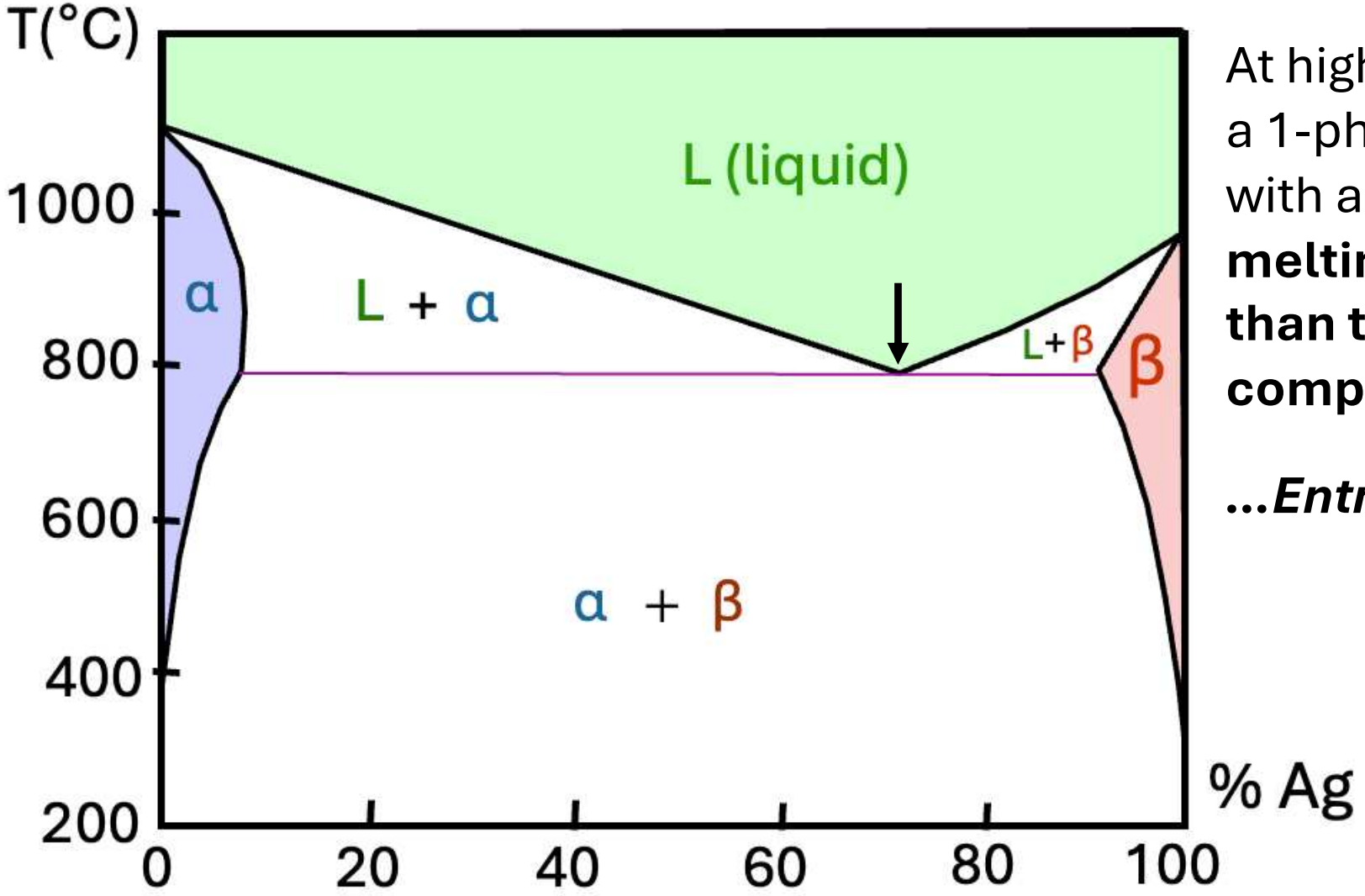


Binary eutectic phase diagram



Binary eutectic phase diagram

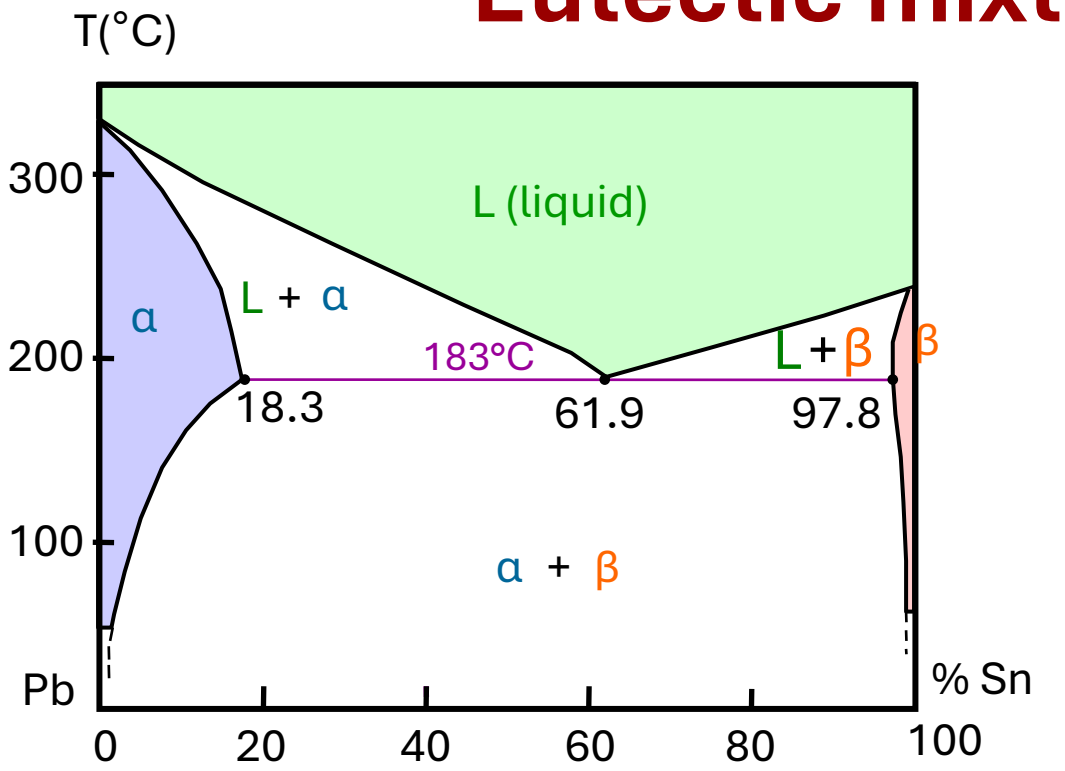
Greek: “easy to melt”



At high T, we have a 1-phase mixture with a **lower melting point than the separate components!**

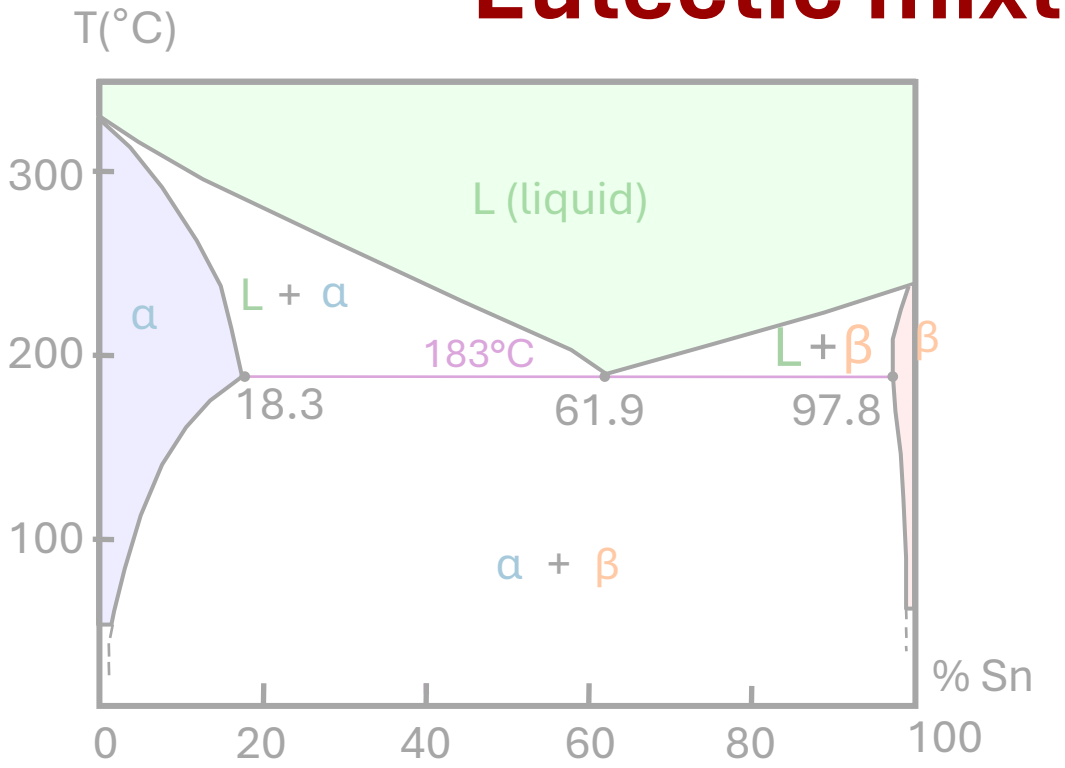
…Entropy…

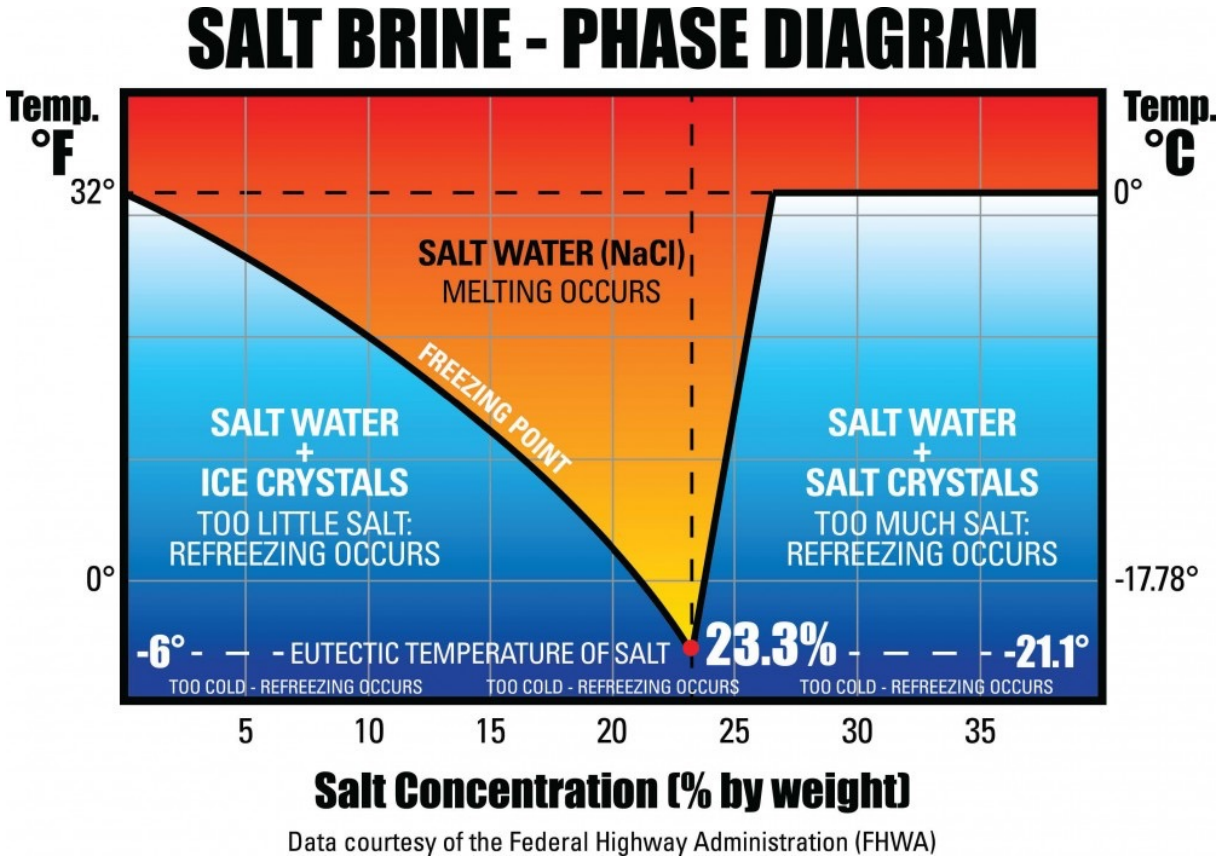
Eutectic mixtures are important!





Eutectic mixtures are important!









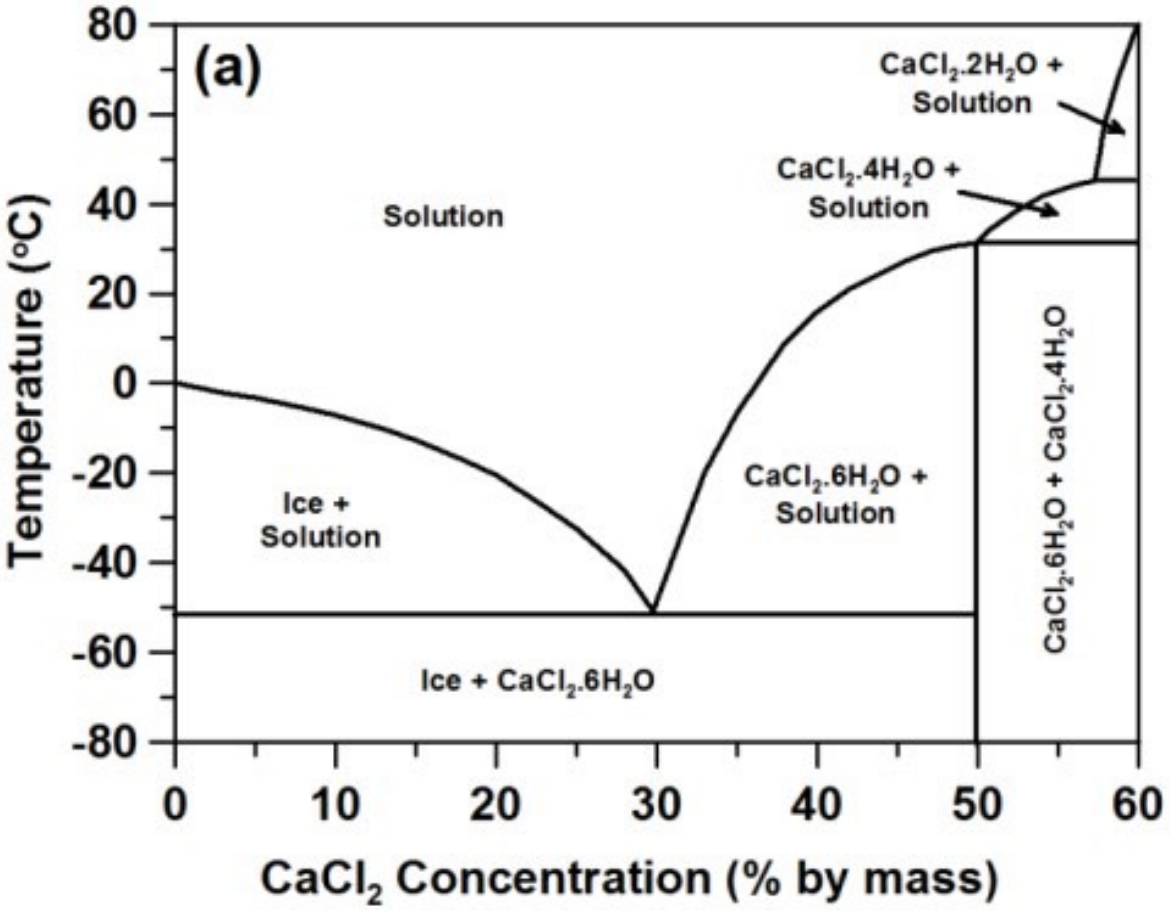
Salt (NaCl) lowers the melting point of water by up to 17 °C

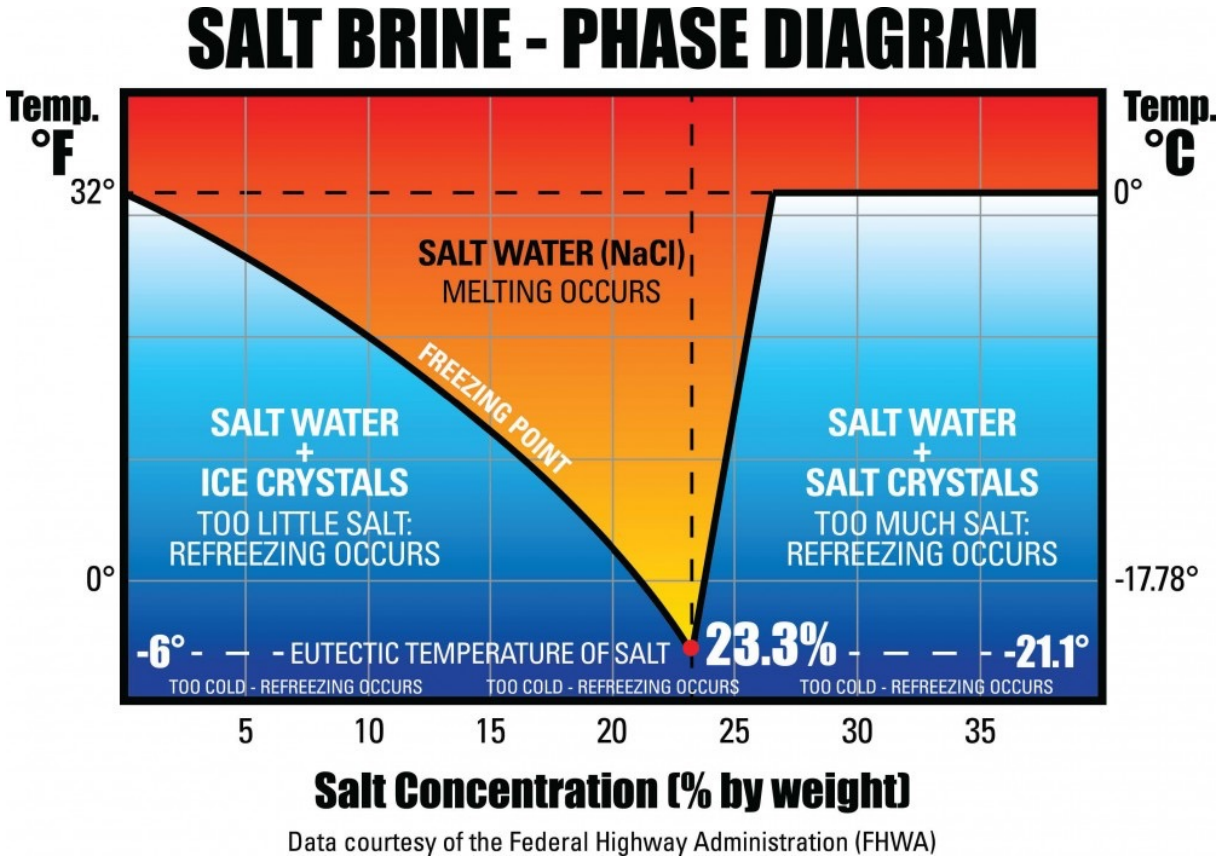

Without salt
With salt
» 64x

Eutectic mixtures are important!



$CaCl_2$ works even better, lowering the melting point of water by up to 50 °C!

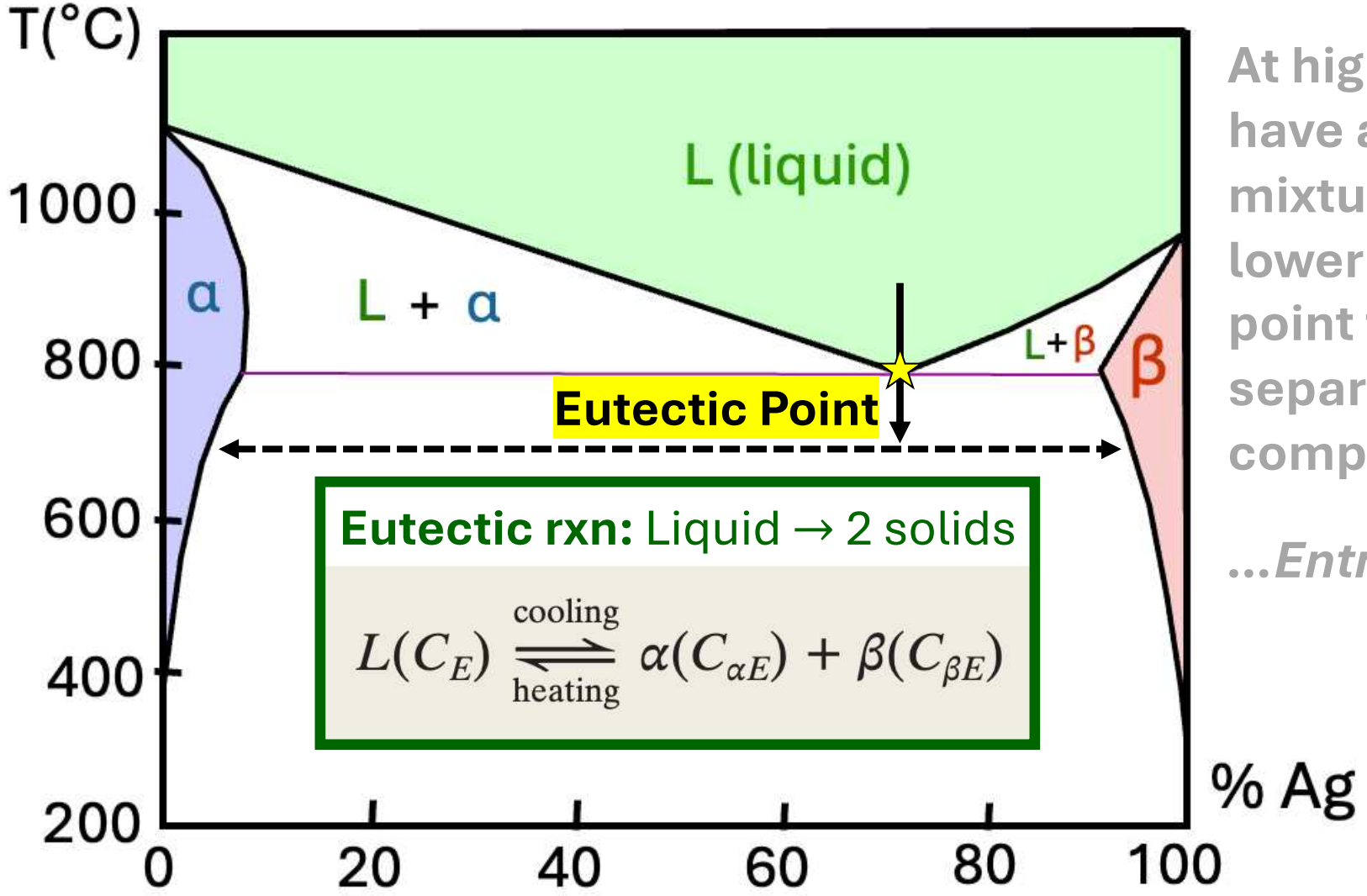




Salt (NaCl) lowers the melting point of water by up to 17 °C

Solidification in a binary eutectic phase diagram

Solidification into to different phases with **very different compositions!**



At high T, we have a 1-phase mixture with a lower melting point than the separate components!

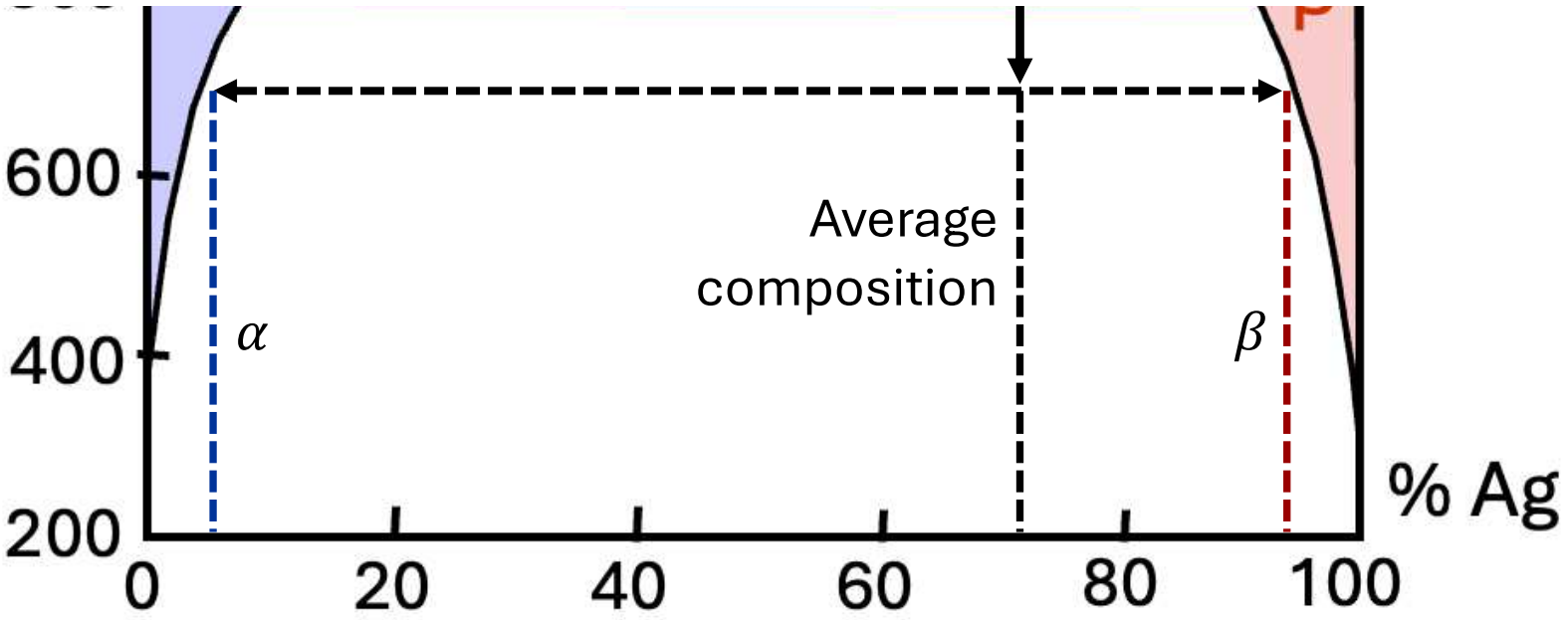
...Entropy...

Solidification in a binary eutectic phase diagram

- Average composition = 72% Ag
- α phase will have 5% Ag
- β phase will have 95% Ag

$$W_\beta = \frac{C_\alpha - C_0}{C_\alpha - C_\beta} = \frac{5 - 72}{5 - 95} = 0.744$$

$$W_\alpha = 1 - 0.744 = 0.256$$



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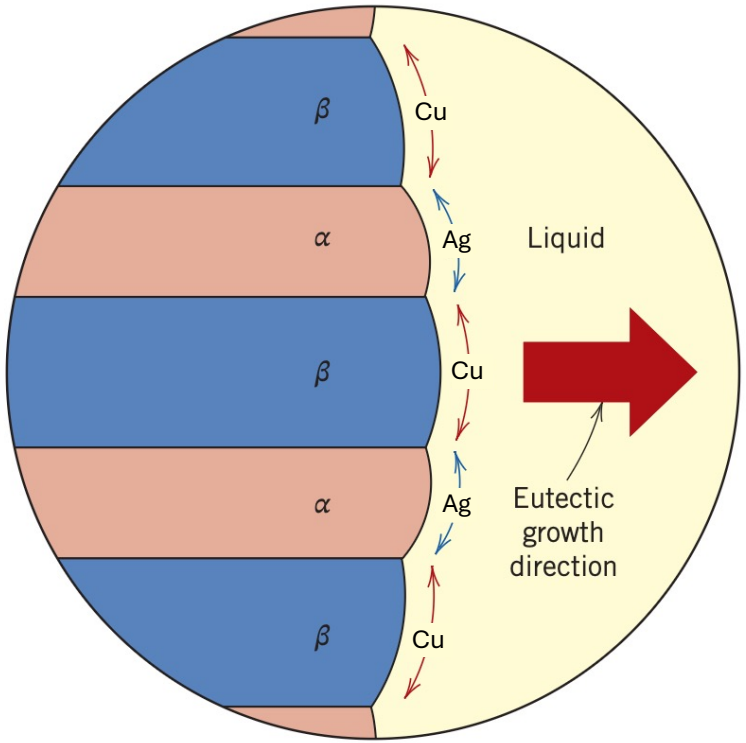


We are forming one phase rich in Ag, and another phase rich in Cu

→ These two phases must ***grow together*** to maintain the average composition

Eutectic microstructure

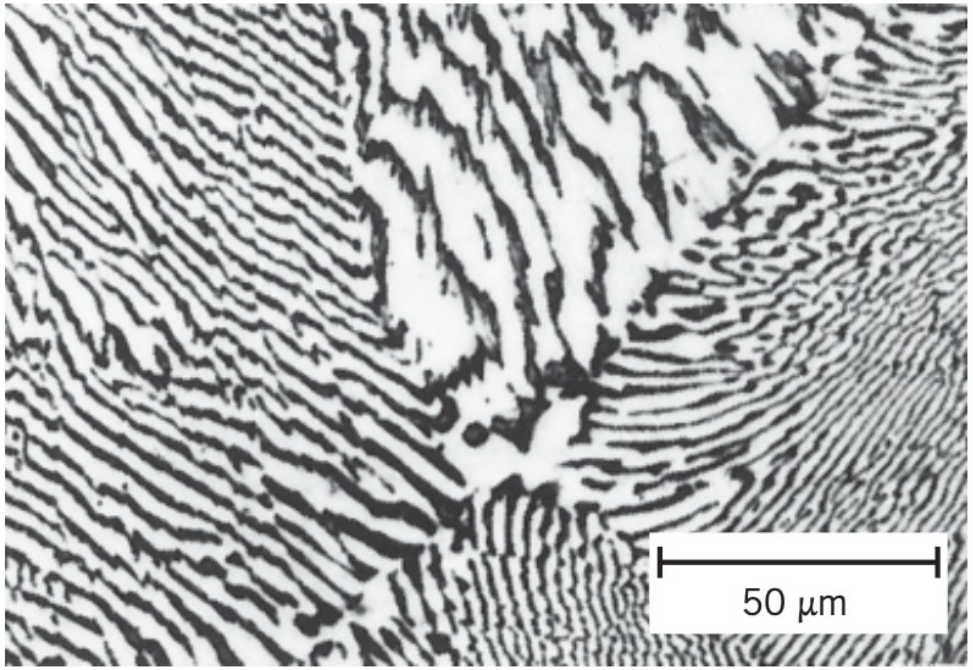
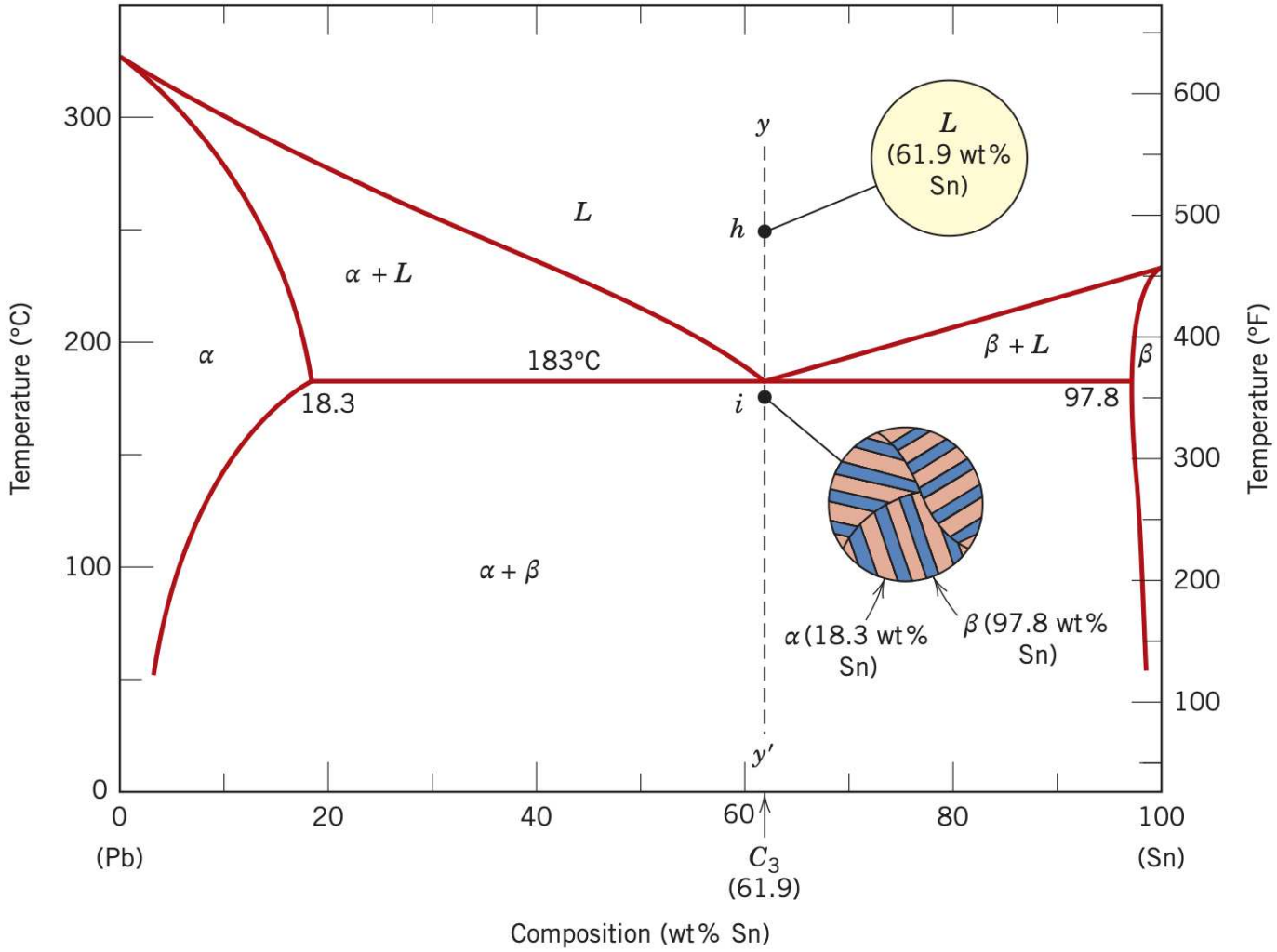
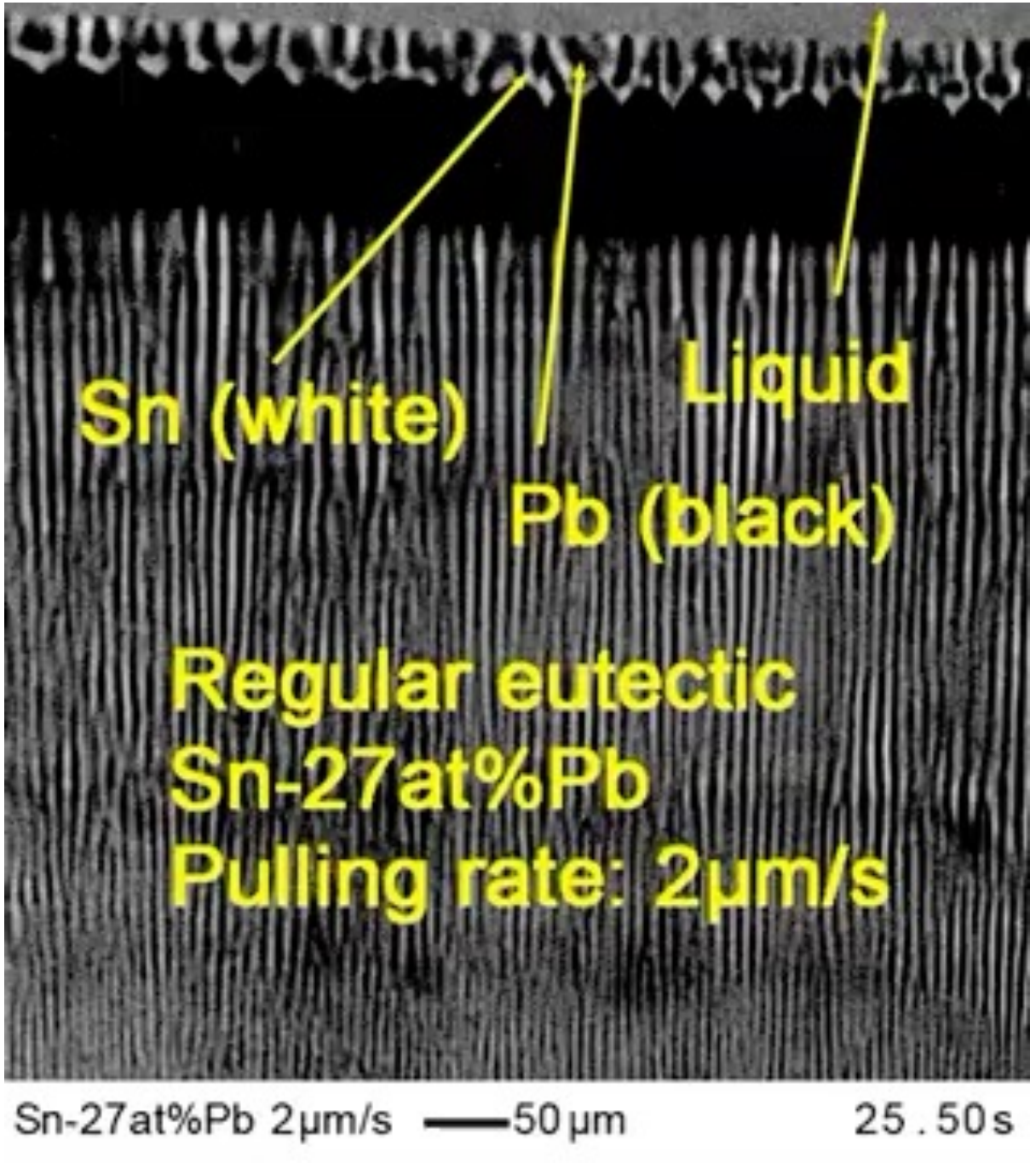


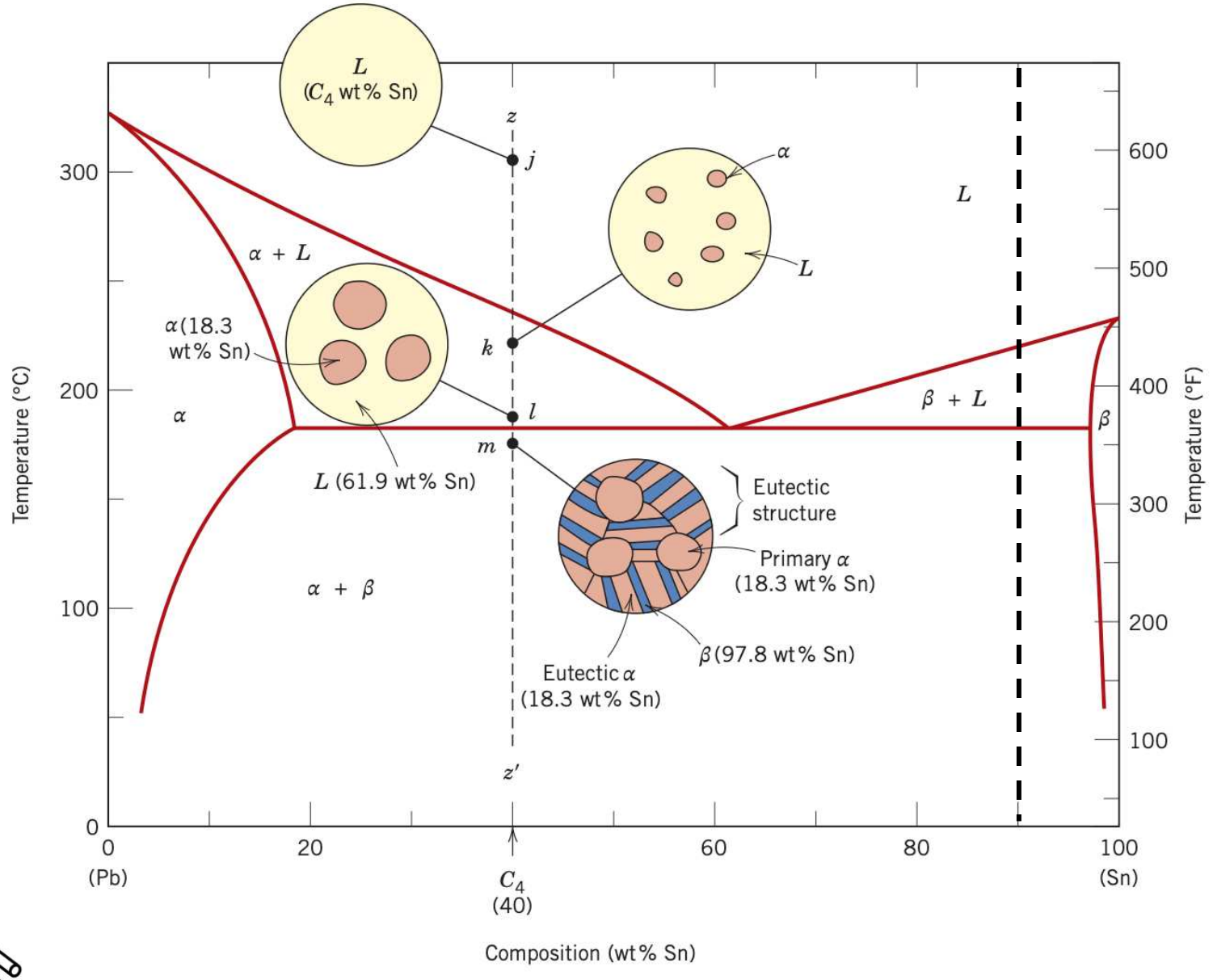
Figure 9.14 Photomicrograph showing the microstructure of a lead–tin alloy of eutectic composition. This microstructure consists of alternating layers of a lead-rich α-phase solid solution (dark layers), and a tin-rich β-phase solid solution (light layers). 375 ×.

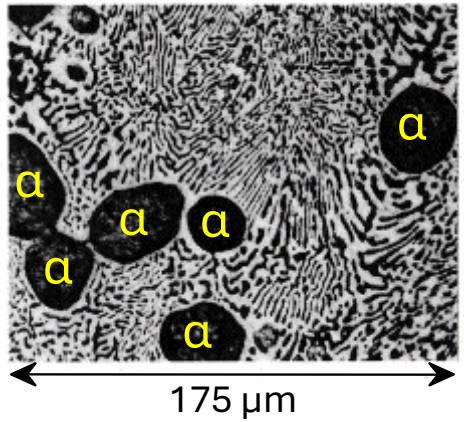




Sn/Pb liquid flows into a cold zone and solidifies

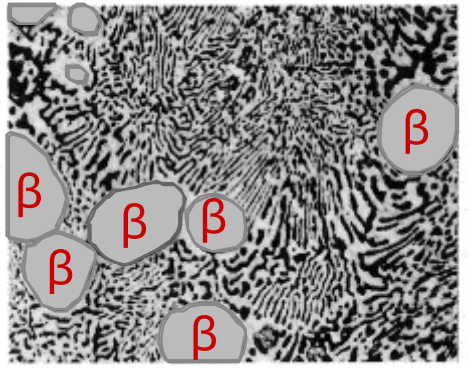
*Hypo*eutectic microstructure





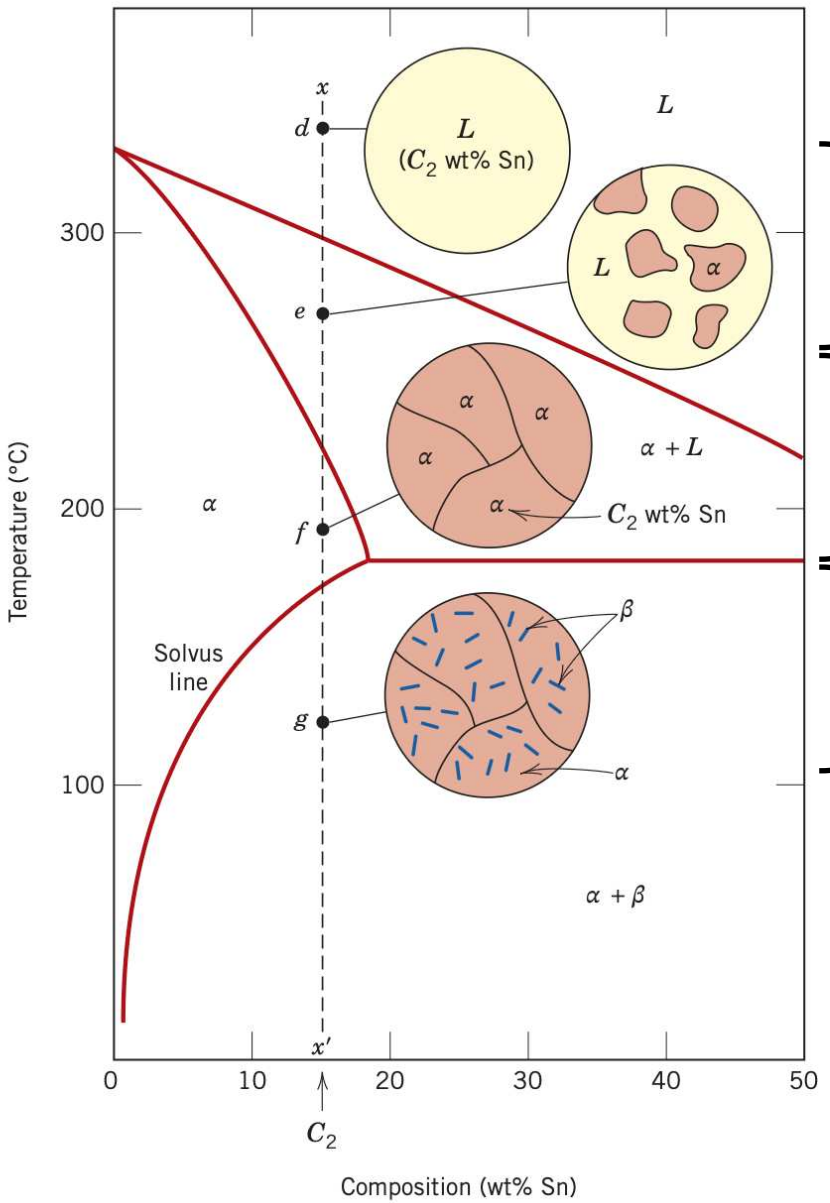
Some α forms

Hypereutectic occurs on the other side of the phase diagram.



Some β forms

Microstructure: cooling through the 1-phase region



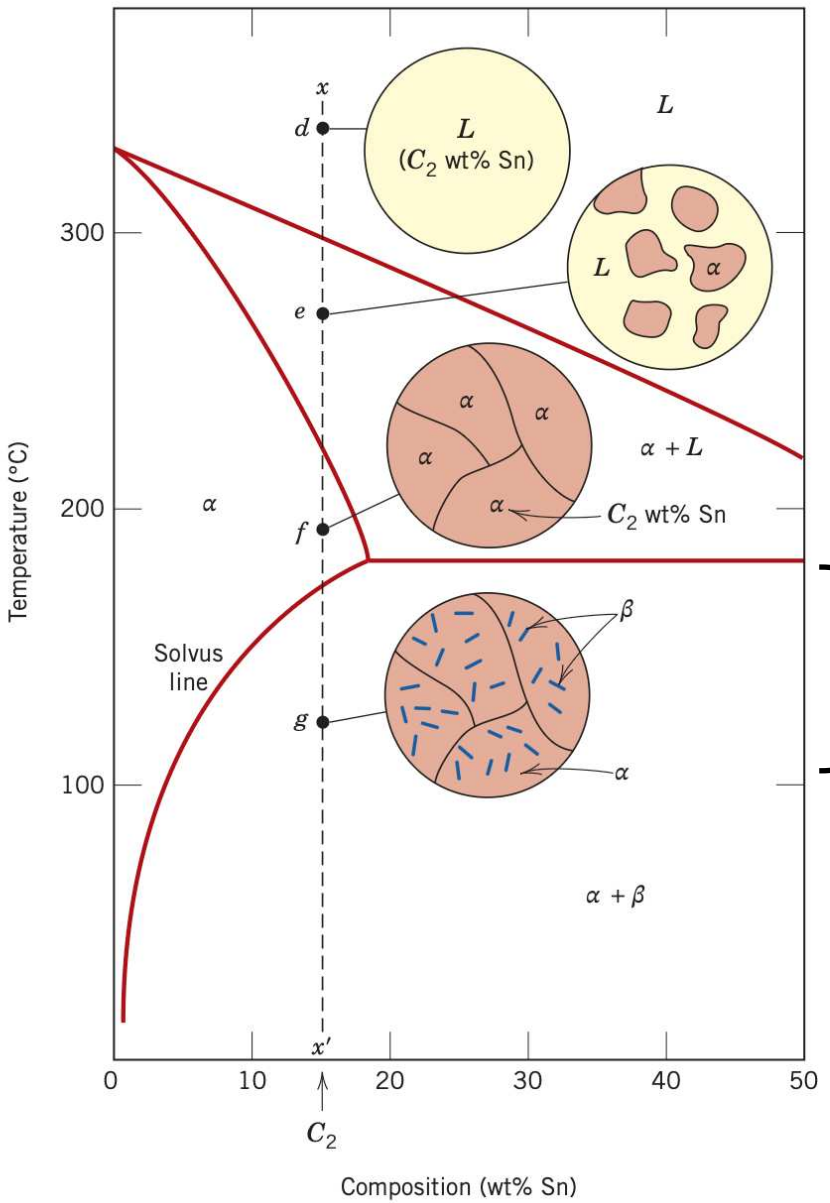
$\boldsymbol{L \rightarrow L + \alpha}$**:** the solid α phase starts to nucleate

$\boldsymbol{L + \alpha \rightarrow \alpha}$**:** complete solidification into α

$\boldsymbol{\alpha \rightarrow \alpha + \beta}$**:** small amounts of β form inside of α

No eutectic microstructure forms since we don't need to simultaneously grow two solid phases with distinct compositions

Microstructure: cooling through the 1-phase region



Side note: this step may or may not happen, depending on the cooling rate

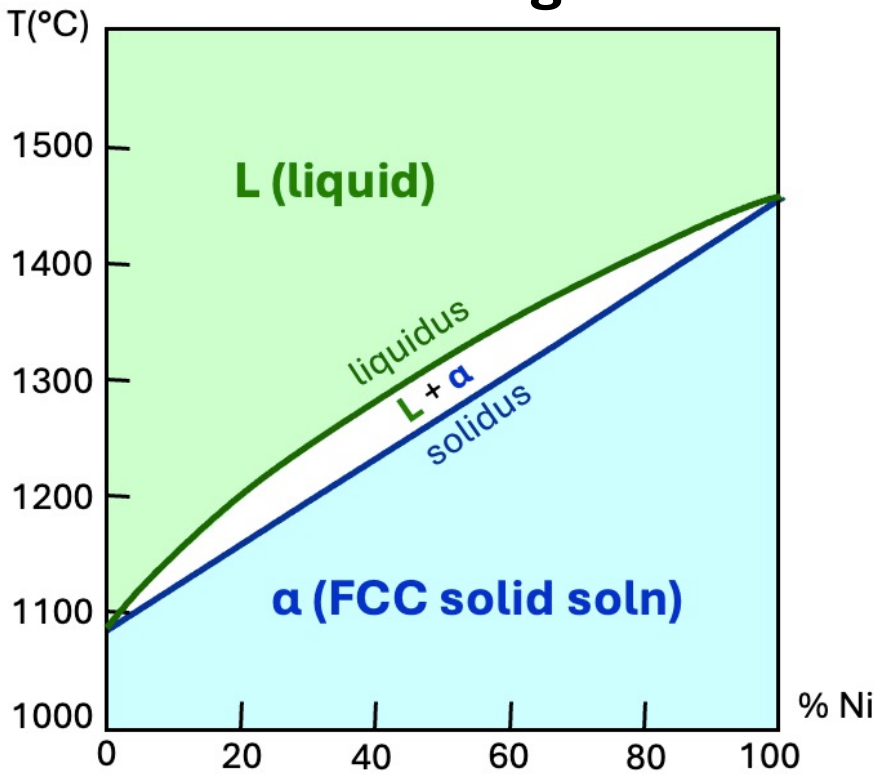
$\alpha \rightarrow \alpha + \beta$: small amounts of β form inside of α

Solid-solid transformations are usually quite slow, especially at low temperature

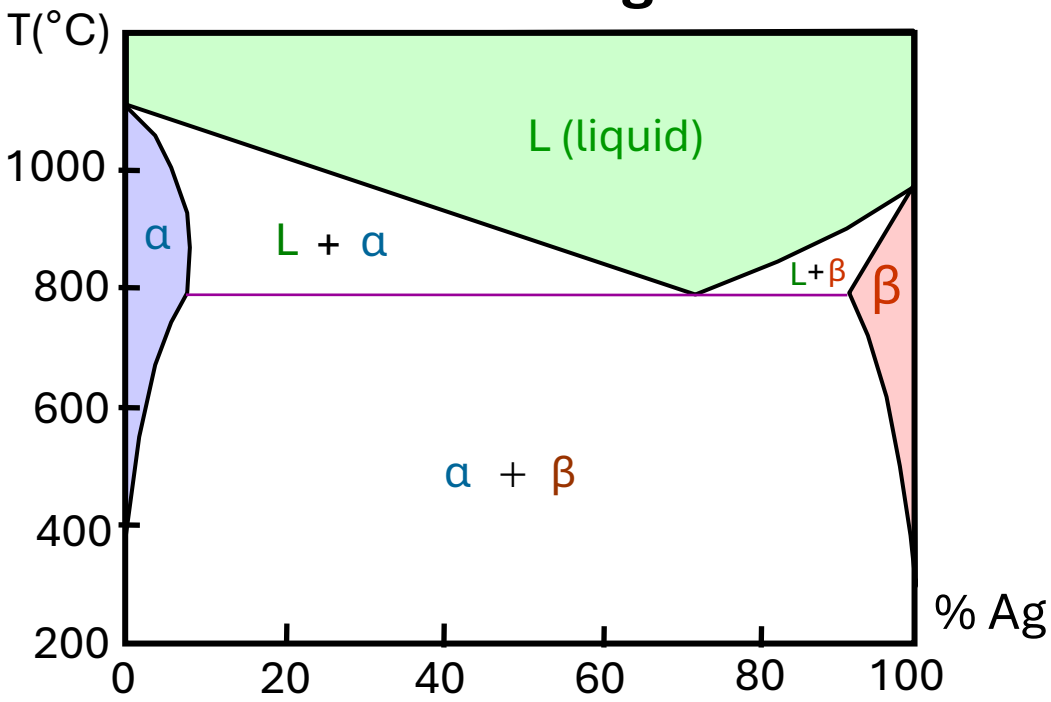
Questions on eutectic phase diagrams?

We've covered two types of binary phase diagrams

"Lens" diagram



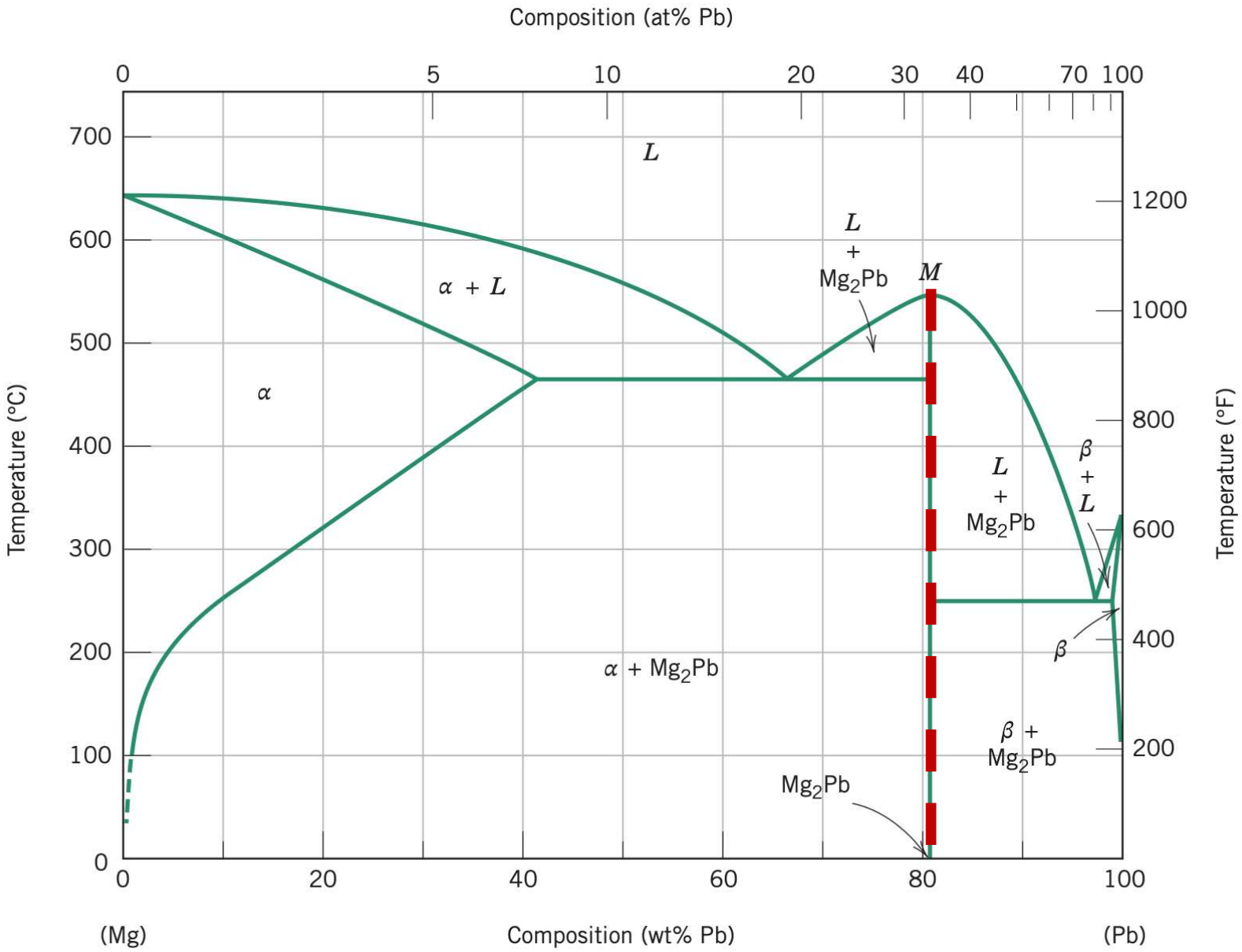
Eutectic diagram



These each involve only two solid phases (α and β) – **what if others form?**

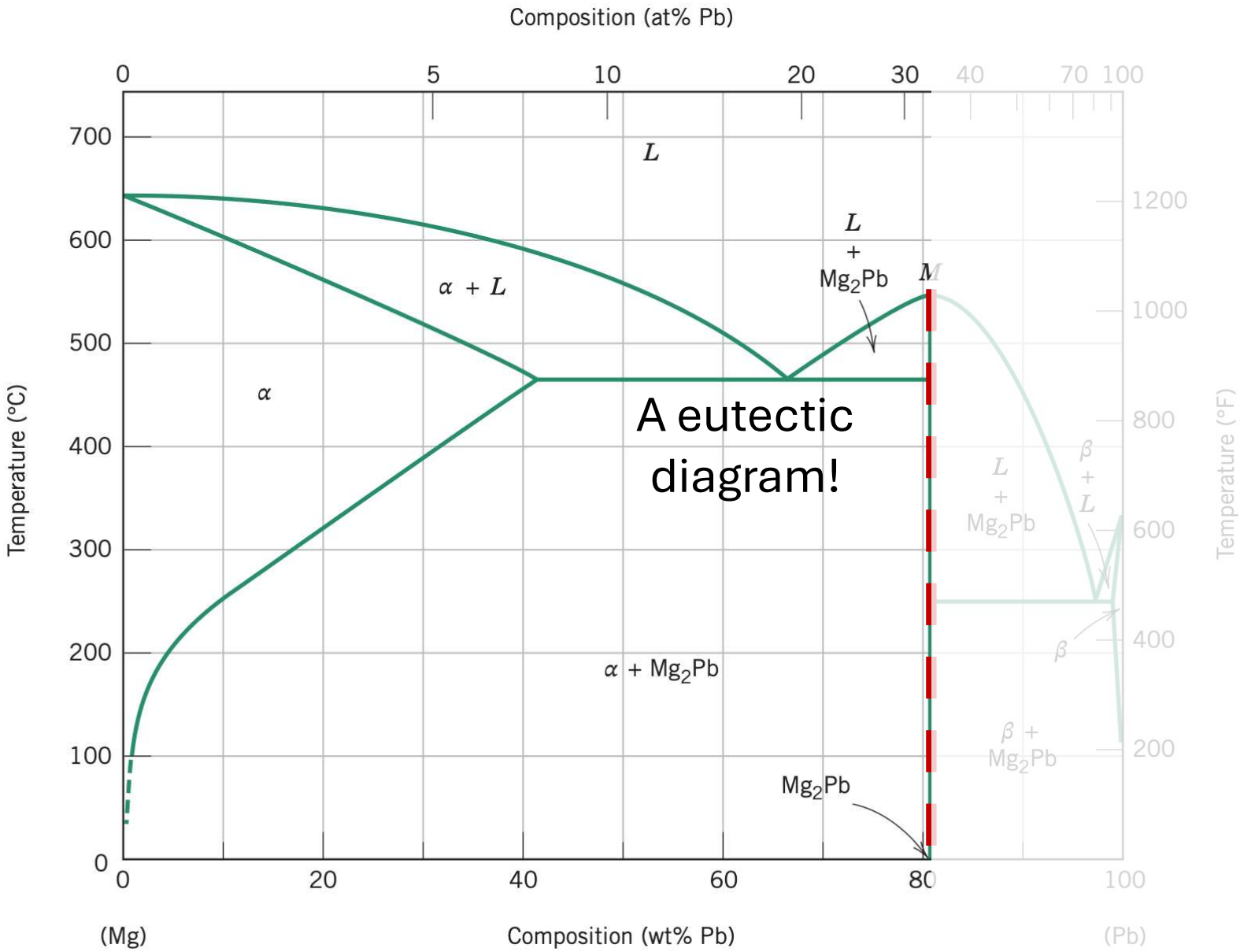
Example: 2 Mg + Pb → Mg_2Pb *(intermetallic)*

Example: Mg-Pb phase diagram



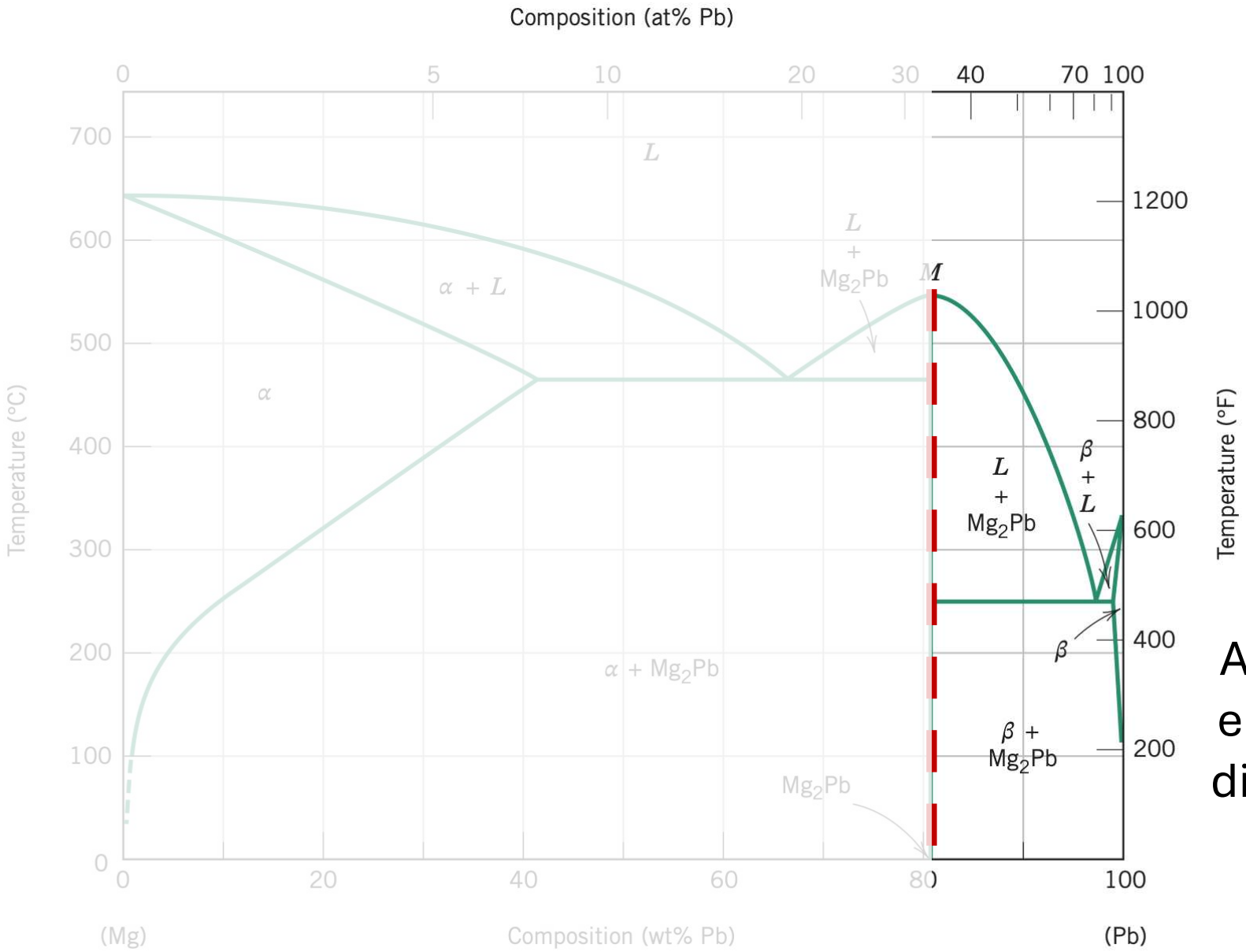
Mg_2Pb is what's known as a "**line compound**" because it has **negligible solubility** of other species. In other words, it does not allow much off-stoichiometry $Mg_{2-x}Pb_{1+x}$

Example: Mg-Pb phase diagram



This looks complicated, but it can be divided into simpler pieces

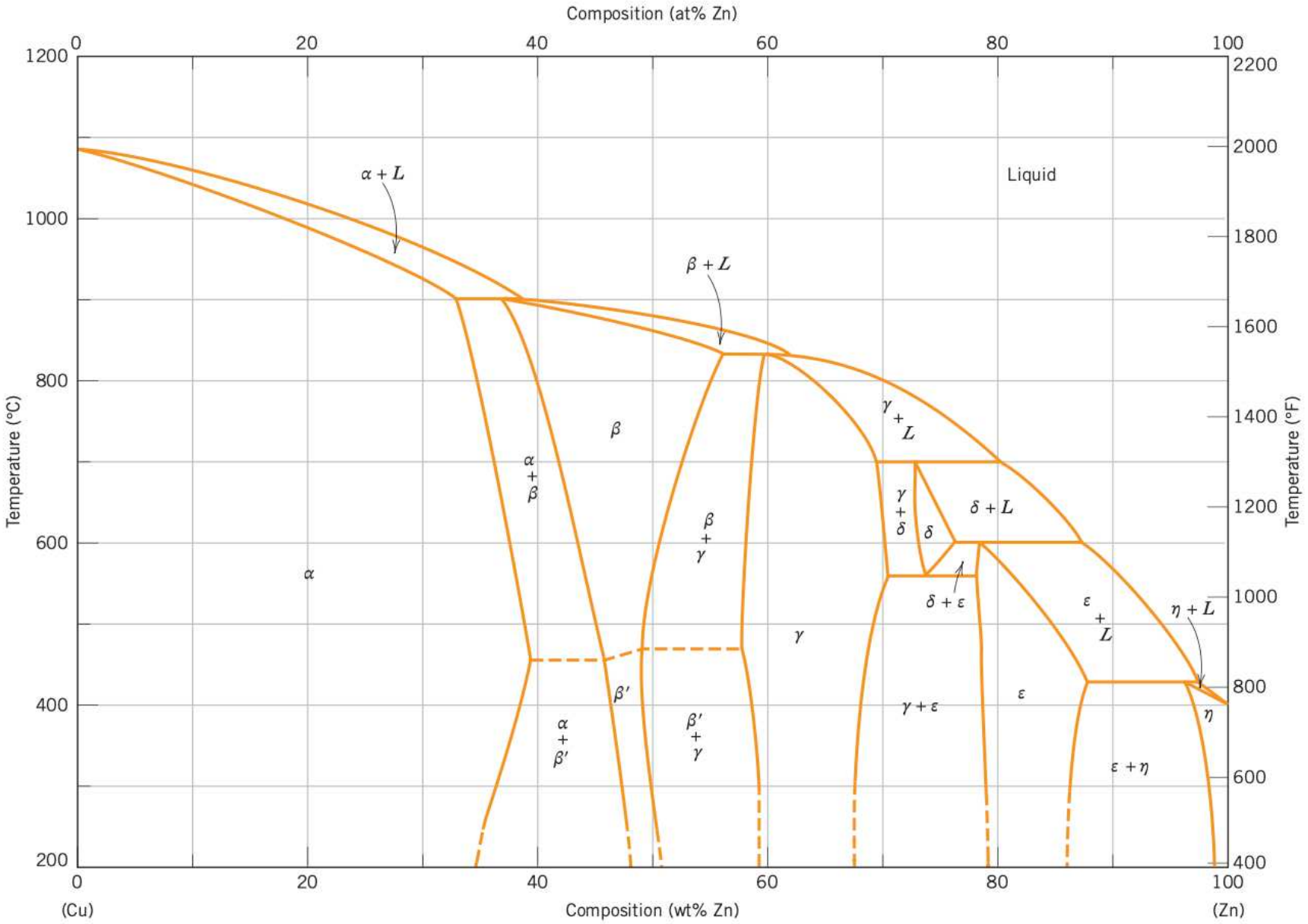
Example: Mg-Pb phase diagram



This looks complicated, but it can be divided into simpler pieces

Another eutectic diagram!

There can be *many* intermetallic compounds



Not all compounds that form are line compounds – some can exhibit a lot of off-stoichiometry (see β and γ)

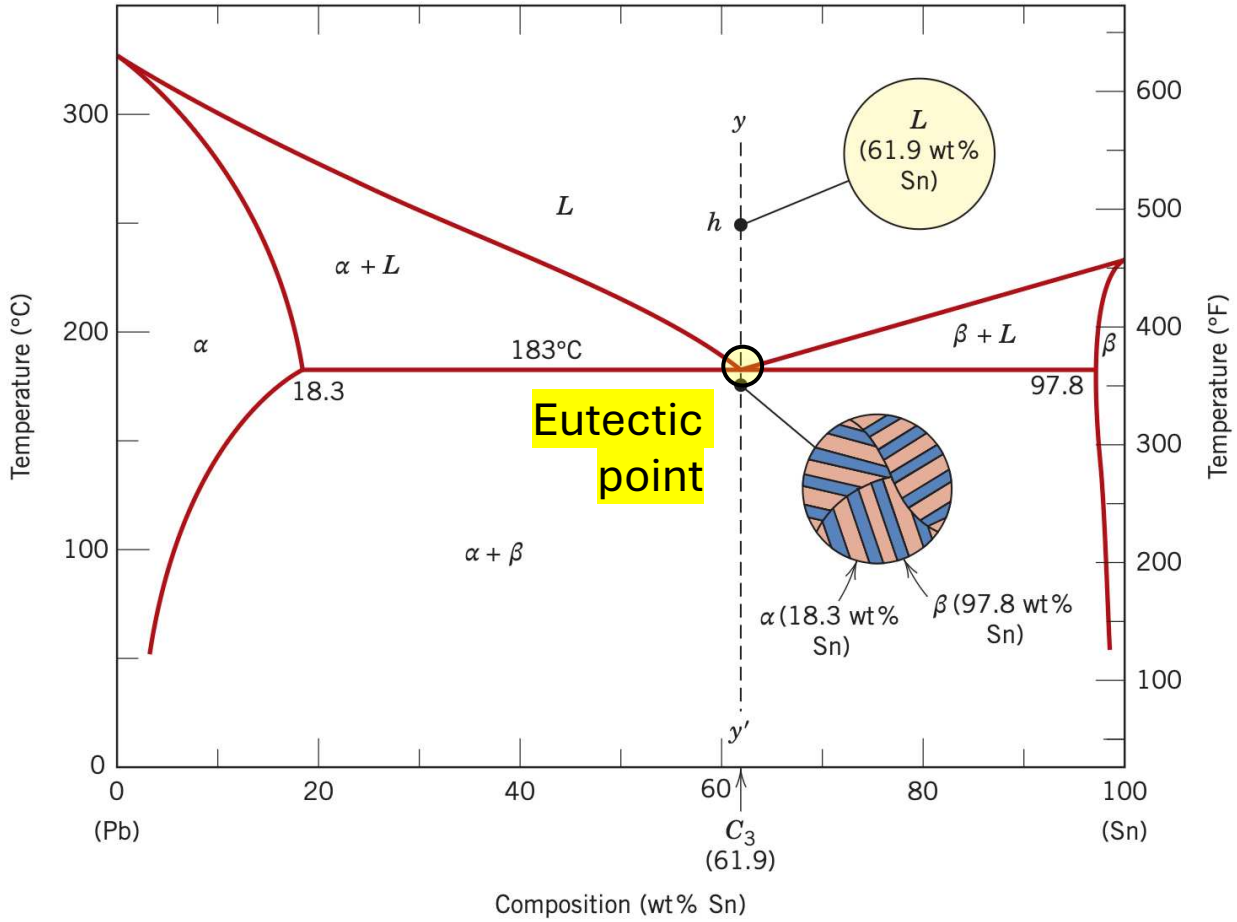
We also find some new points of interest in this phase diagram

Types of reactions on the phase diagram

Eutectic reaction:

Liquid → Two solid phases upon cooling

$$L(C_E) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$



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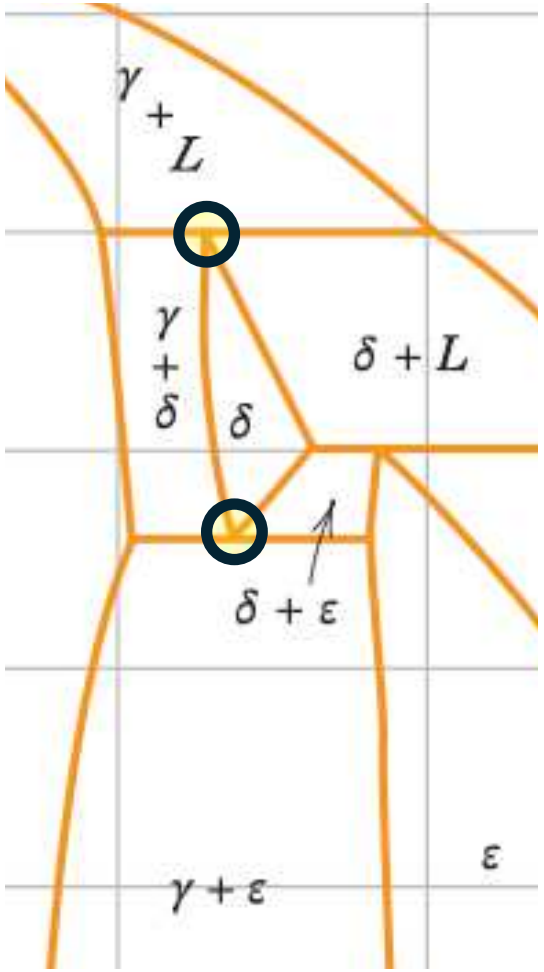


$$\delta \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \gamma + \varepsilon$$

Eutectoid reaction:
One solid solution → Two solid phases upon cooling

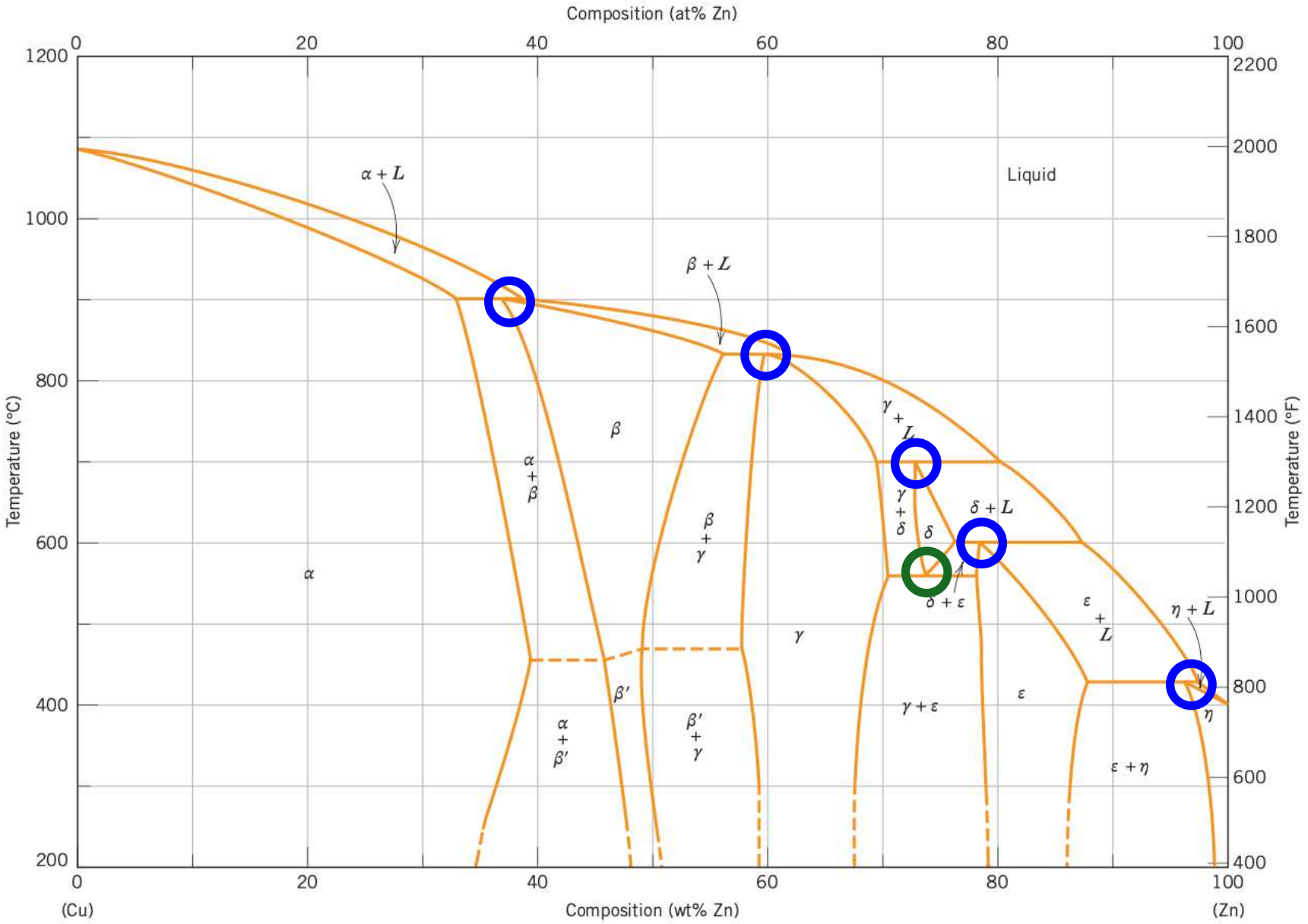
$$\delta + L \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \varepsilon$$

Peritectic reaction:
Solid + liquid → one solid solution upon cooling

"Peritectic" looks like "Pants"

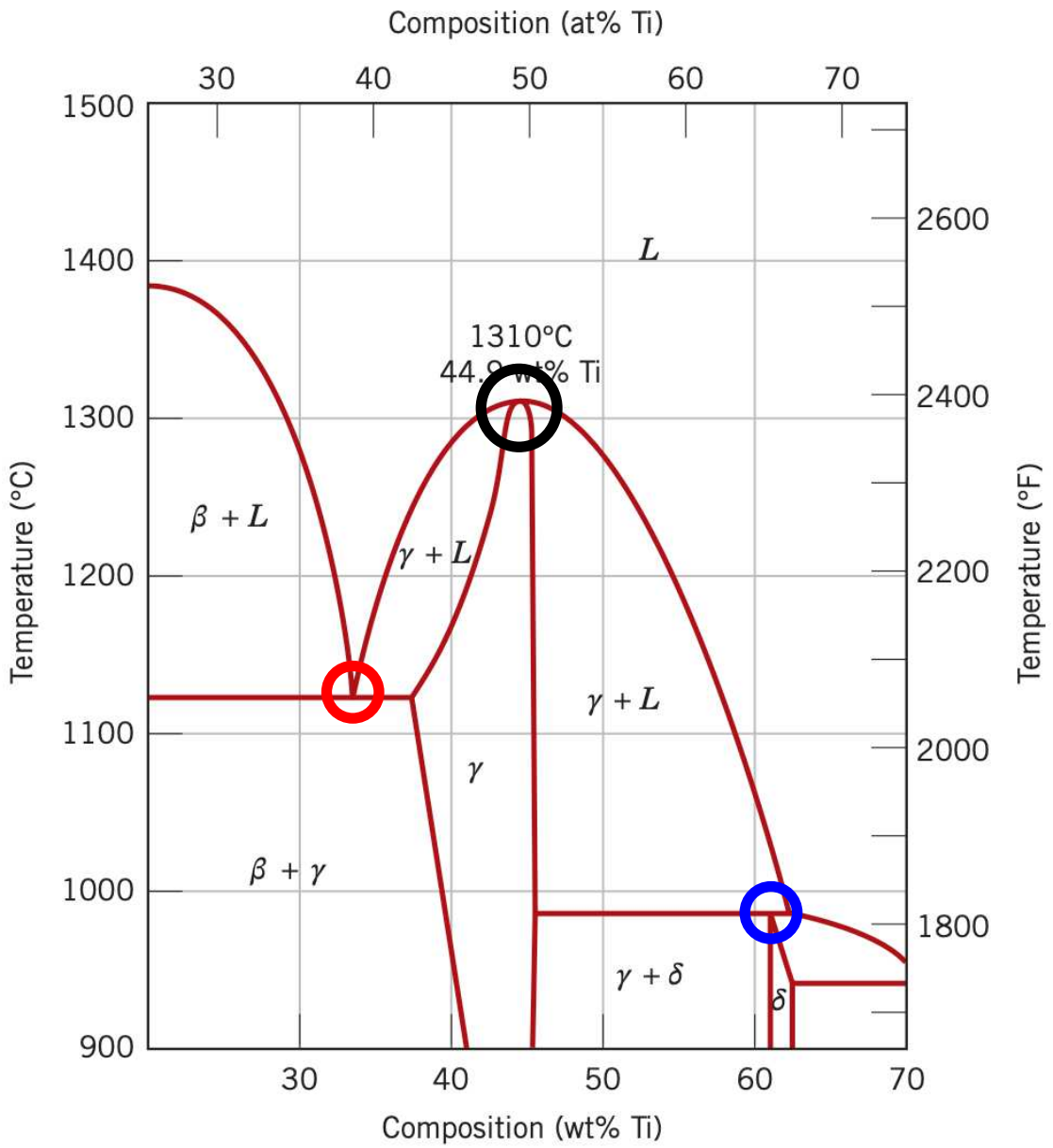


Can you identify all the “special” points?



- 4 peritectic points
- 1 eutectoid point

Another example: where are the special points?



1 eutectic point

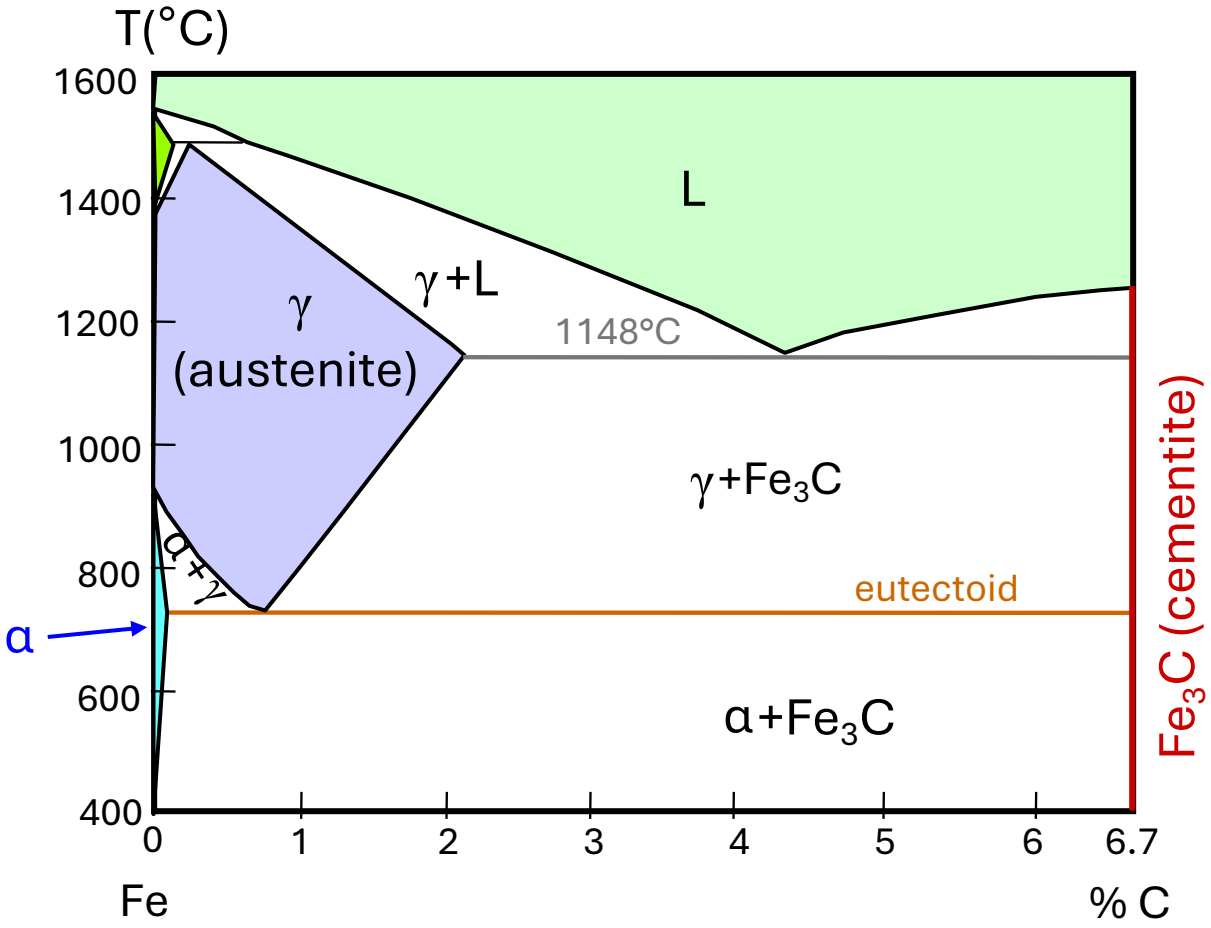
1 peritectic points

Another case: *congruent melting*

- **Liquid ↔ solid without any change in composition**
- Much nicer from a synthesis standpoint…No coring or secondary phase formation

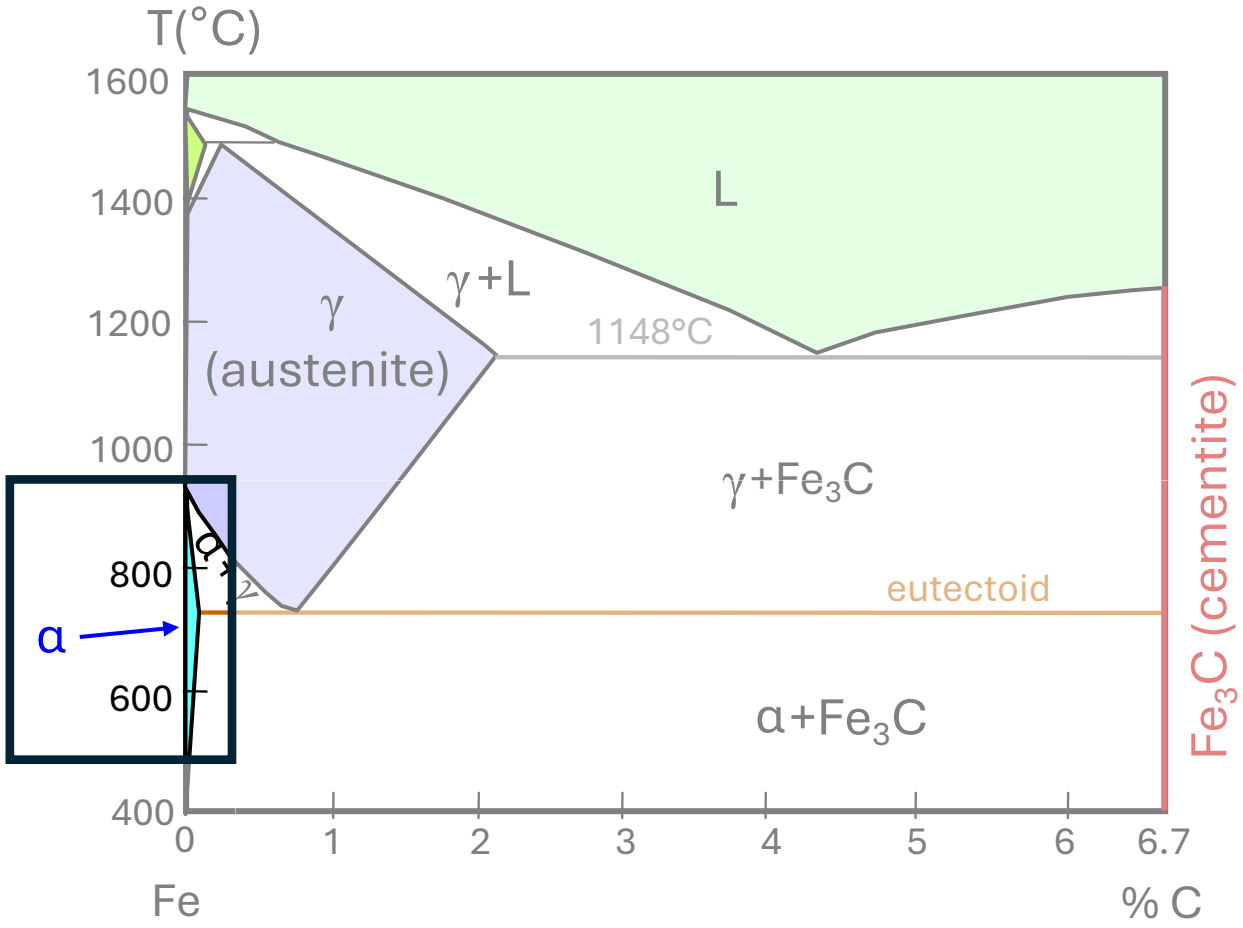
A special phase diagram: steel (Fe-C)





A special phase diagram: steel (Fe-C)



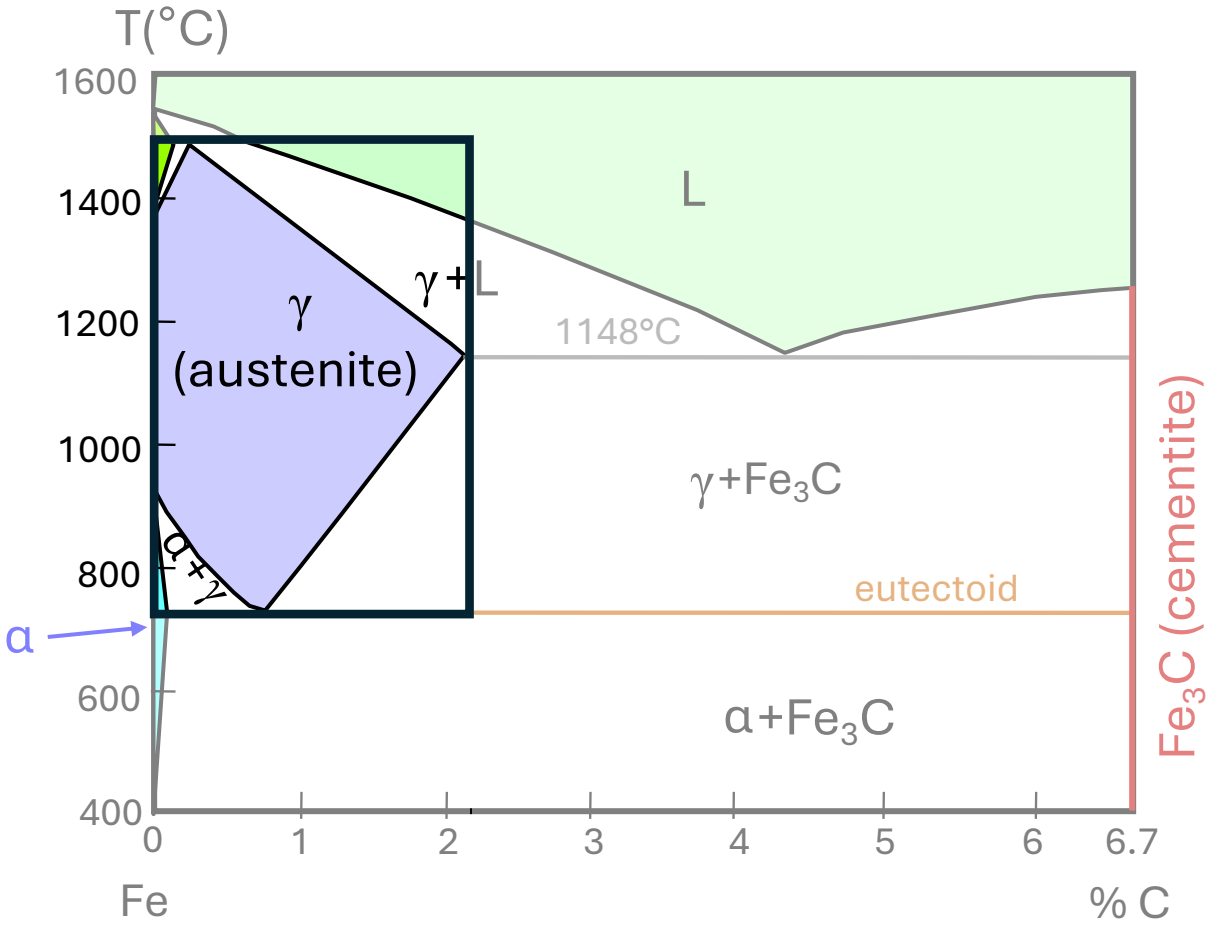


Ferrite (α) is BCC, relatively weak, and often used in magnets

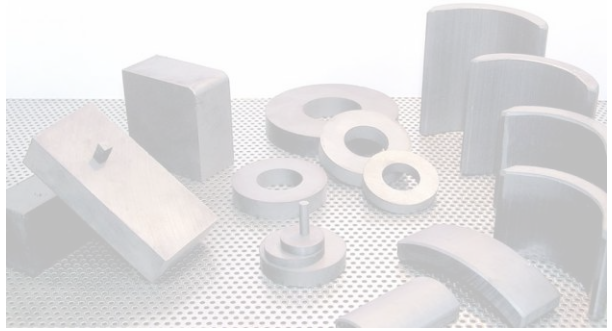


A special phase diagram: steel (Fe-C)





Ferrite (α) is BCC, relatively weak, and often used in magnets

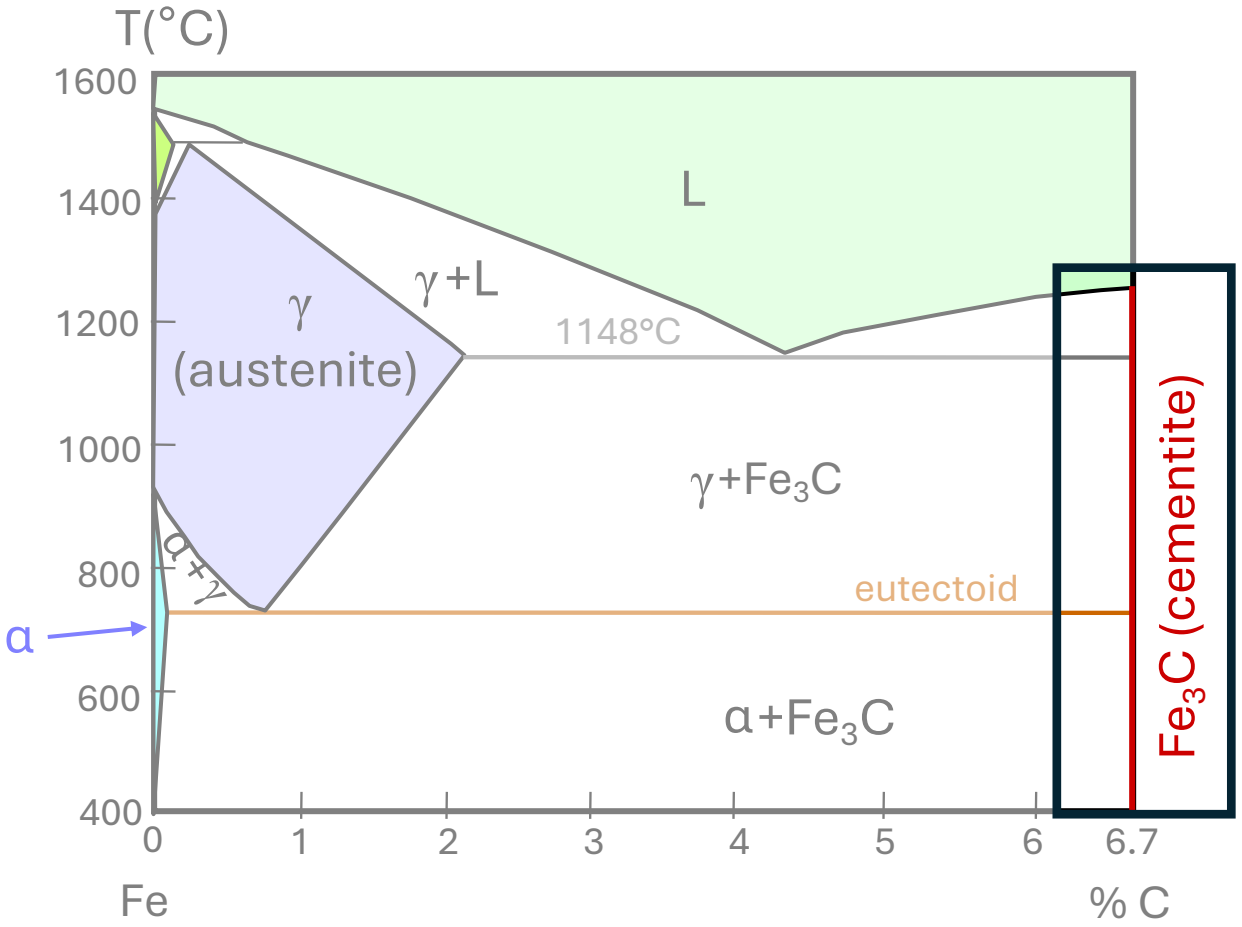




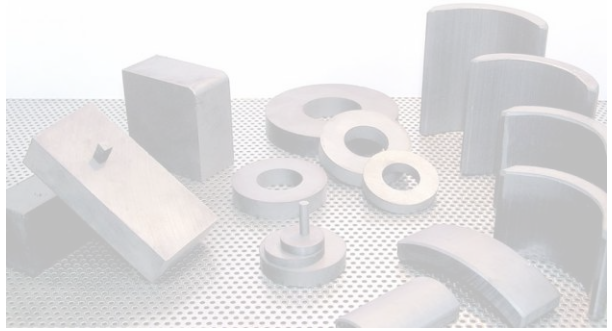
Austenite (γ) is FCC, much stronger while still being ductile

A special phase diagram: steel (Fe-C)





Ferrite (α) is BCC, relatively weak, and often used in magnets





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Cementite (Fe_3C) is hard but very brittle – not used on its own



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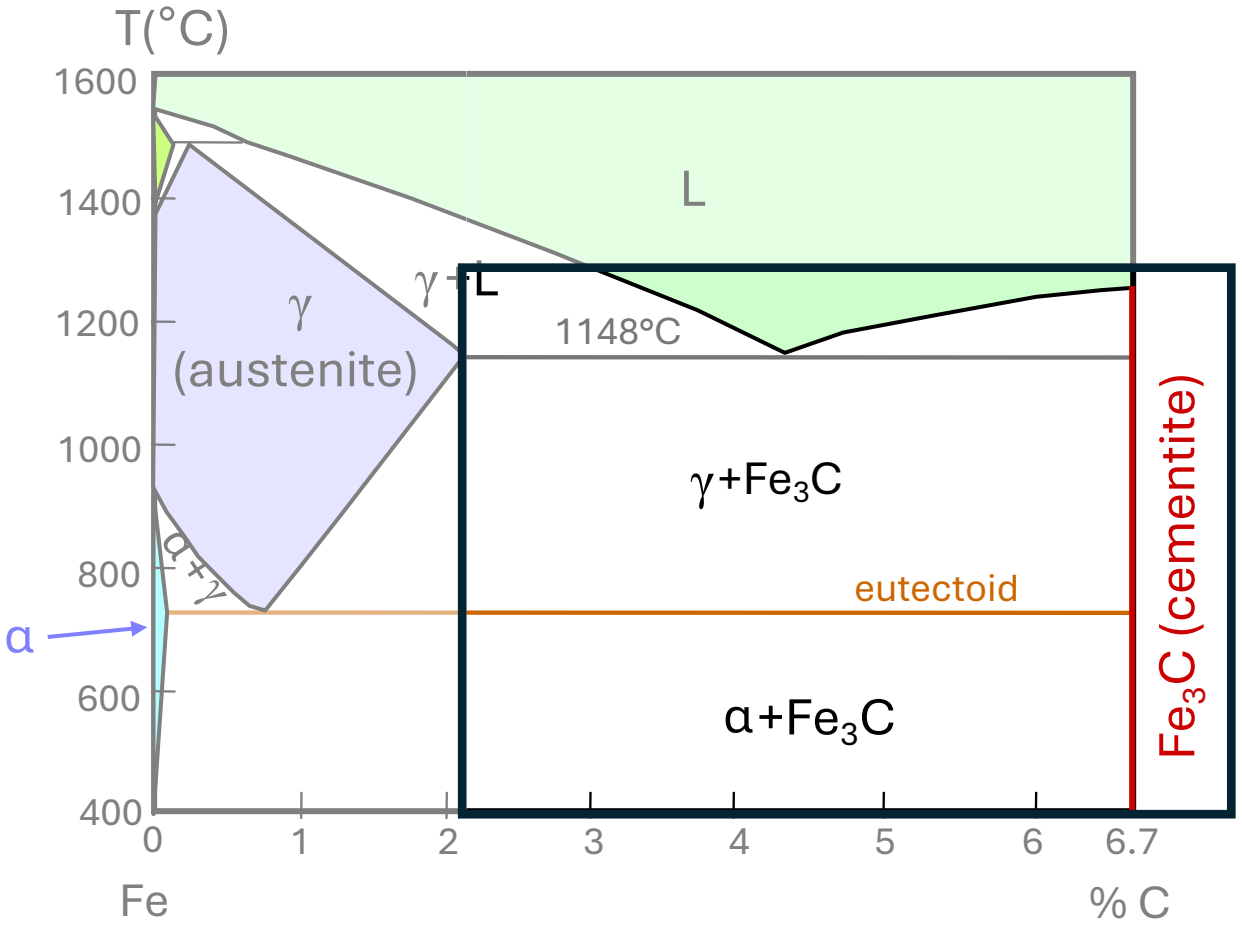

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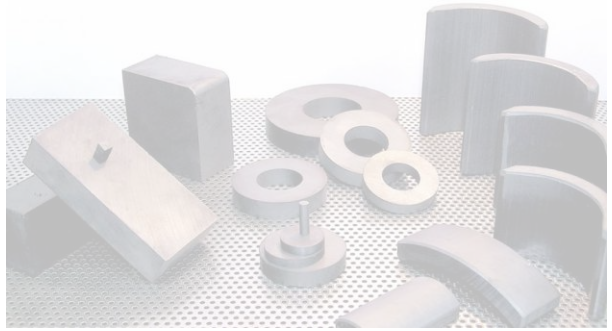




Austenite (γ) is FCC, much stronger while still being ductile

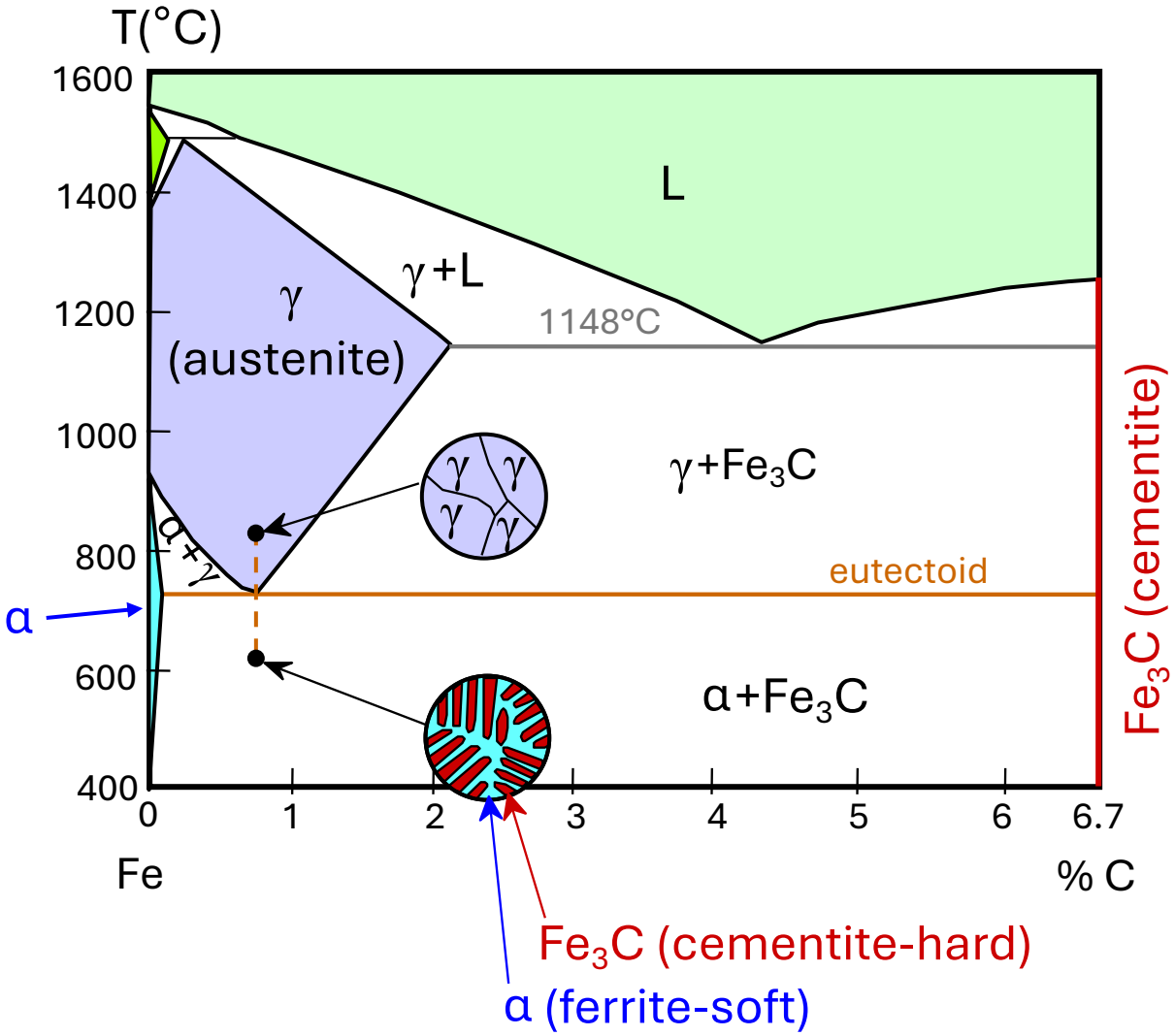
Cementite (Fe_3C) is hard but very brittle – not used on its own



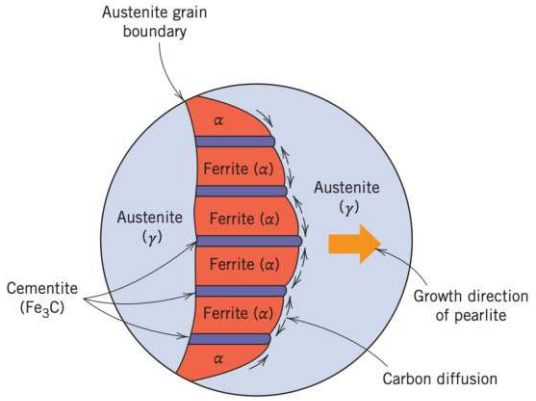
But is used in two-phase mixtures! ←

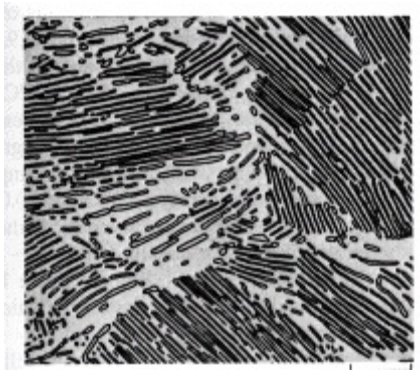
A special phase diagram: steel (Fe-C)





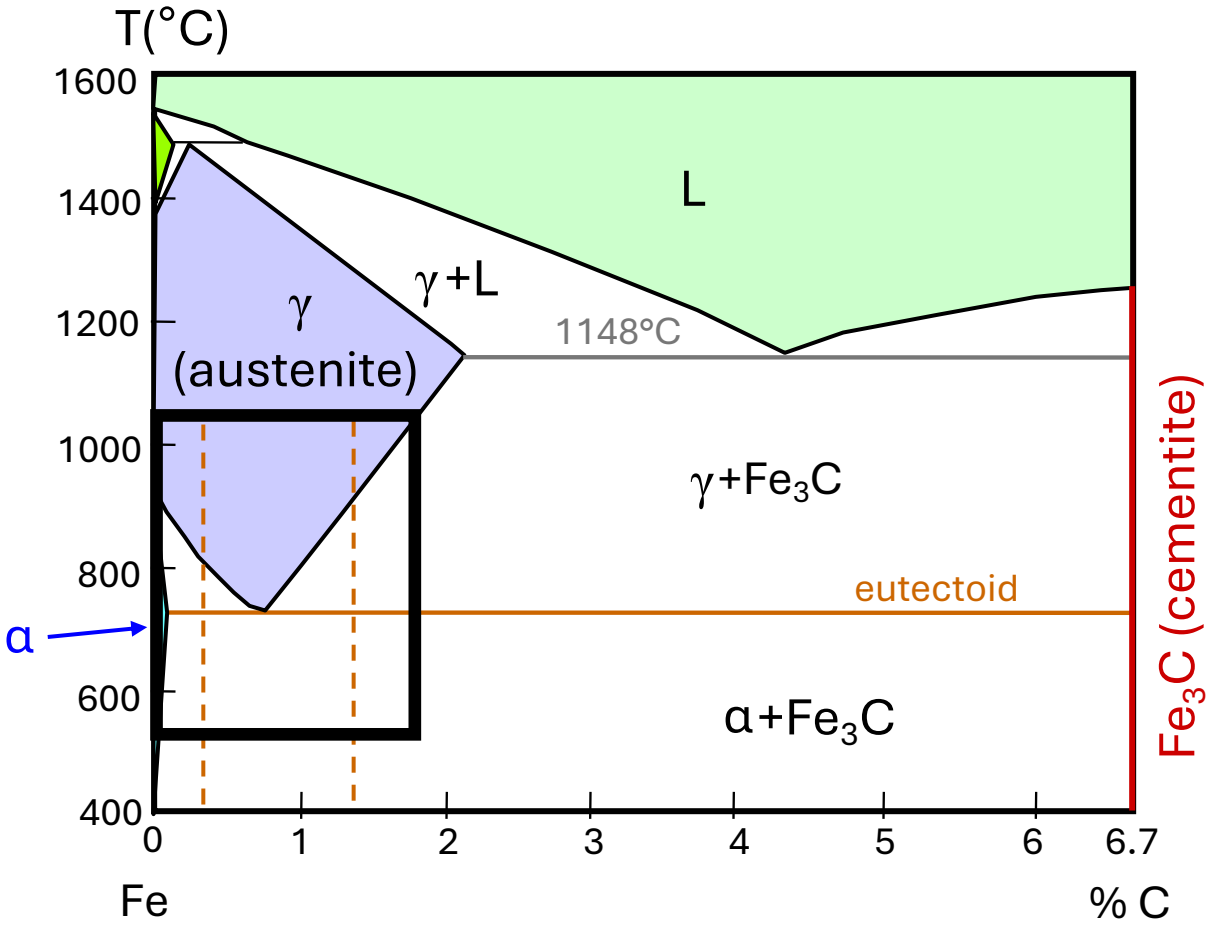
If we cool from austenite through the **eutectoid** into α + **Fe_3C**, we can form **pearlite**: a common steel that **takes advantage of both phases** to achieve high strength and reasonable ductility





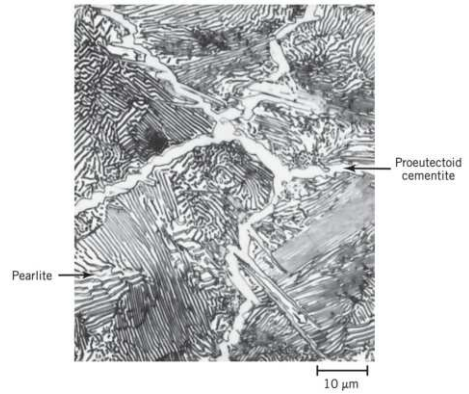
A special phase diagram: steel (Fe-C)



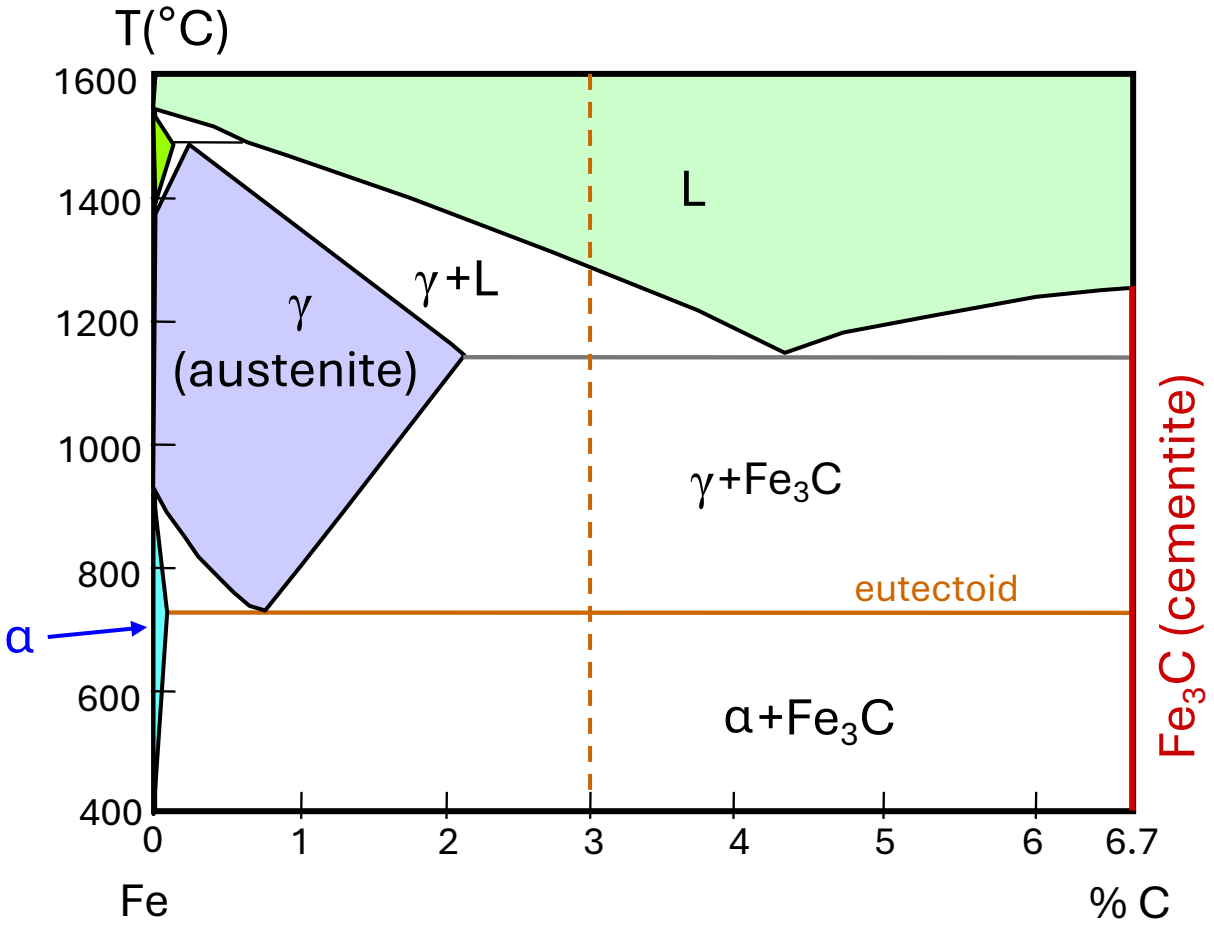


We can tune the properties of our steel by cooling at different composition, rates, *etc.*





An example problem



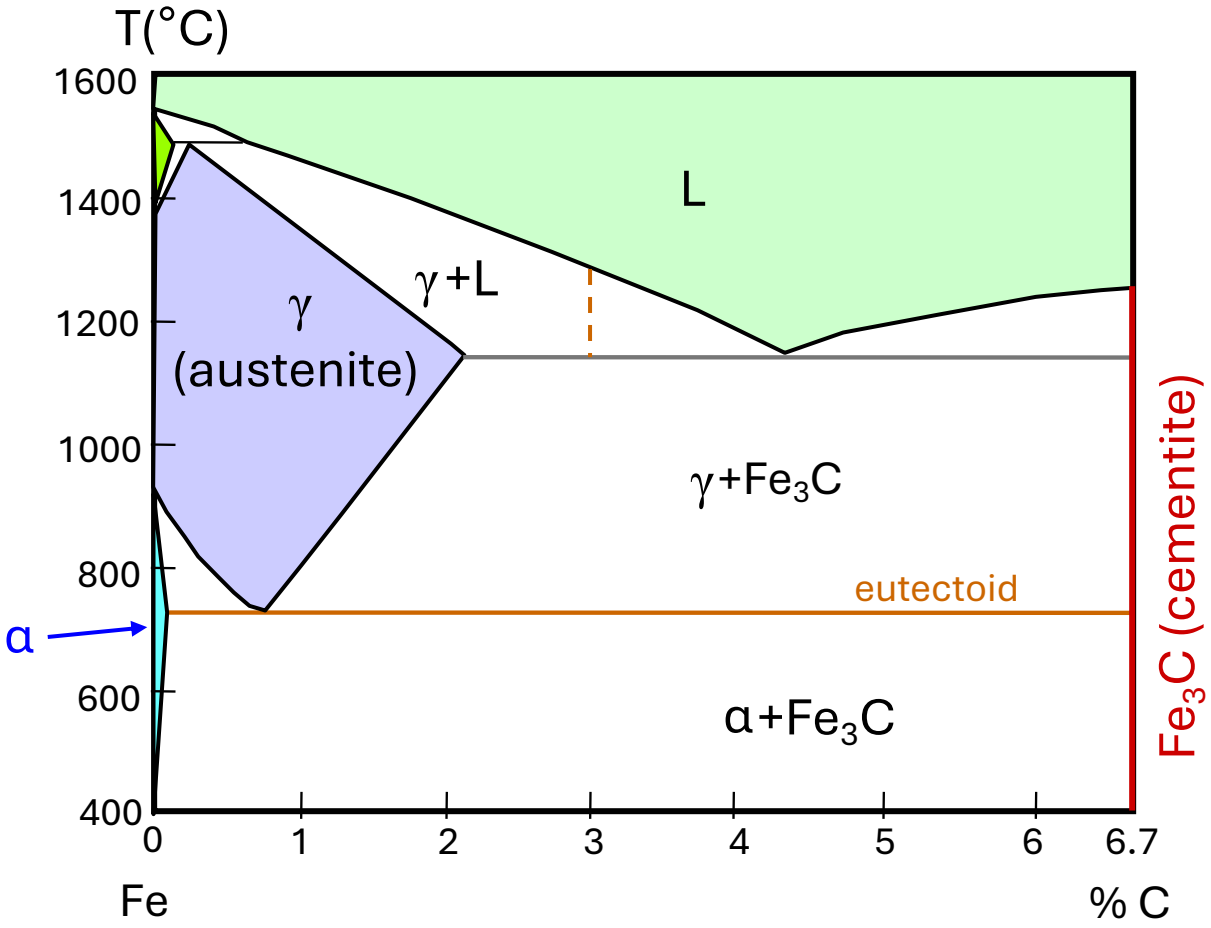
Suppose we melt a mixture of **97% Fe and 3% C** by heating it to **1400 °C.**

Then, we **slowly cool** the melt to room temperature.

What is the order of solid phases that will appear?

How will their composition change with cooling?

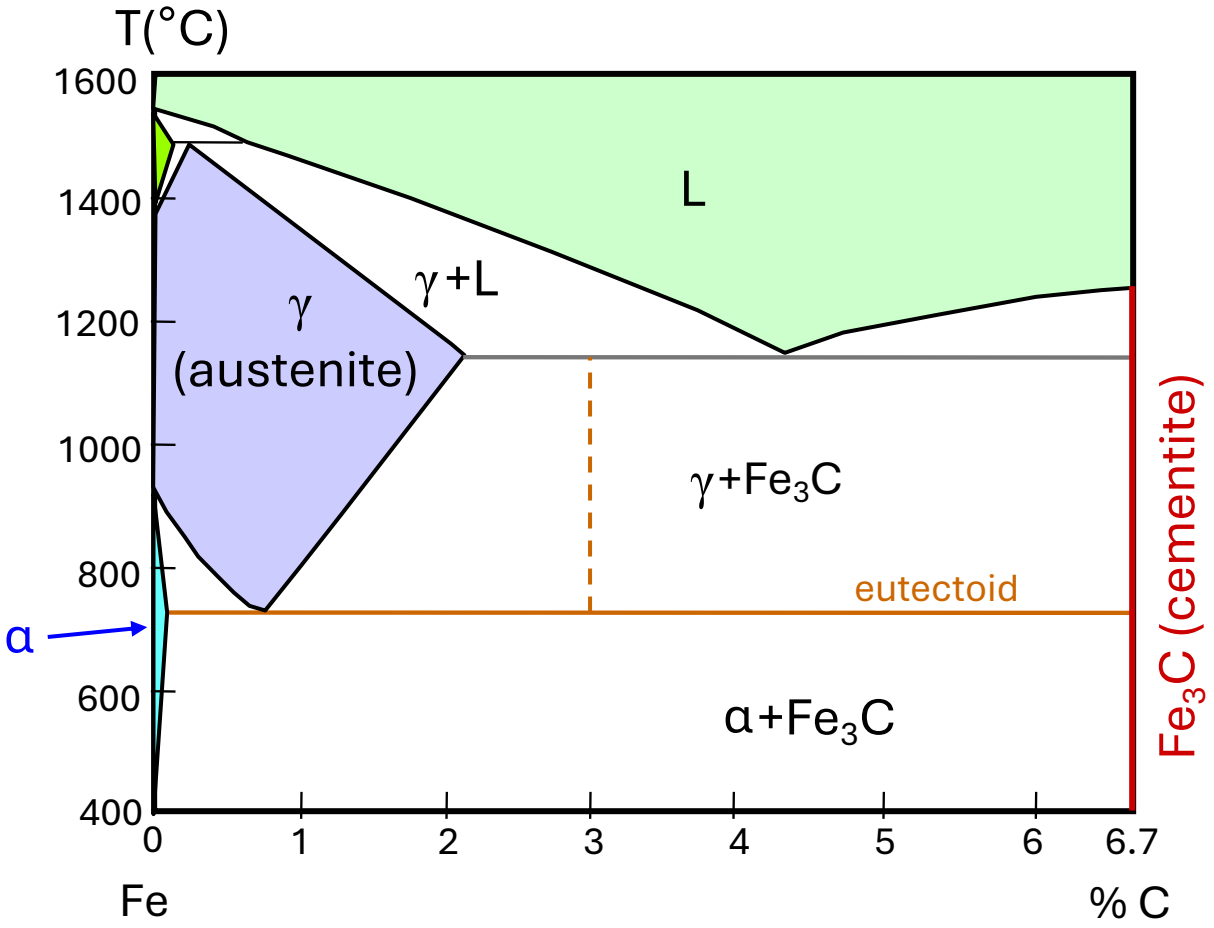
An example problem



Stage 1) 1300 °C → 1150 °C

- Austenite (γ) forms
- It becomes rich in C upon cooling

An example problem



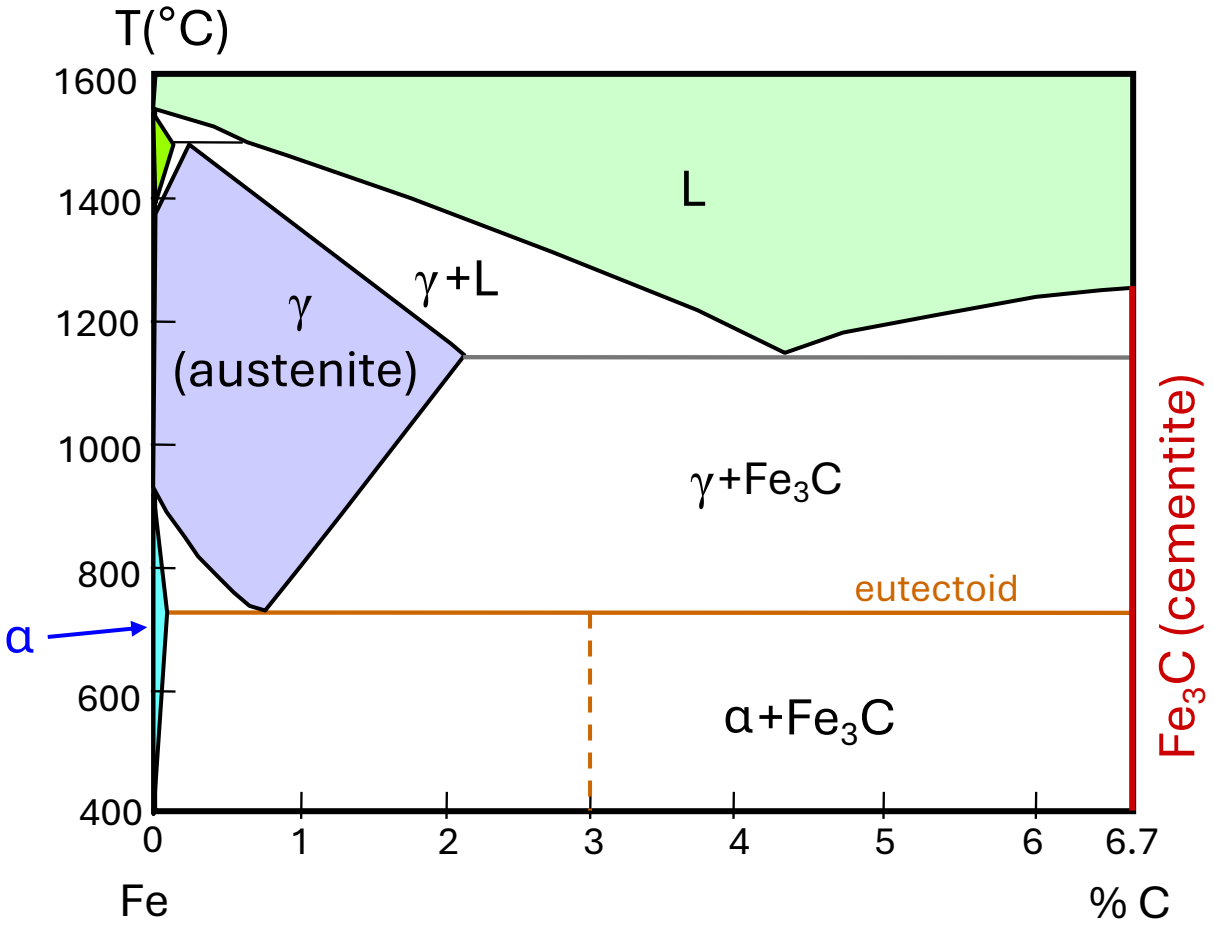
Stage 1) 1300 °C → 1150 °C

- Austenite (γ) forms
- It becomes rich in C upon cooling

Stage 2) 1150 °C → 750 °C

- Cementite (Fe_3C) forms
- Austenite loses C upon cooling

An example problem



Stage 1) 1300 °C → 1150 °C

- Austenite (γ) forms
- It becomes rich in C upon cooling

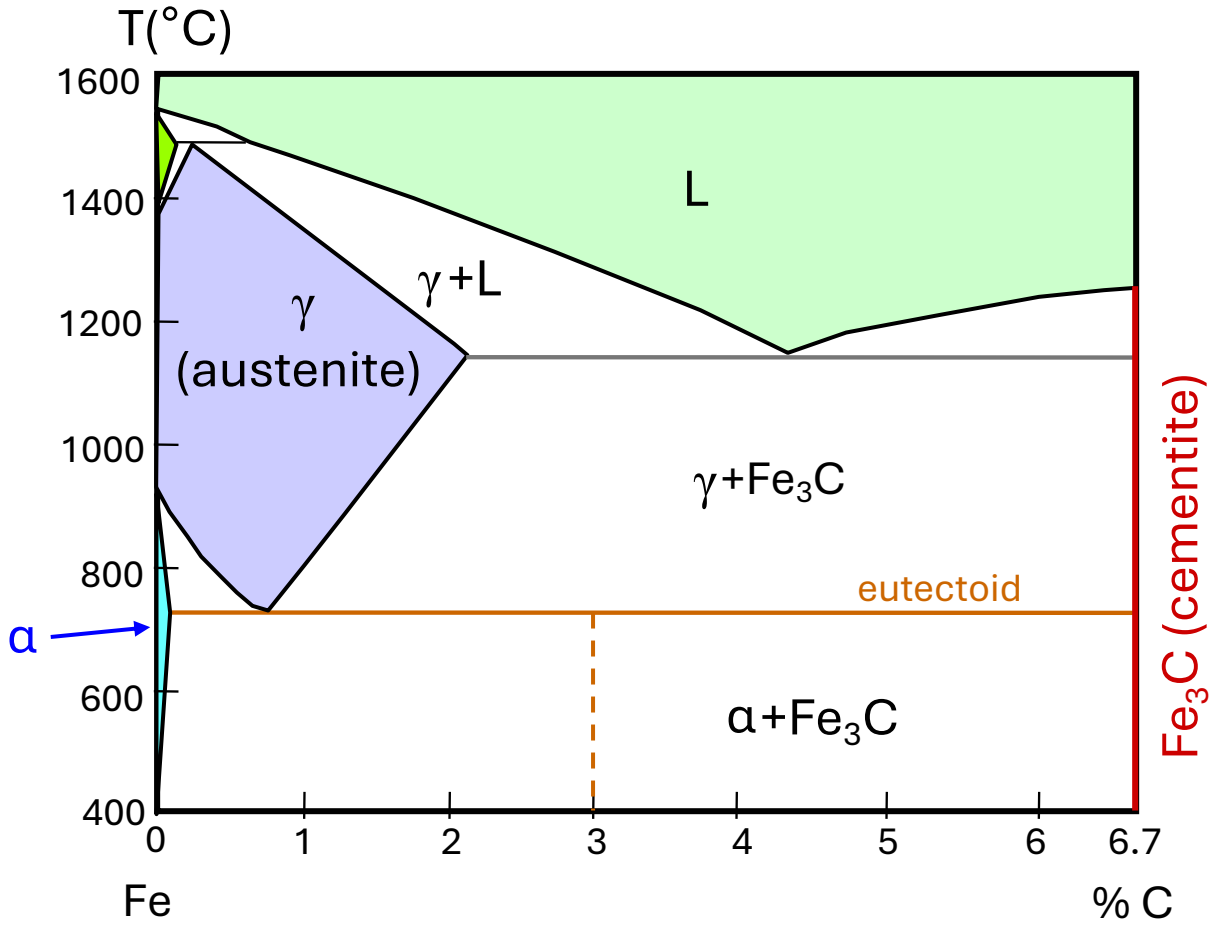
Stage 2) 1150 °C → 750 °C

- Cementite (Fe_3C) forms
- Austenite loses C upon cooling

Stage 3) 750 °C → RT

- Ferrite (β) forms
- Compositions mostly unchanged

An example problem



What is the weight % if each phase in the final product?

$$W_{Fe_3C} = \frac{C_\alpha - C_0}{C_\alpha - C_{Fe_3C}} = \frac{0 - 3}{0 - 6.7}$$

$$W_{Fe_3C} = 0.448$$

$$W_\alpha = 0.552$$

Phase diagrams can have more than two components

Many useful materials have > 2 elements. For example, stainless steel:

Composition	Percentage by weight
Carbon	0.030
Manganese	2.00
Silicon	0.75
Chromium	16.00-18.00
Nickel	10.00-14.00
Molybdenum	2.00-3.00
Phosphorus	0.045
Sulphur	0.030
Nitrogen	0.10
Iron	7.0

What we've learned about phase diagrams still applies, but more difficult to visualize

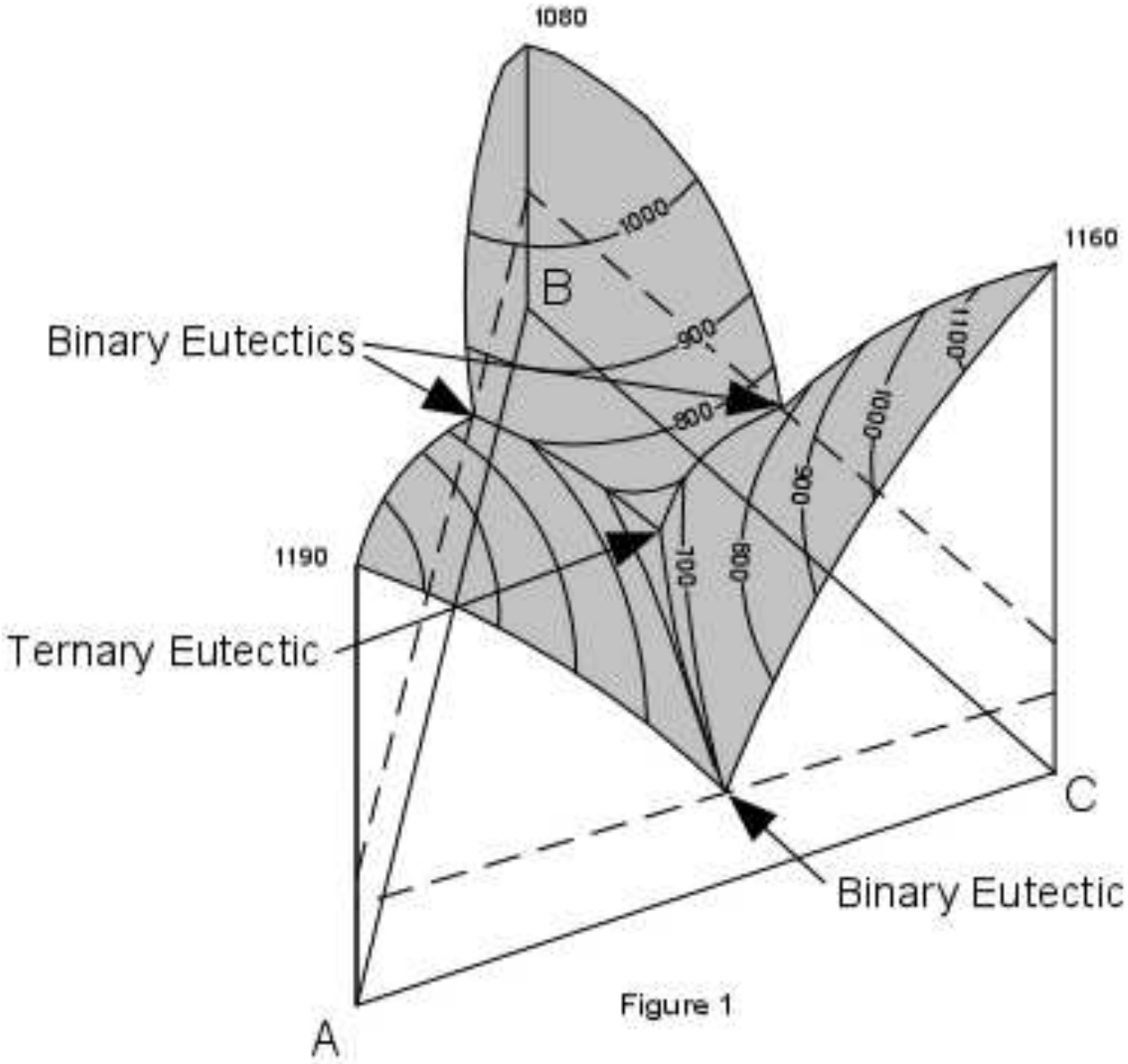
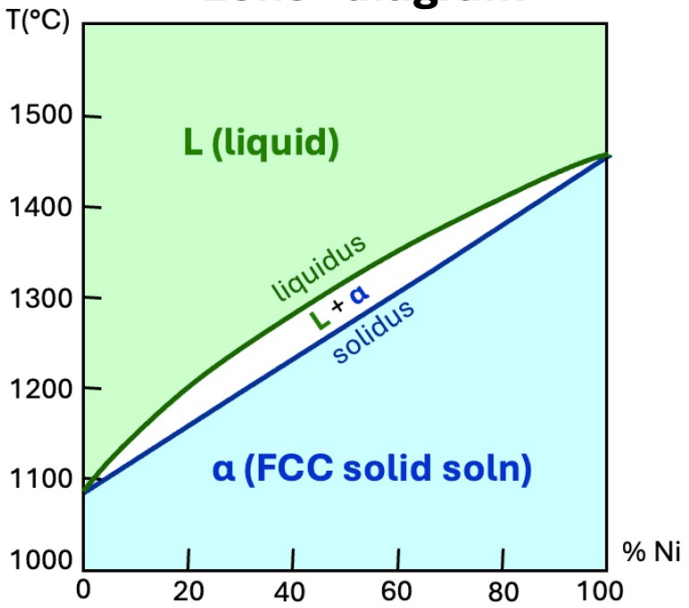


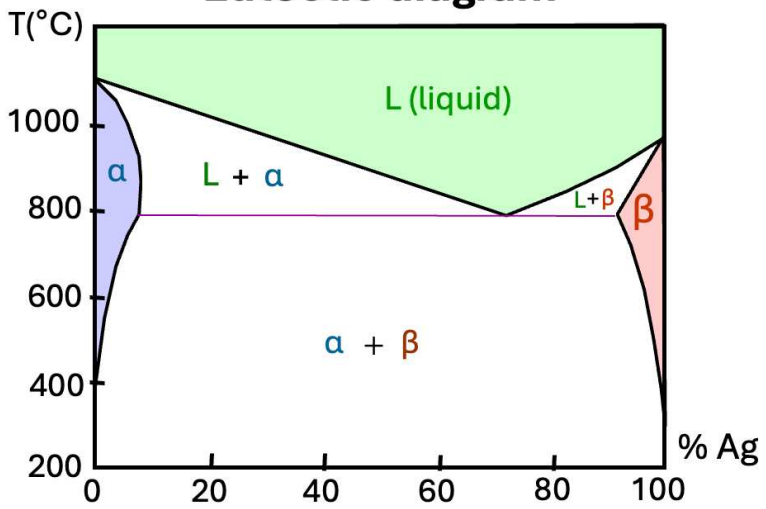
Figure 1

Summary

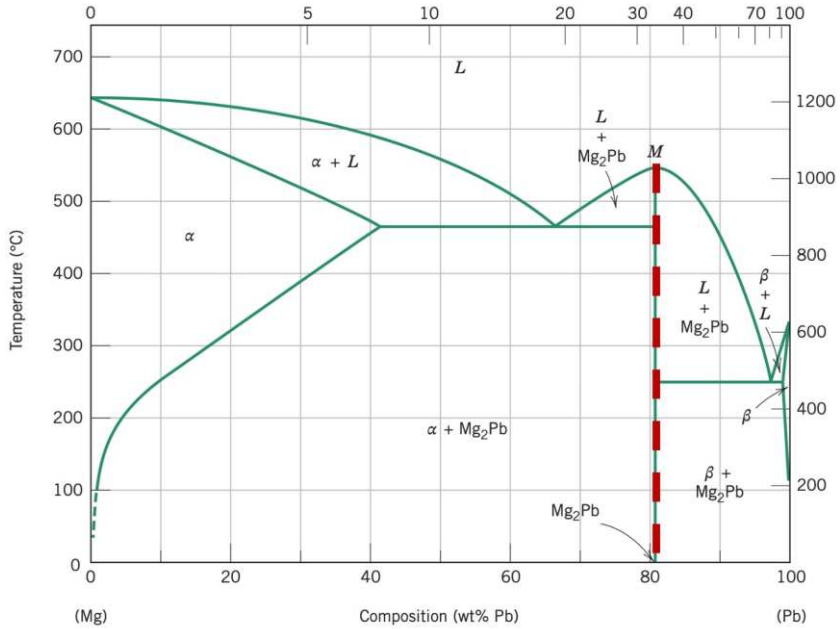
"Lens" diagram

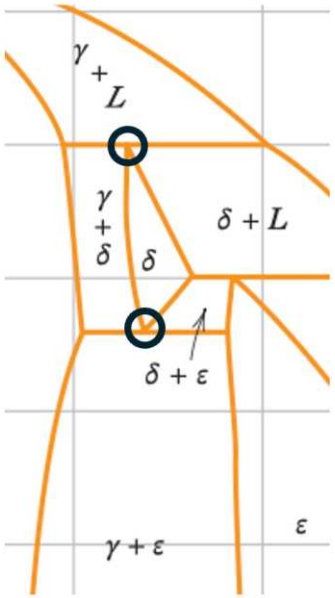


Eutectic diagram



Intermetallic formation





$$\delta \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \gamma + \varepsilon$$

Eutectoid reaction:
One solid solution → Two solid phases upon cooling

$$\delta + L \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \varepsilon$$

Peritectic reaction:
Solid + liquid → one solid solution upon cooling

