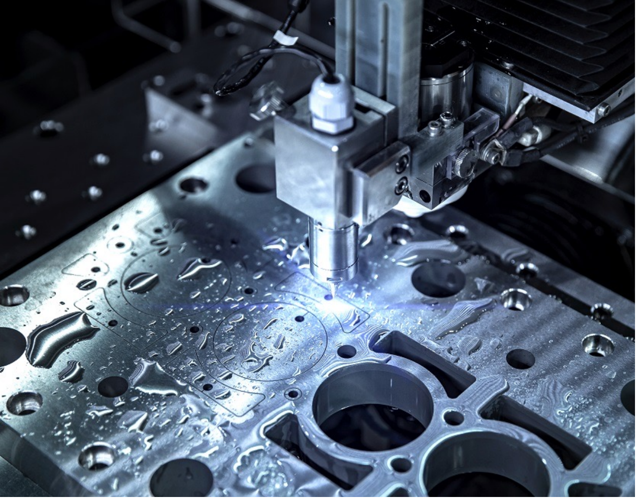
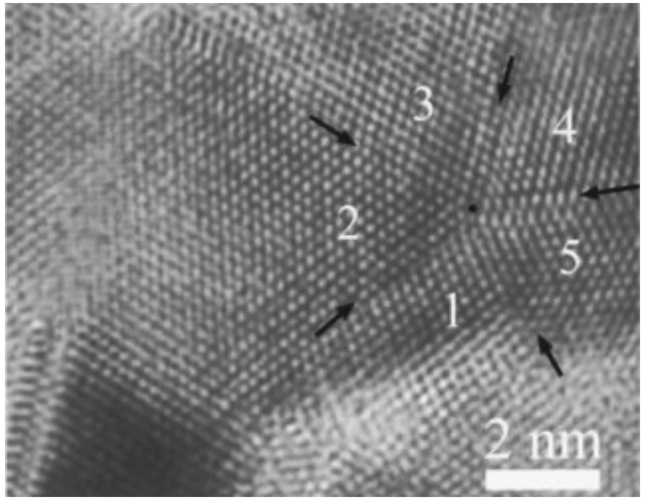




Materials Engineering I (MSE 214)

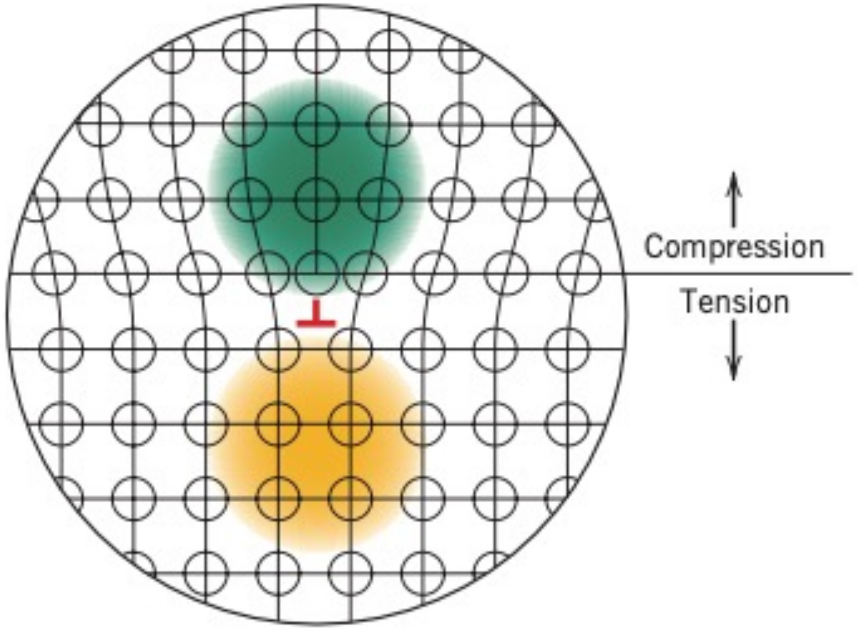
Lecture 9: Metals – Properties and Phase Diagram (II)

Prof. Daryl W. Yee

Email: (daryl.yee@epfl.ch)

EPFL

Recap: Dislocations create a strain field



Dislocations have a strain field around them

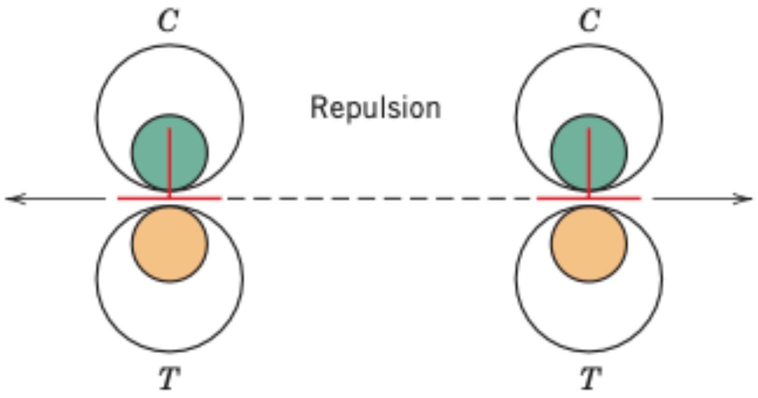
The extra half-plane of atoms distorts the surrounding lattice

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)

Implication:

Dislocation mobility is impacted by its surrounding strain field

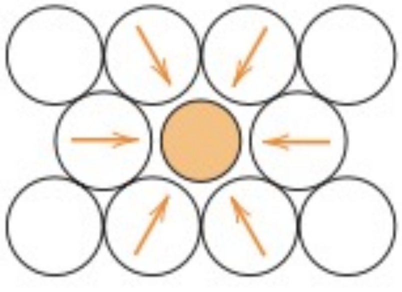


Recap: Solid-solution strengthening

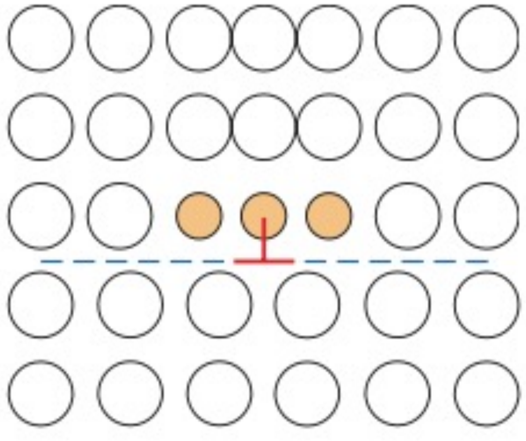
Size mismatch of atoms strains the lattice

Strain field between dislocation and substitutional atoms can interact

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



→



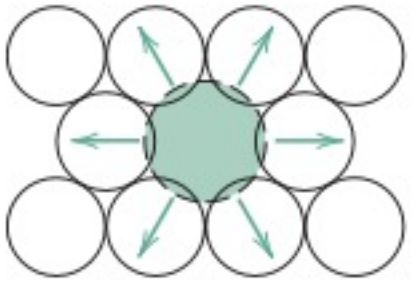
Effect 1

Pins the dislocation

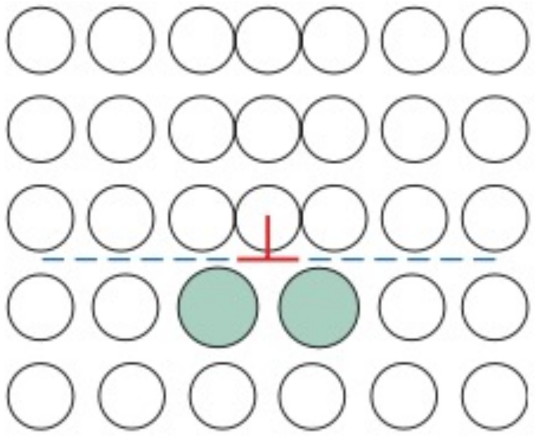
↓

Harder to start moving

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



→



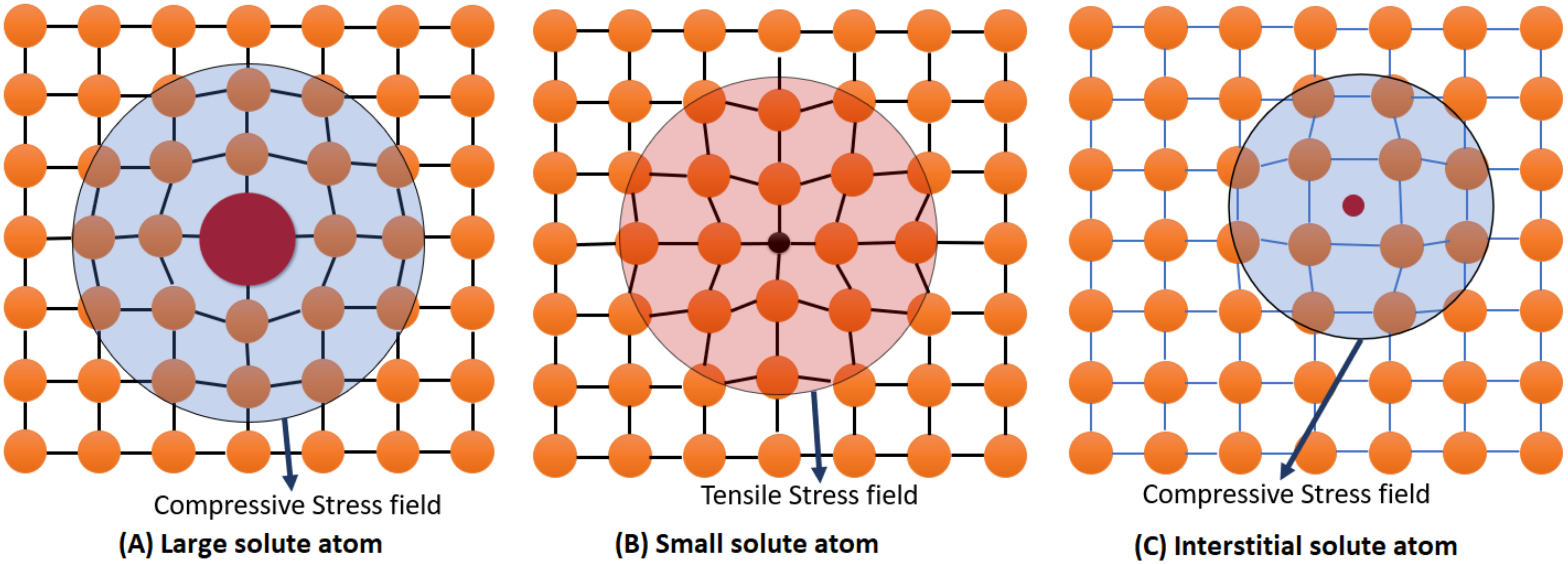
Effect 2

Strain field impedes dislocation movement

↓

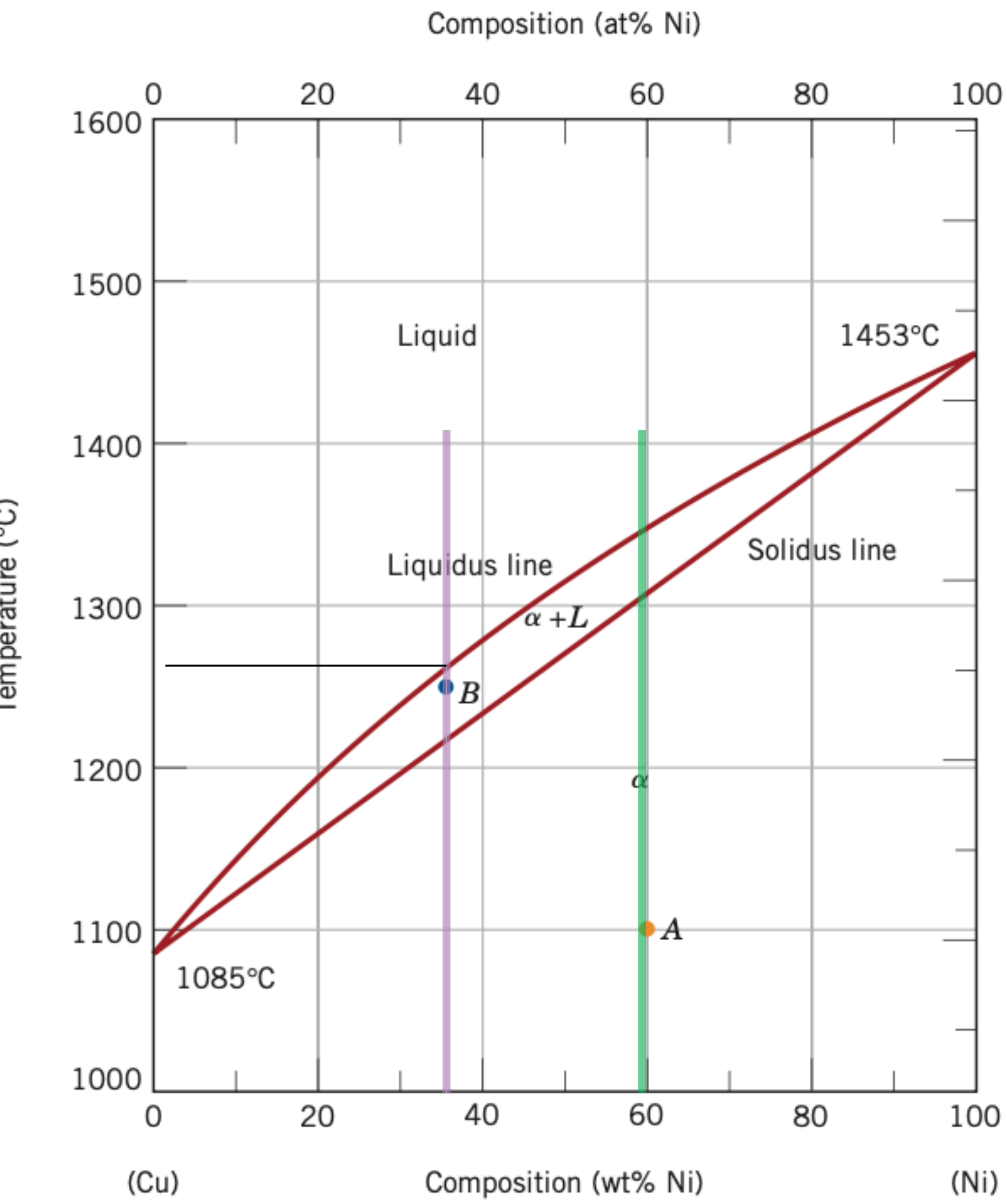
Harder to keep moving

Recap: Solid-solution strengthening



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

Recap: Binary phase diagrams



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

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

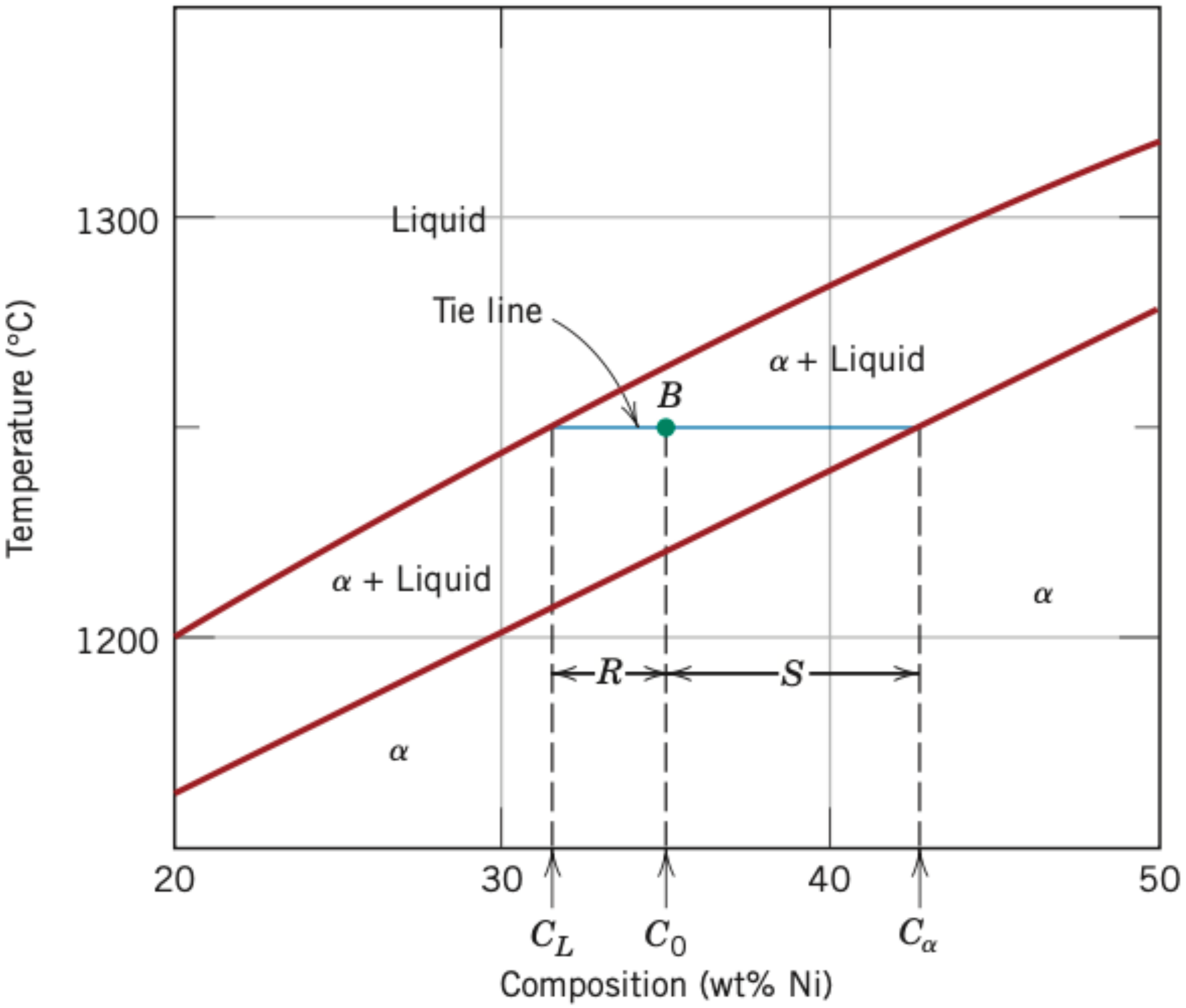
Example 4:
$Cu_{65}Ni_{35}$

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

Recap: Tie lines to determine phase compositions



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

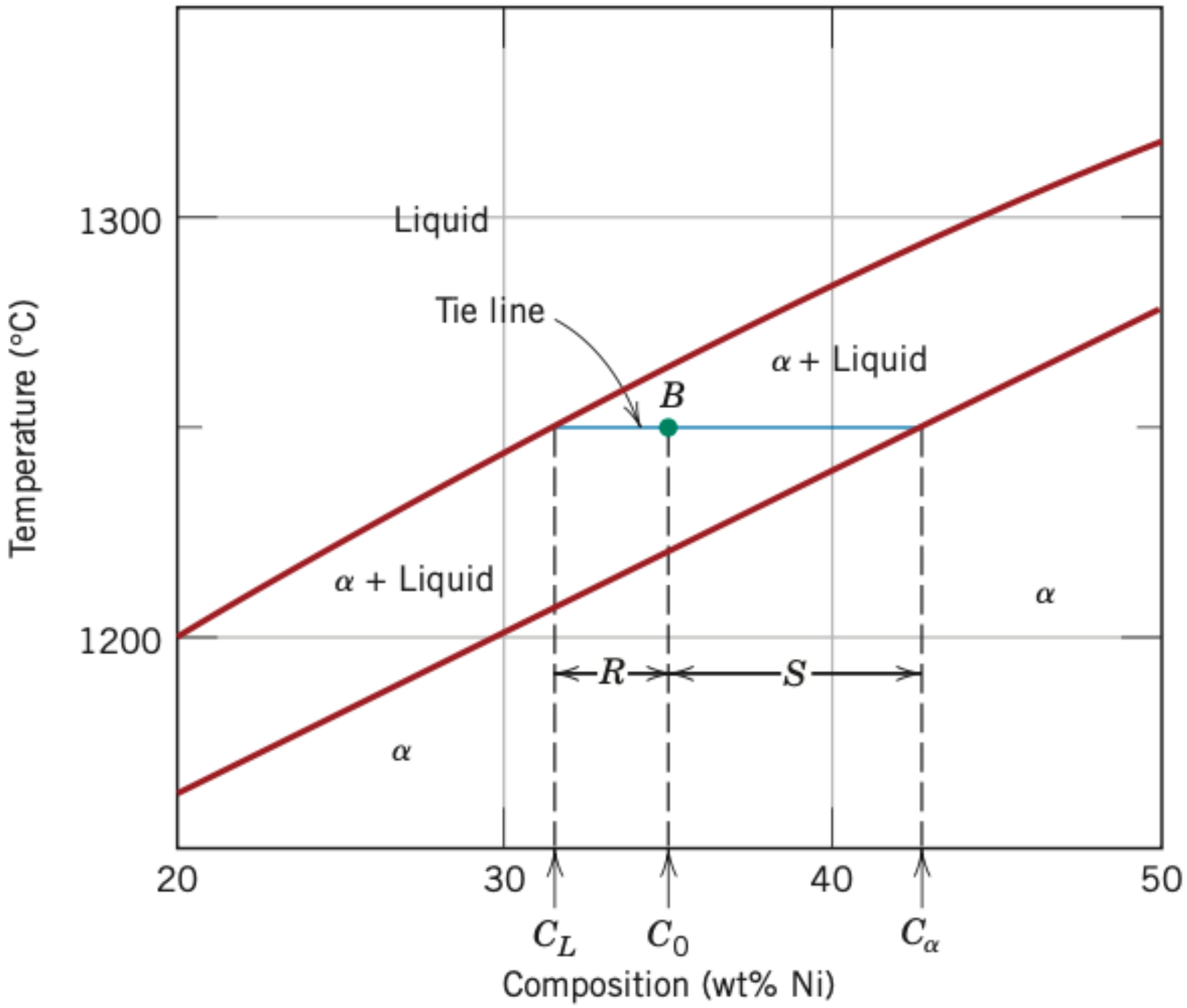
Note: This horizontal line is called a tie line

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) = $Cu_{57.5}Ni_{42.5}$

Recap: Lever rule to determine phase amounts



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

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

Precise: Use the compositions on the x axis

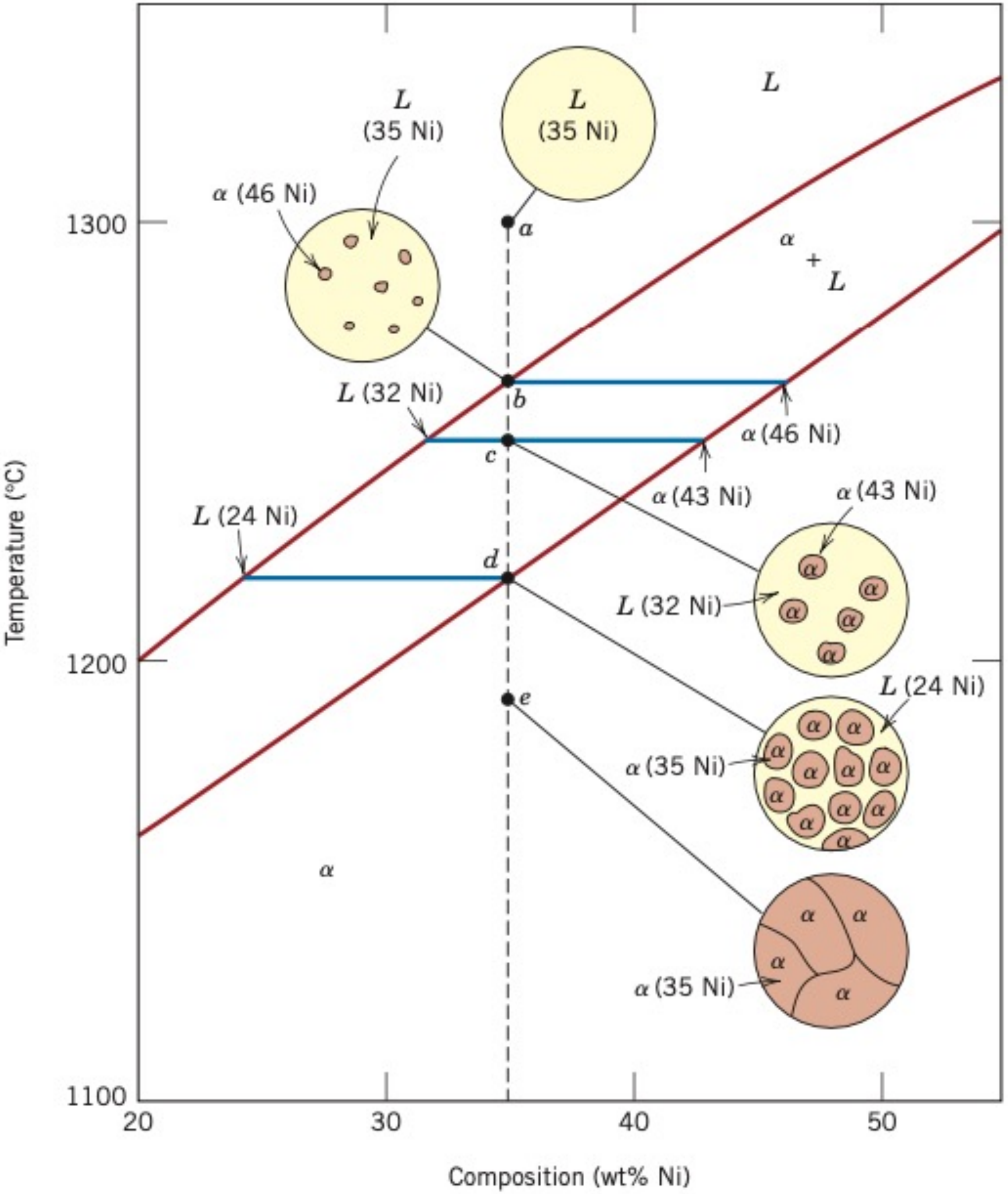
Only need to use one of the element values to calculate the composition

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!

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

Is this a fair assumption?

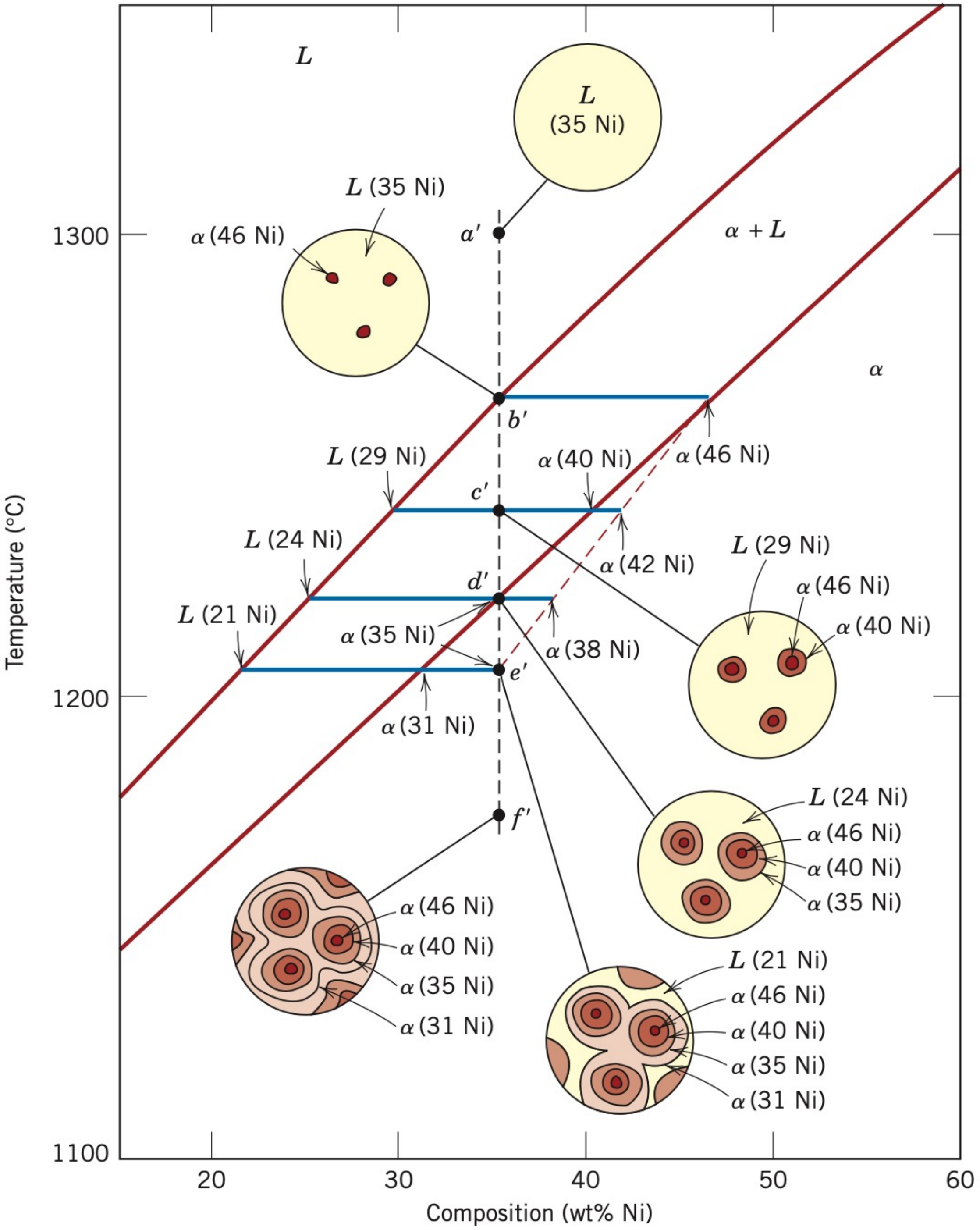
Diffusion needs to occur in:

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



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

Outcome of rapid cooling = Inhomogeneous grain

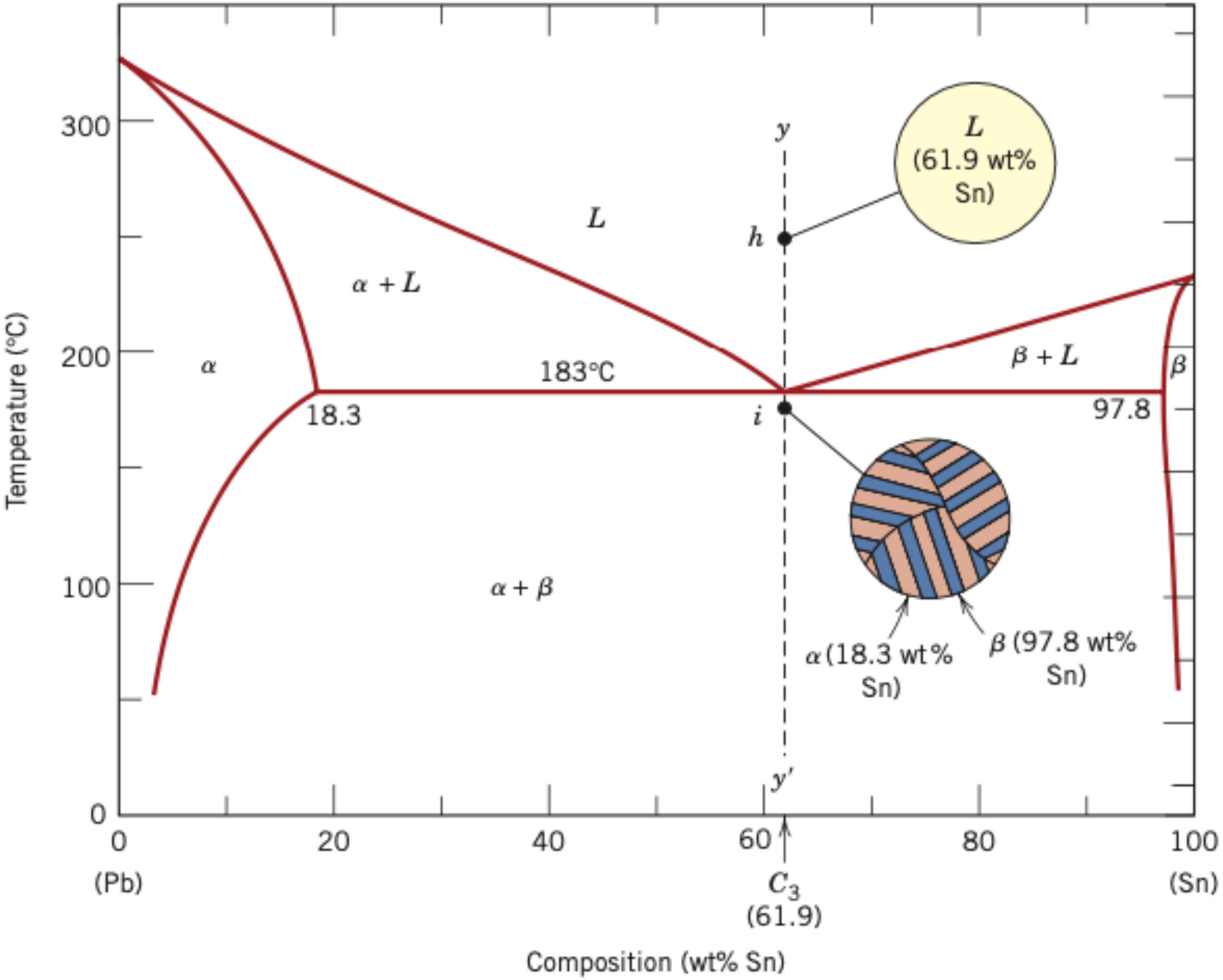
Cored structure

Implication 1: Changes to mechanical properties

Implication 2: Reduced temperature stability

*For simplicity

Recap: Eutectic

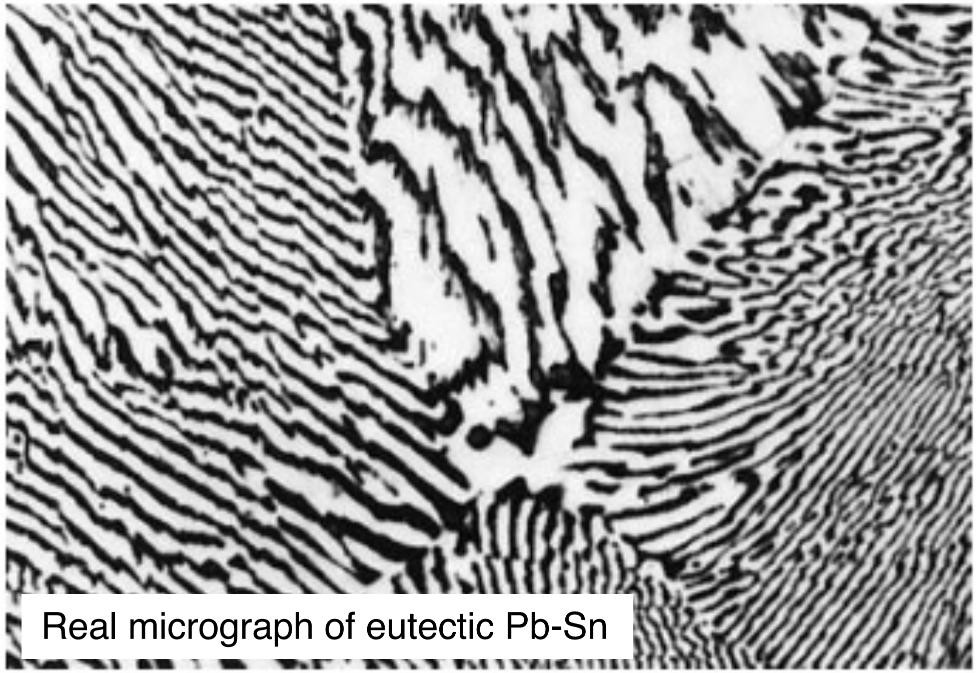


Important things about eutectics:

Lowest melting temperature

No L + solid region

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

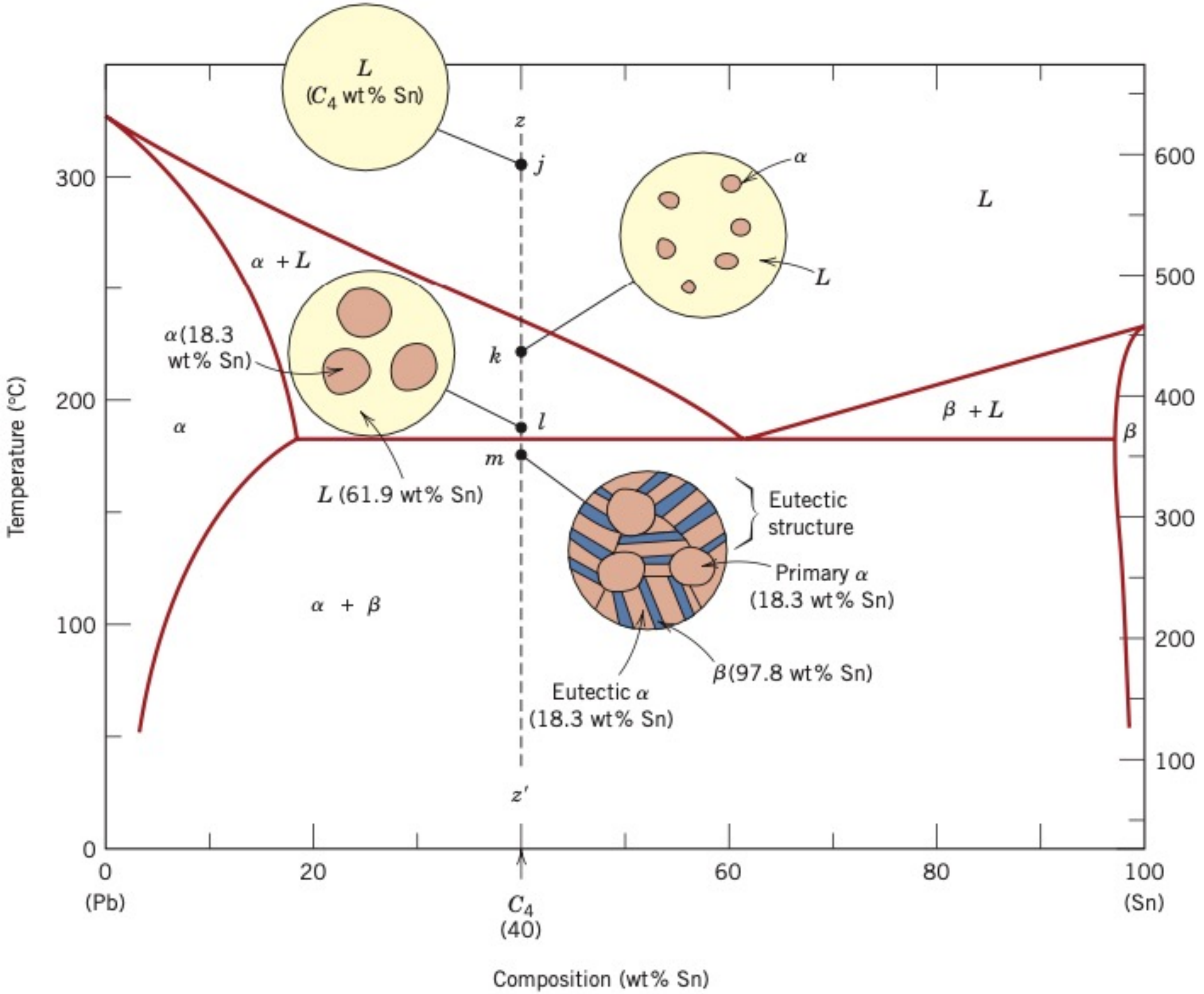


Real micrograph of eutectic Pb-Sn

Week 9 Learning Objectives

- **Understand how to calculate phase fractions in hypo/hypereutectic metals**
- **Understand what a slip system is**
- **Understand why BCC metals have a ductile to brittle transition temperature**
- **Understand what martensite is and why it is strong and brittle**
- **Understand what a TTT diagram is and how to use it**
- **Understand what a CCT diagram is and how to use it**

Calculating phase fractions in hypo/hypereutectics



How much α and β phase is there?

Let's introduce a new term:
microconstituent

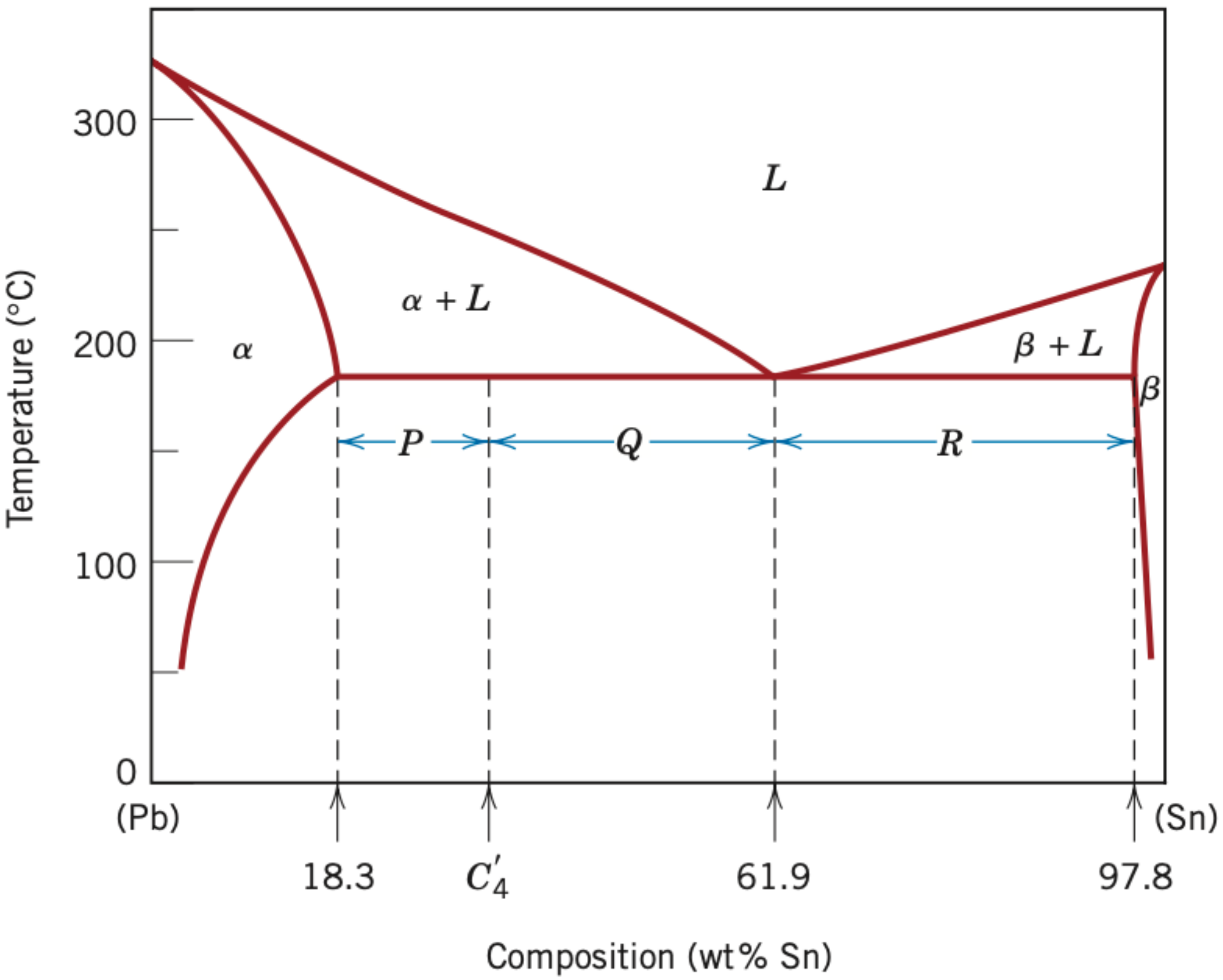
↓

Element of the microstructure that has a distinct and characteristic structure

At point *m*, we have two microconstituents: primary α and the eutectic structure

Important: Each microconstituent has a different amount of the α and β phase

Calculating phase fractions in hypo/hypereutectics



Let us consider an alloy of composition C_4':

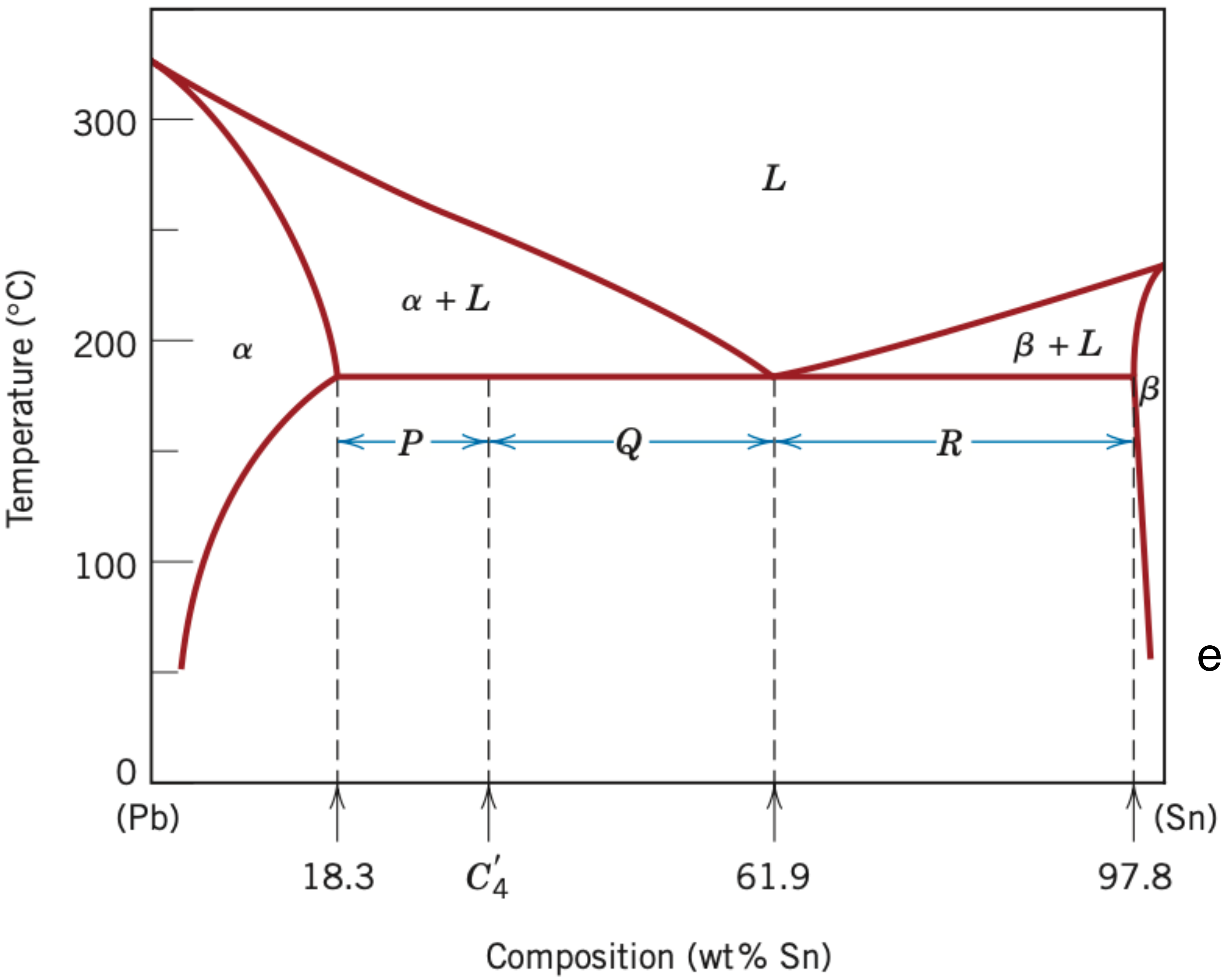
The fraction of the eutectic microconstituent W_e is the same as the fraction of liquid W_L from which it transforms

$$W_e = W_L = \frac{P}{P+Q}$$

The fraction of primary α, $W_{\alpha'}$ is just the fraction of the α phase the existed prior to the eutectic transformation

$$W_{\alpha'} = \frac{Q}{P+Q}$$

Calculating phase fractions in hypo/hypereutectics



Let us consider an alloy of composition C_4':

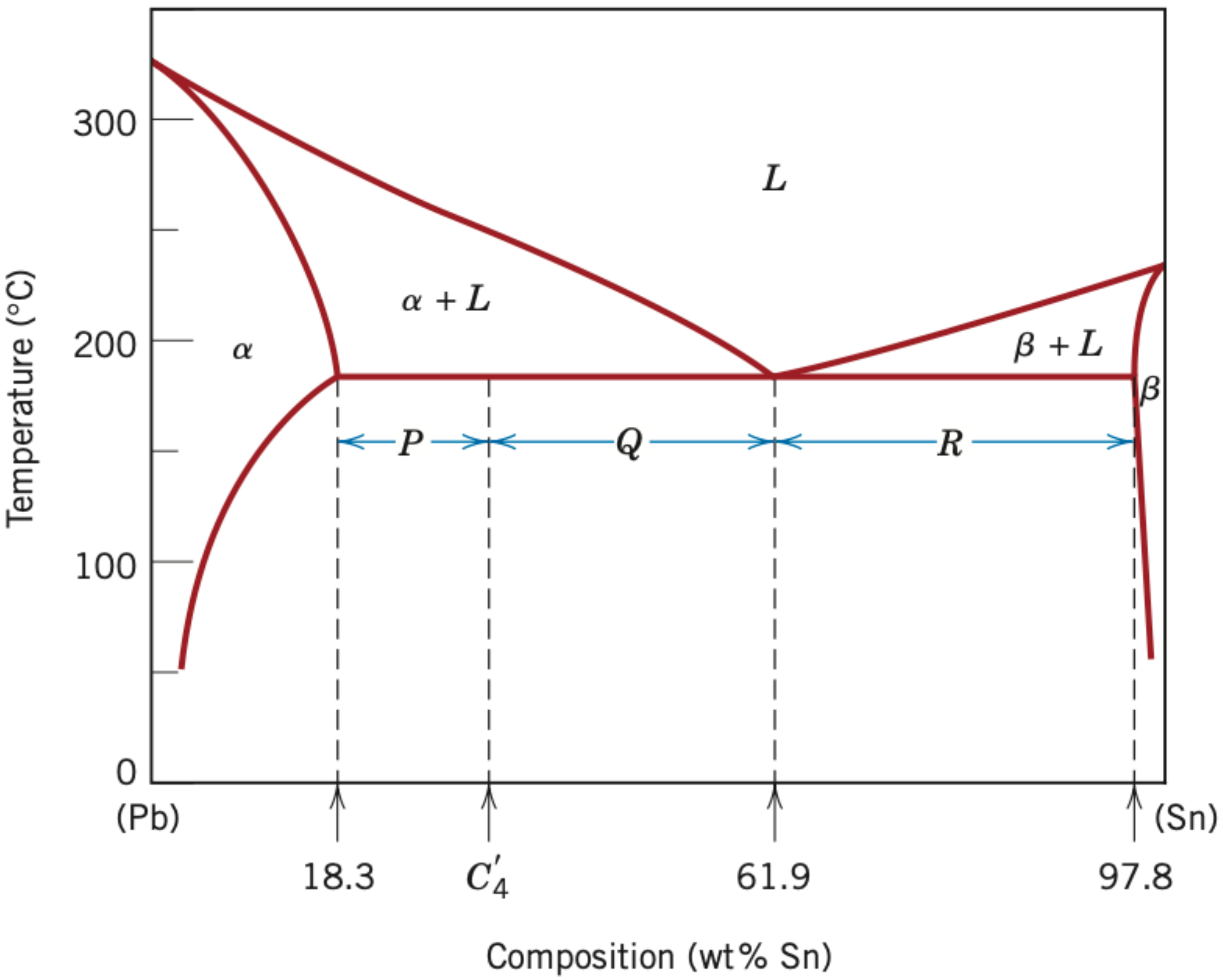
The fraction of α in the eutectic, $W_{\alpha,e}$ is determined by a tie line that extends across the entire α + β phase field from $C_{eutectic}$

$$W_{\alpha,e} = \frac{R}{P+Q+R}$$

Important: This is the fraction of α in the eutectic phase. Not the fraction of α in the alloy

The fraction of α from the eutetic in the alloy as a whole is $W_{a,e}$ x W_e

Calculating phase fractions in hypo/hypereutectics



Let us consider an alloy of composition C_4':

The fraction of the total α, W_α is determined by the a tie line that extends across the entire $\alpha + \beta$ phase field

$$W_\alpha = \frac{Q+R}{P+Q+R}$$

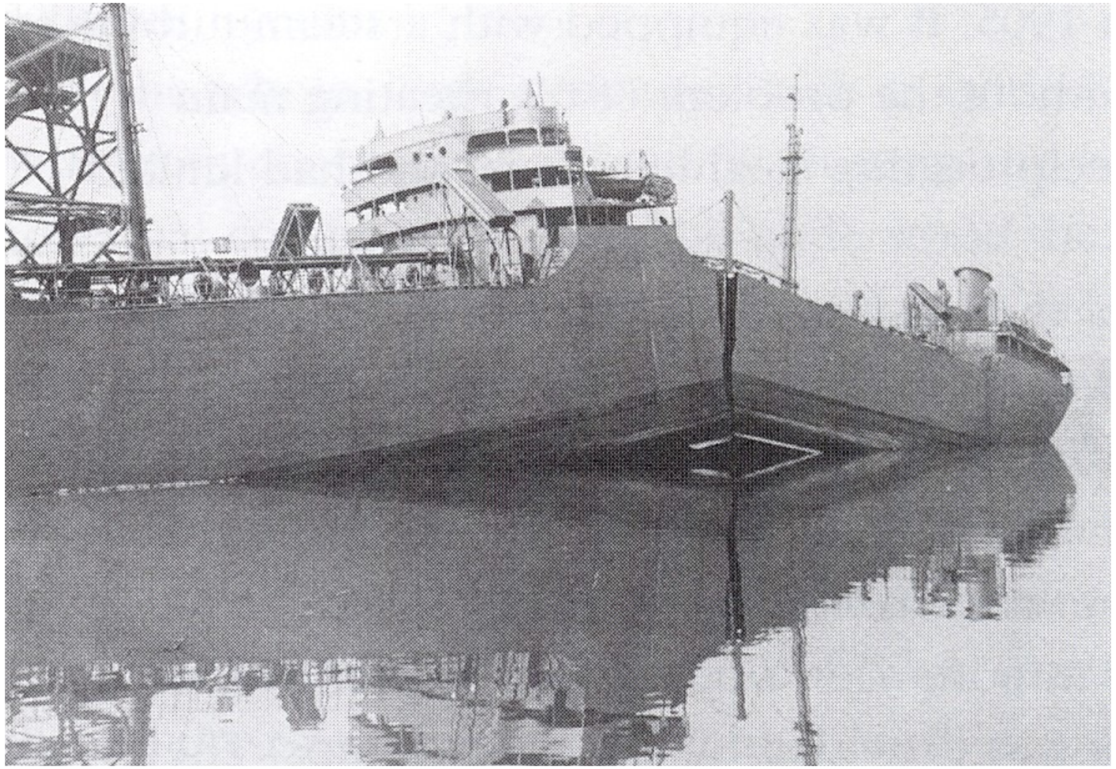
Same goes for total β, W_β

$$W_\beta = \frac{P}{P+Q+R}$$

Today's Focus: Temperature and Metal

Why do we do this in sword making?

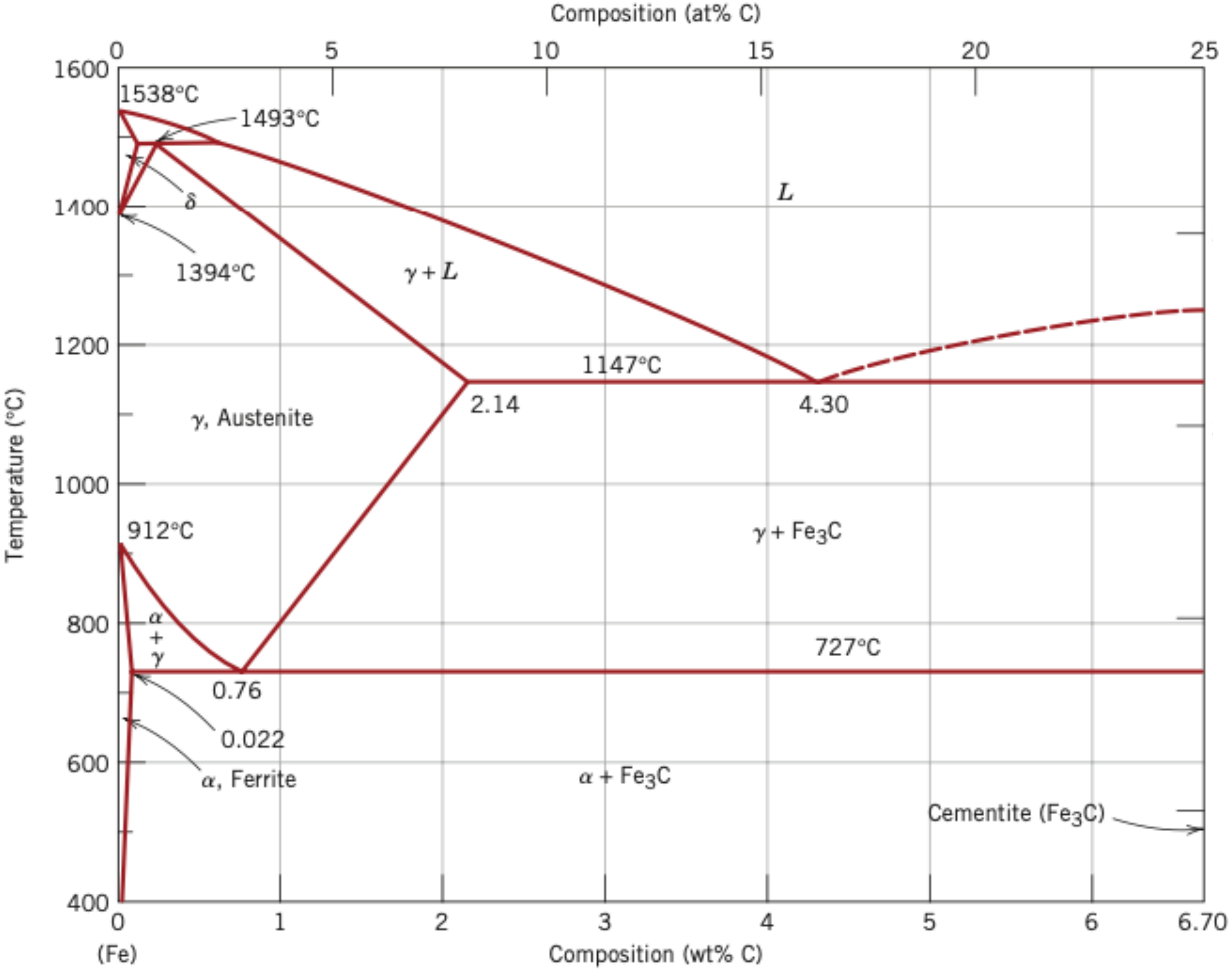
Why did this ship fracture in two?



Examples where we see the impact of temperature on the properties of metals

To understand both phenomena, we need to look at steel

Steel is the most commonly used metal in the world → Good to have a basic knowledge of it



At its most basic, steel is Fe + C

Everything below 1400˚C is similar to what we covered last week

Two eutectic points:

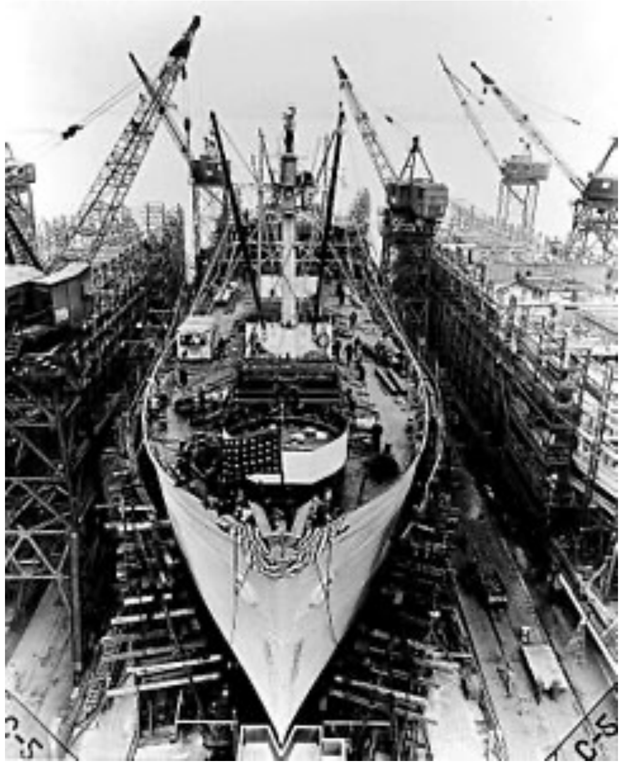
1. 4.30 wt% C
2. 0.76 wt% C

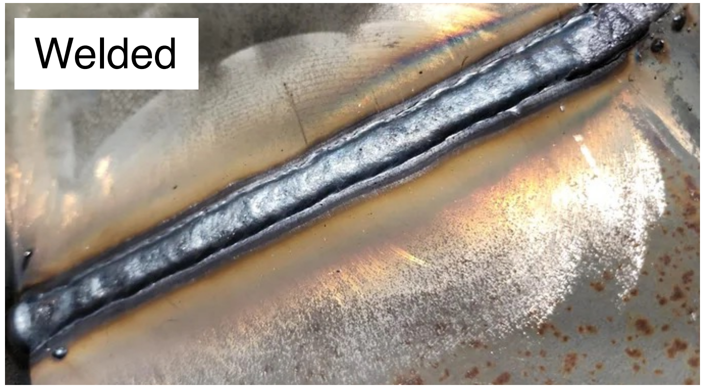
Biggest differences with Pb-Sn are:

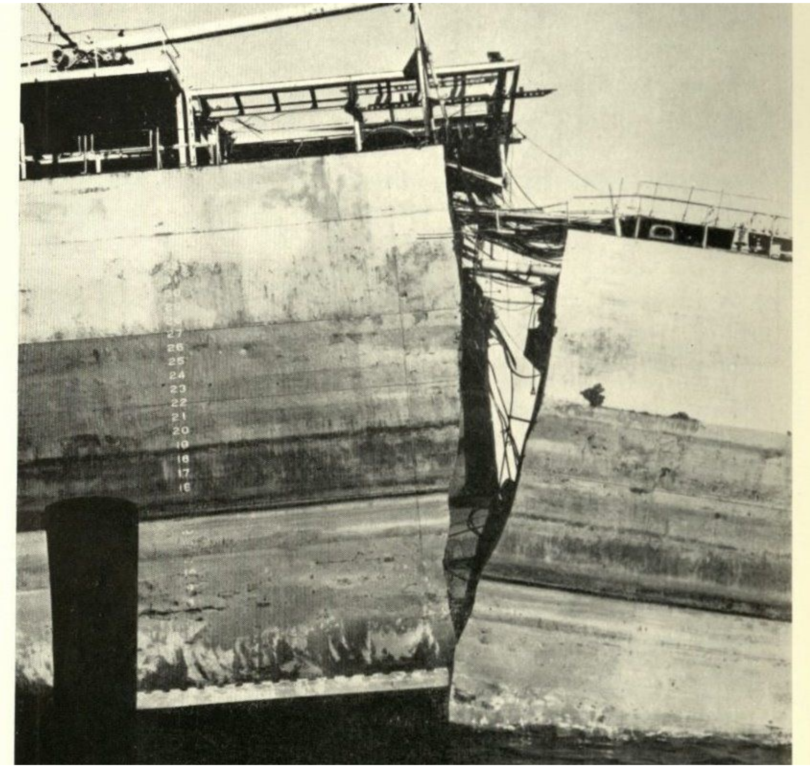
1. Much higher temperatures
2. More solid-solid phase transformations

We will not cover the *peritectic* reaction that occurs >1400˚C.

Story 1 (The simpler one): Liberty ship and fracture







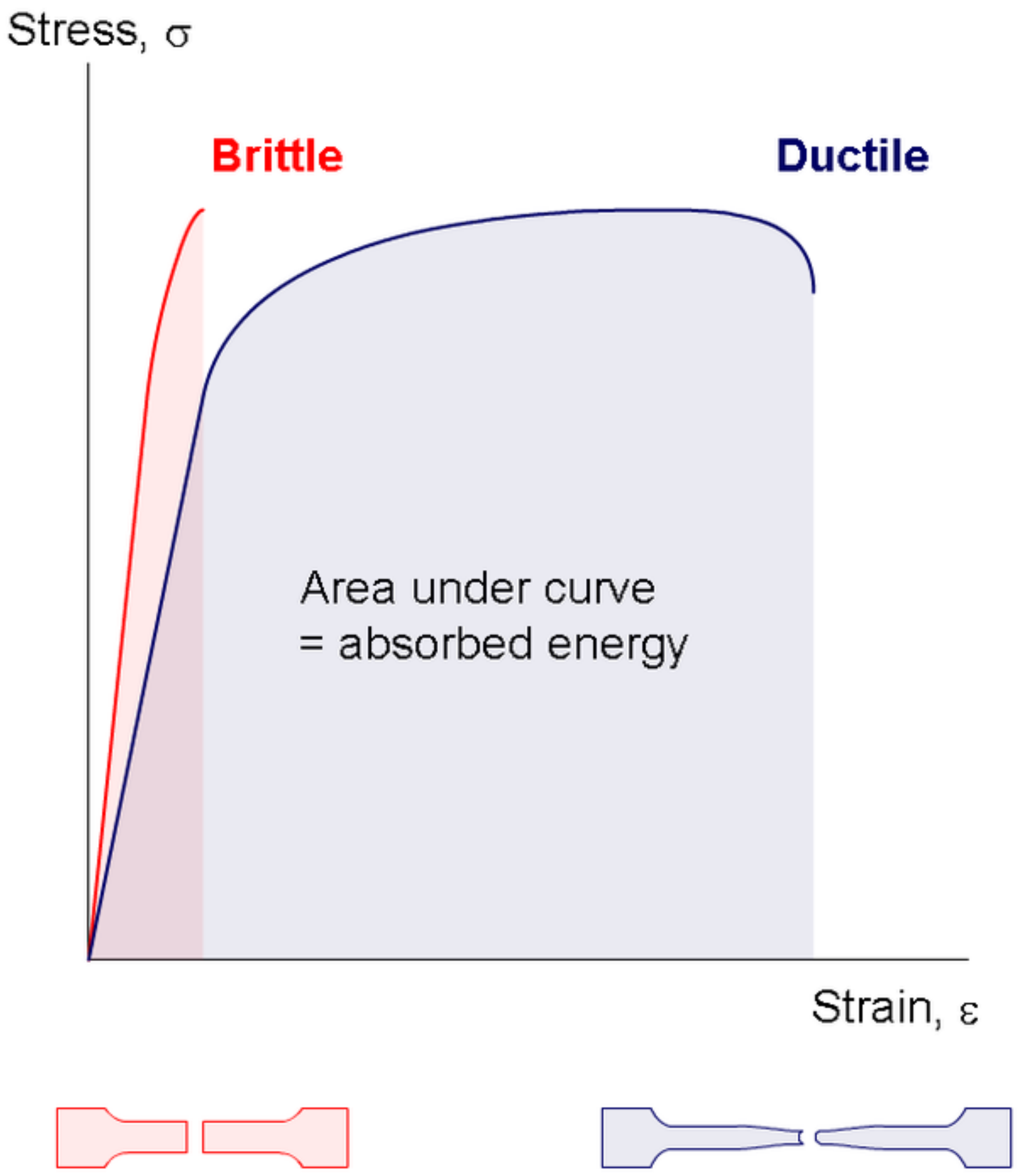
German U-Boats were very successful in sinking British ships

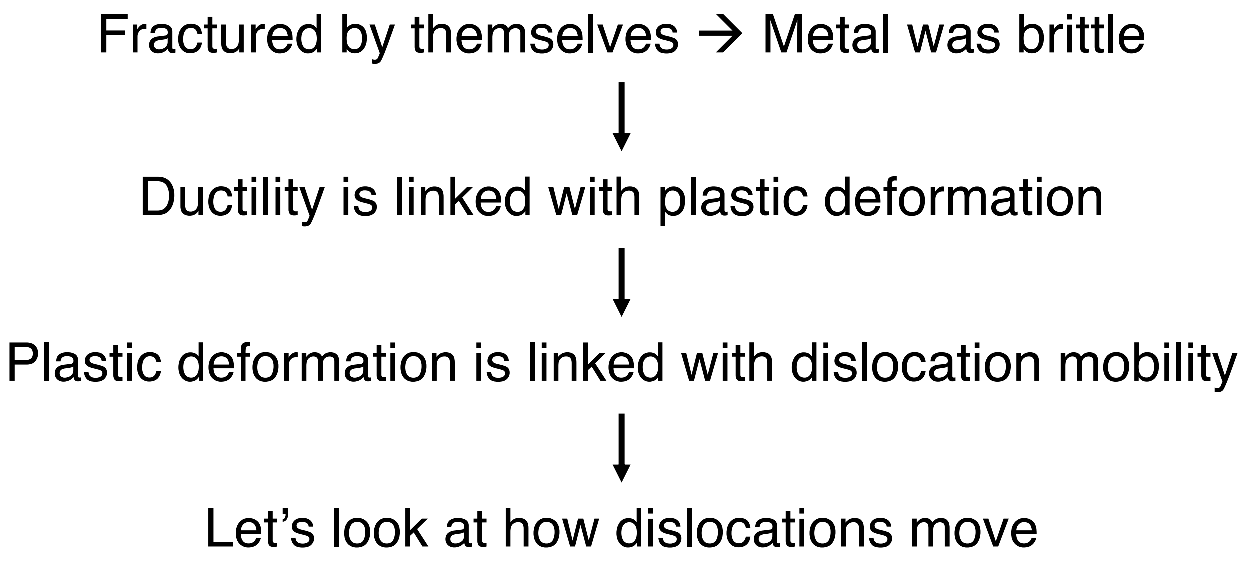
To combat losses, Allied forces developed methods to mass produce these “Liberty Ships”

Key innovation: “Liberty Ships” were welded together instead of being riveted together

Problem: The hull of the “Liberty Ships” started to fracture by themselves

Ductility and Dislocations




Fractured by themselves → Metal was brittle

Ductility is linked with plastic deformation

Plastic deformation is linked with dislocation mobility

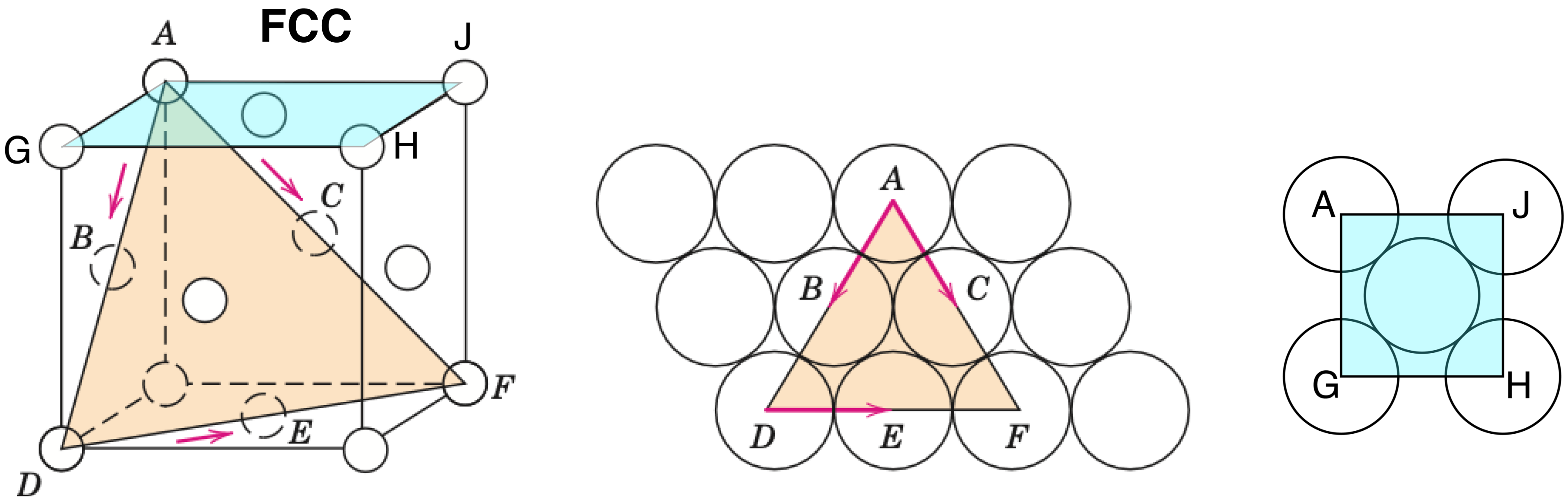
Let’s look at how dislocations move

Crystal structure and slip planes

Dislocations do not move with the same ease in all directions

Preferred plane of dislocation movement → Slip plane
Preferred direction of movement → Slip direction

→ Slip system → The system that allows dislocations to move with lowest applied energy



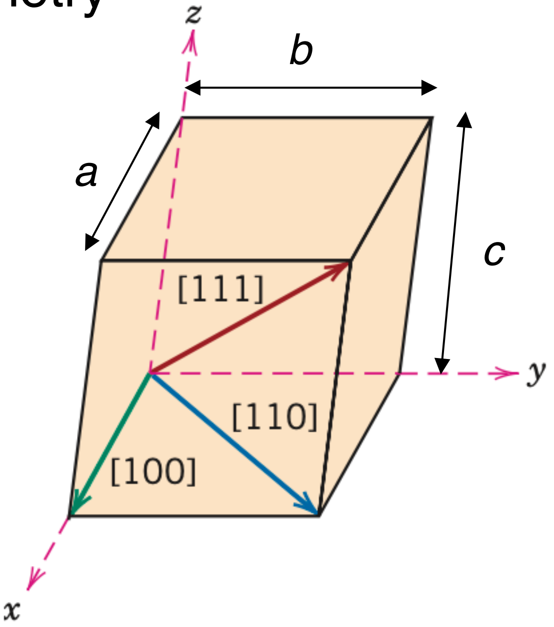
→ Which is easier?

Recap on Miller indices

Miller indices: Notation used to describe parts of a crystal lattice

---

[hkl] = denotes a direction in the lattice (vector)
<hjl> = denotes the set of all directions that are equivalent to [hkl] by symmetry



How to determine a direction?

A direction is basically a line between two points, i.e. a vector

1. Starting from the origin, find the length of the vector projection on each of the three axes in terms of the unit cell dimensions *a, b, c.*

2. The three numbers are multiplied or divided by a common factor to reduce them to the smallest integer values

Eg. Red line	**x**	**y**	**z**
Projections (red line)	a	b	c
Projections (in terms of *a*, *b*, and *c*)	1	1	1
Reduction	1	1	1

Recap on Miller indices

Miller indices: Notation used to describe parts of a crystal lattice

---

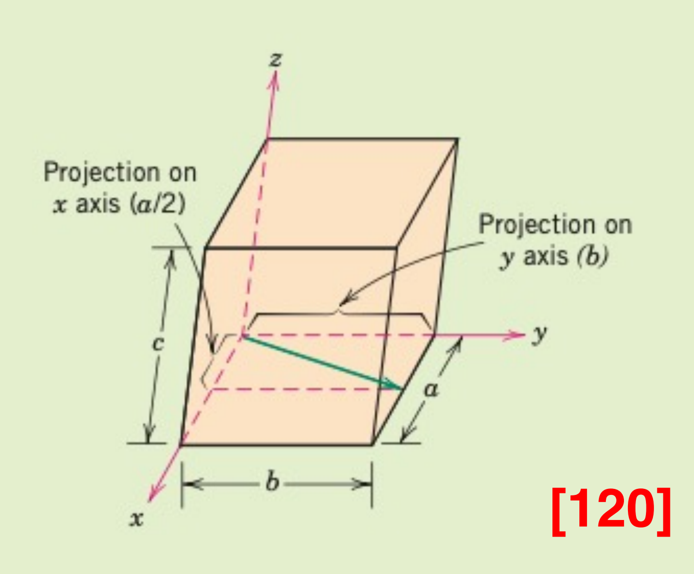
[hkl] = denotes a direction in the lattice (vector)
<hjl> = denotes the set of all directions that are equivalent to [hkl] by symmetry

How to determine a direction?

A direction is basically a line between two points, i.e. a vector

1. Starting from the origin, find the length of the vector projection on each of the three axes in terms of the unit cell dimensions *a, b, c.*

2. The three numbers are multiplied or divided by a common factor to reduce them to the smallest integer values



Eg. Green line	**x**	**y**	**z**
Projections (red line)	*a*/2	*b*	0*c*
Projections (in terms of *a*, *b*, and *c*)	1/2	1	0
Reduction	1	2	0

Recap on Miller indices

Miller indices: Notation used to describe parts of a crystal lattice

---

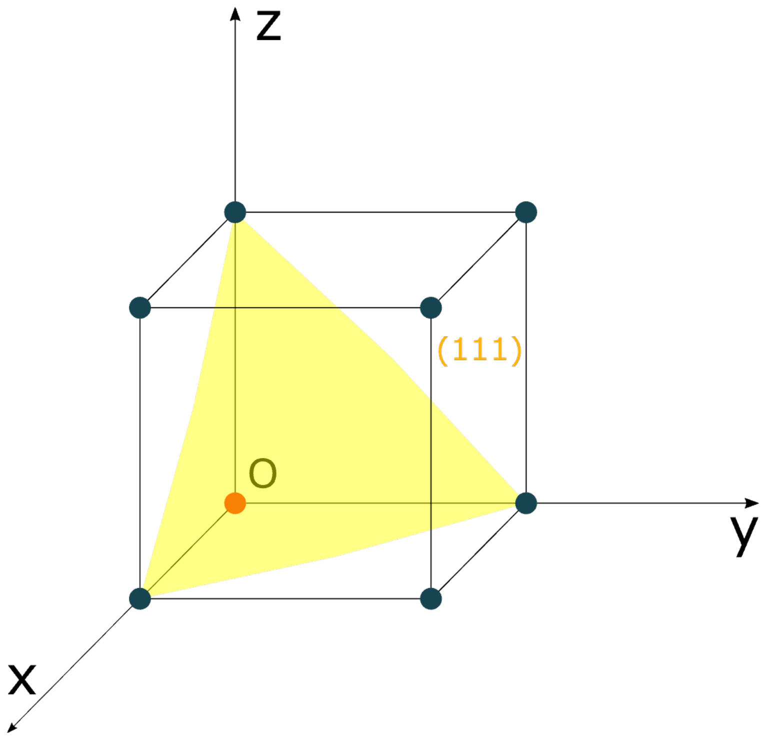
(hkl) = denotes family of parallel planes in the lattice
{hkl} = denotes the set of all planes that are equivalent to (hkl) by symmetry

How to determine a plane?

1. Check: Does the plane pass through the origin?
If no, proceed to **3.**
If yes, proceed to **2.**

2. Establish a new origin at the corner of another unit cell such that the plane does not pass through this new origin

3. At this point, the plane either intersects or parallels each of the three axes



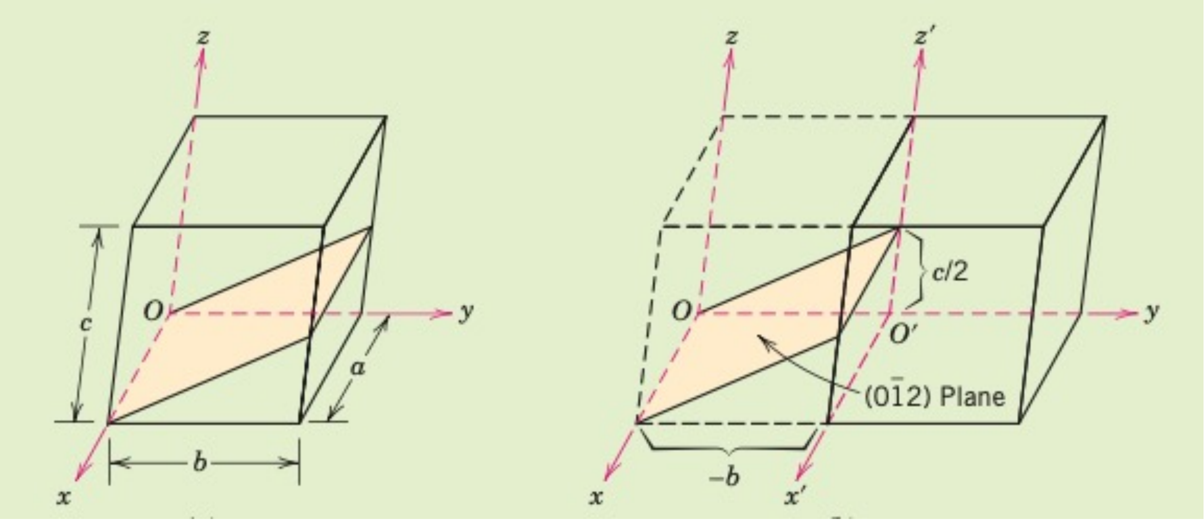
Recap on Miller indices

Miller indices: Notation used to describe parts of a crystal lattice

---

(hkl) = denotes family of parallel planes in the lattice
{hkl} = denotes the set of all planes that are equivalent to (hkl) by symmetry

How to determine a plane?



1. Check: Does the plane pass through the origin?
If no, proceed to **3.**
If yes, proceed to **2.**

2. Establish a new origin at the corner of another unit cell such that the plane does not pass through this new origin

3. At this point, the plane either intersects or parallels each of the three axes

Recap on Miller indices

Miller indices: Notation used to describe parts of a crystal lattice

---

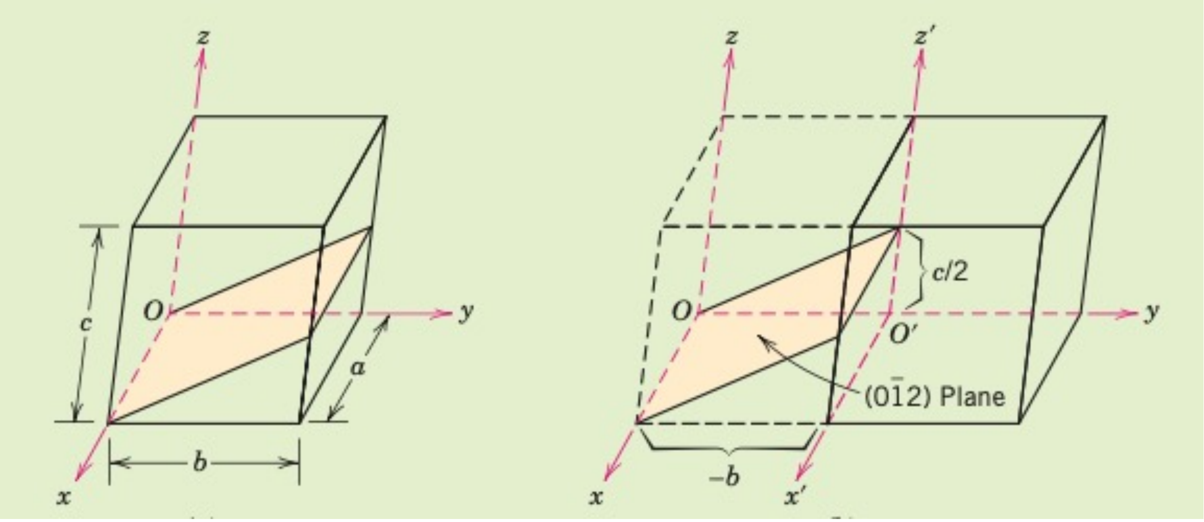
(hkl) = denotes family of parallel planes in the lattice
{hkl} = denotes the set of all planes that are equivalent to (hkl) by symmetry

How to determine a plane?

4. The length of the planar intercept for each axis is determined in terms of *a*, *b*, and *c*

5. The reciprocal of these numbers are taken. A plane that parallels an axis is considered to have an intercept of ∞. Thus a zero index

6. From the three numbers, find the smallest set of integers via a common factor



Eg. Plane	**x**	**y**	**z**
Intercepts	∞*a*	-*b*	*c/2*
Intercepts (in terms of *a*, *b*, and *c*)	∞	-1	1/2
Reciprocal	0	-1	2

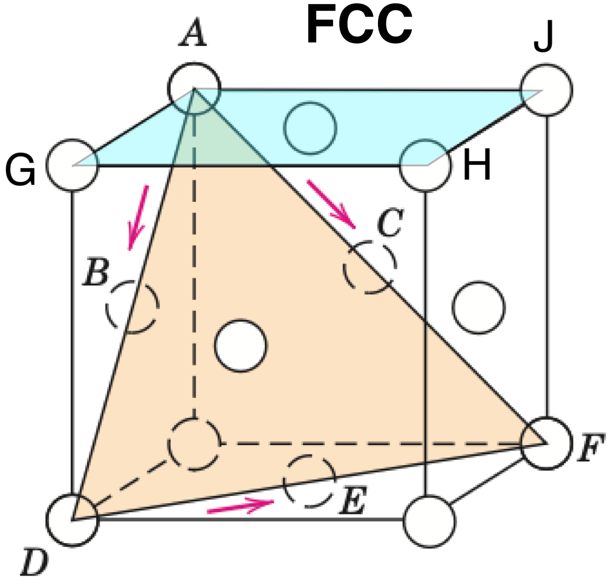
Crystal structure and slip planes

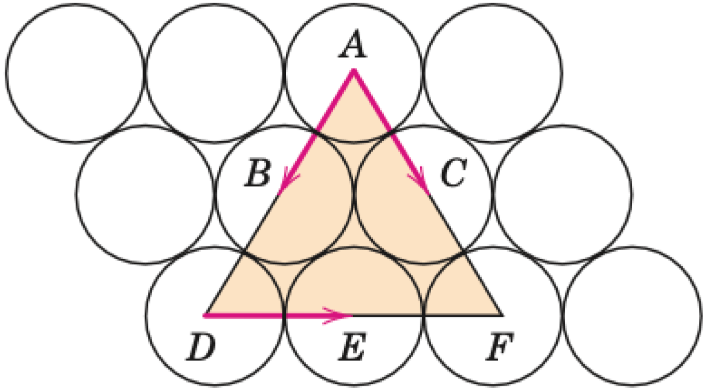
Dislocations do not move with the same ease in all directions

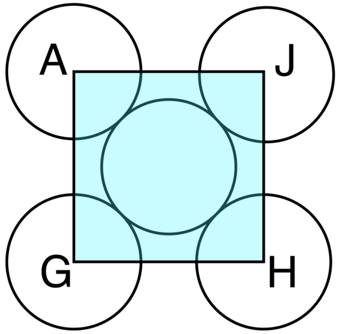
Preferred plane of dislocation movement → Slip plane
Preferred direction of movement → Slip direction

→ Slip system → The system that allows dislocations to move with lowest applied energy

FCC





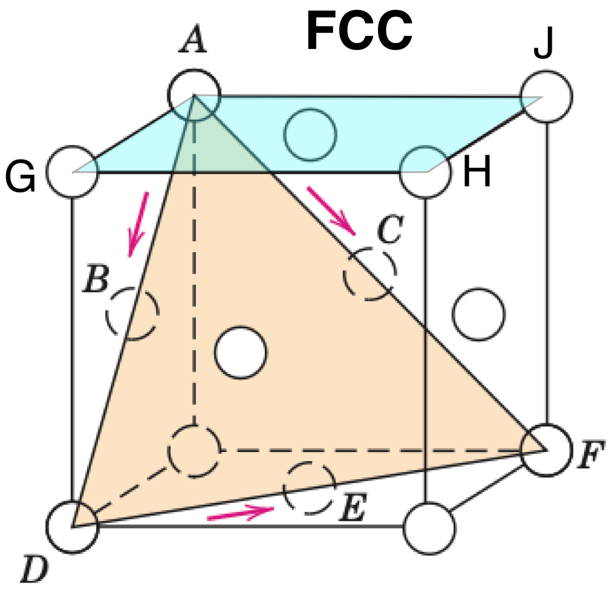


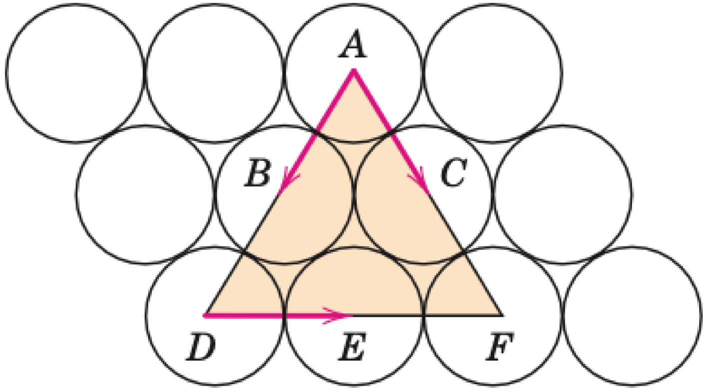
Which is easier?

Crystal structure and slip planes

<u>Slip plane</u> is the plane that has the most dense packing

<u>Slip direction</u> corresponds to the direction, in the <u>slip plane</u>, that is most closely packed with atoms





<u>FCC:</u>

Slip plane: {111} family
Slip direction: <110>

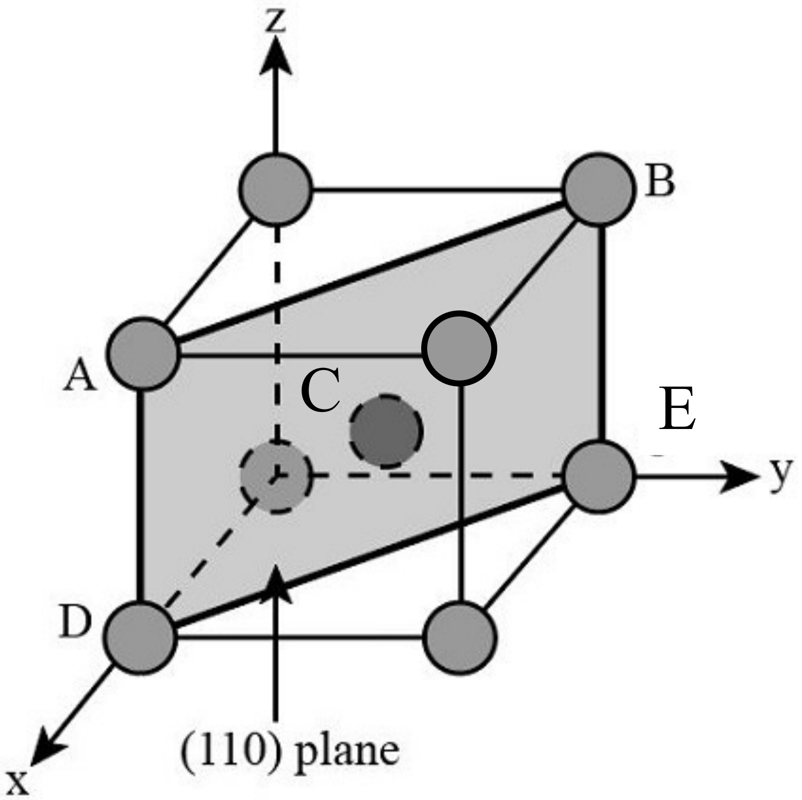
Slip system: {111} <110>

<u>Total of 12 slip systems for FCC</u> (4 unique {111} planes, each with 3 <110> directions in them.

Crystal structure and slip planes

Slip plane is the plane that has the most dense packing

Slip direction corresponds to the direction, in the slip plane, that is most closely packed with atoms



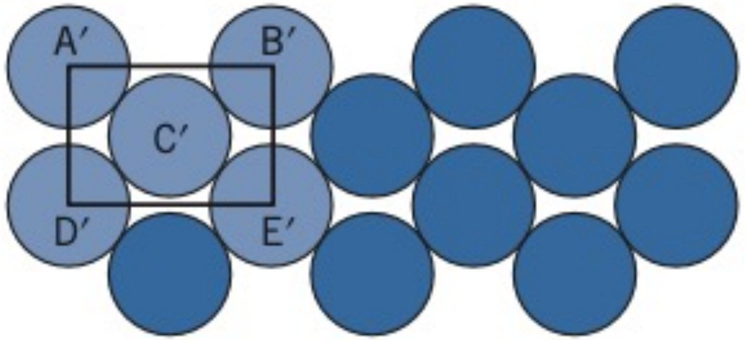
BCC:

Slip plane: {110}, {211}, {321)
Slip direction: <111>

Slip systems: {111} <111>, {211}<111>, {321}<111>

Up to 48 slip systems for BCC

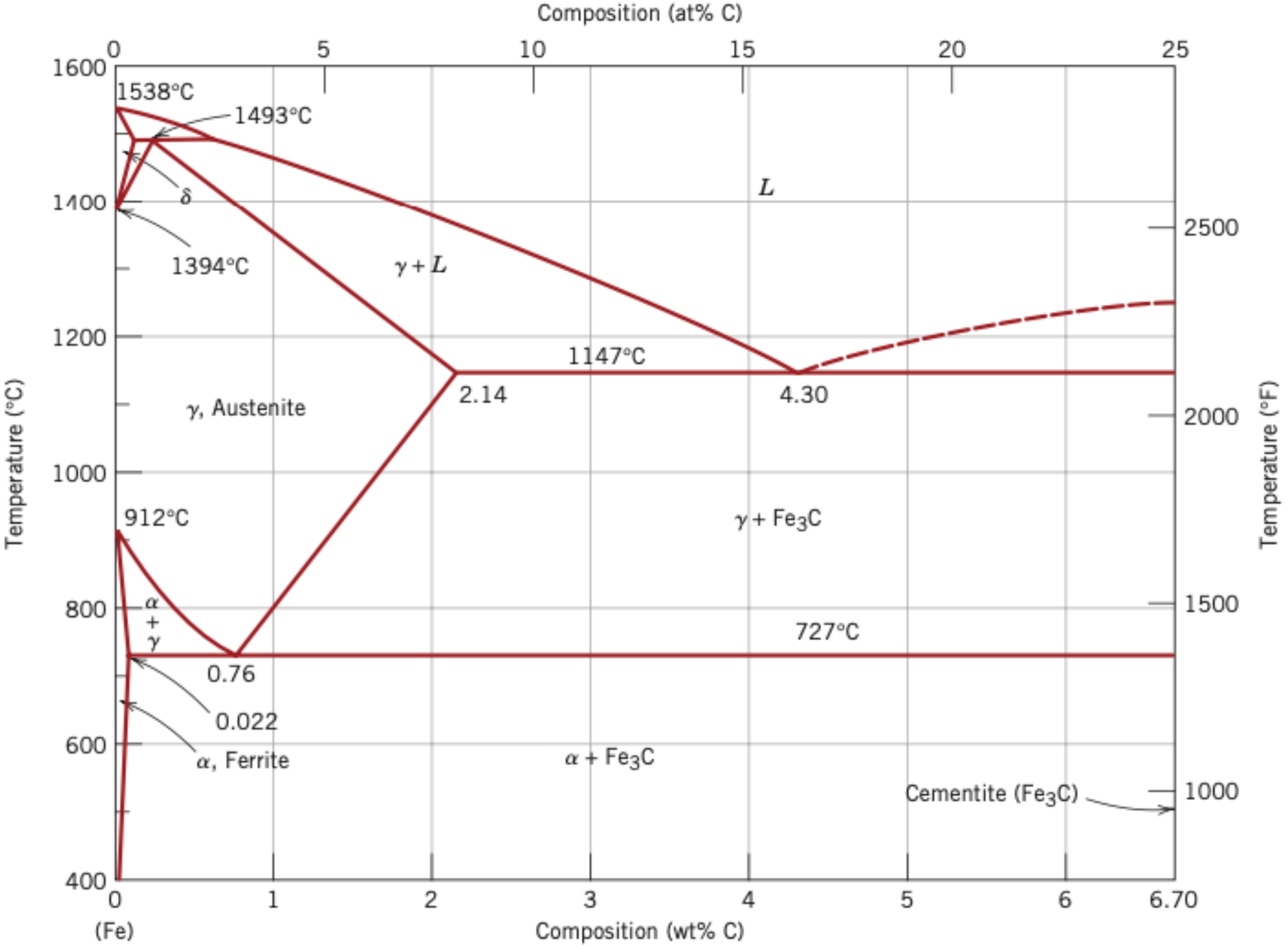
BUT no truly closed packed planes in BCC



Some slip systems in BCC are thermally activated

So why did the ships fail?

Reason 1: Used mild steel, which is mostly BCC ferrite



Ships were exposed to cold water

↓

BCC slip systems became inactivated

↓

Dislocation movements became difficult

↓

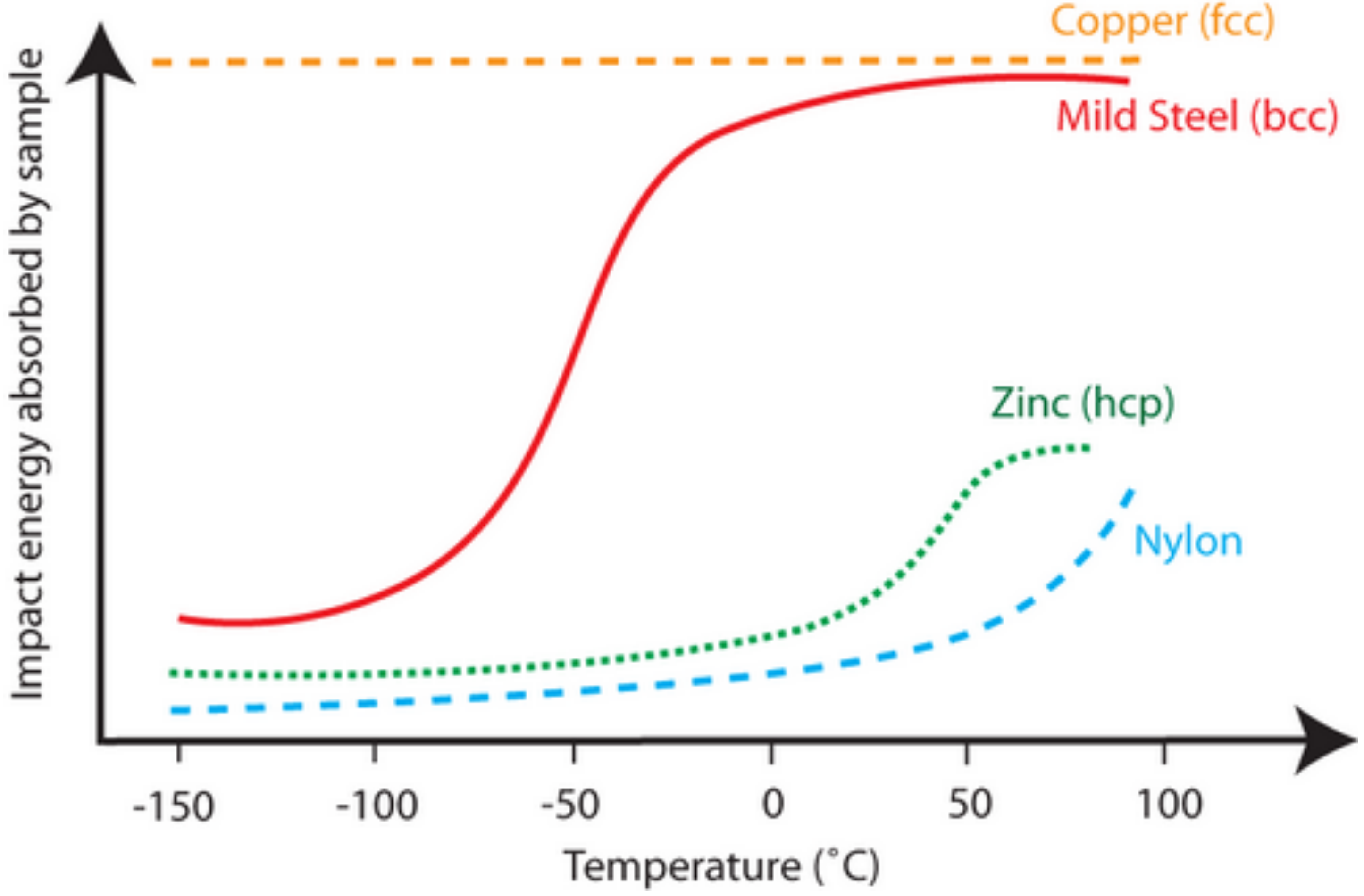
Metal lost ductility = Became brittle

↓

Any stress in the boat could lead to crack initiation and propagation

Some metals have a ductile-to-brittle transition temperature

Ductile–to-Brittle Transition Temperature (DBTT)



Can think of energy absorbed as area under the stress-strain plot

↓

More energy absorbed = more ductile

Temperature does not affect FCC metals much

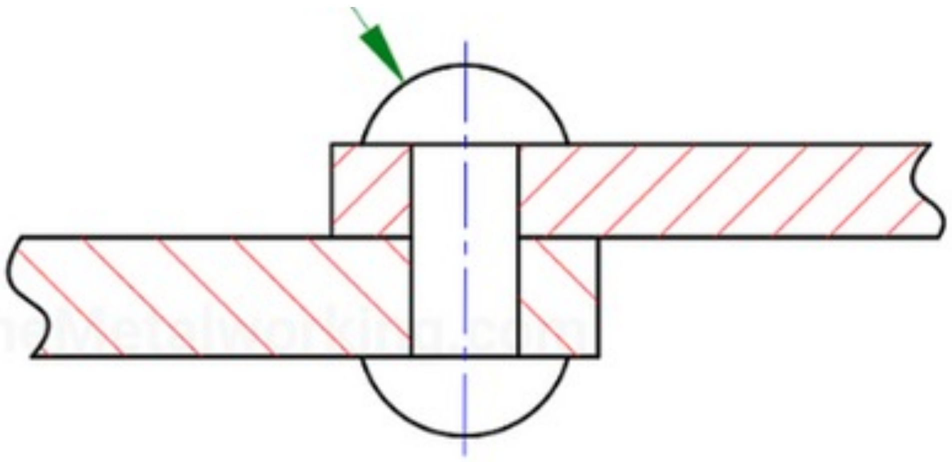
BCC and HCP have temperature-dependent behavior!

Nylon does as well. Why? (Recap polymers)

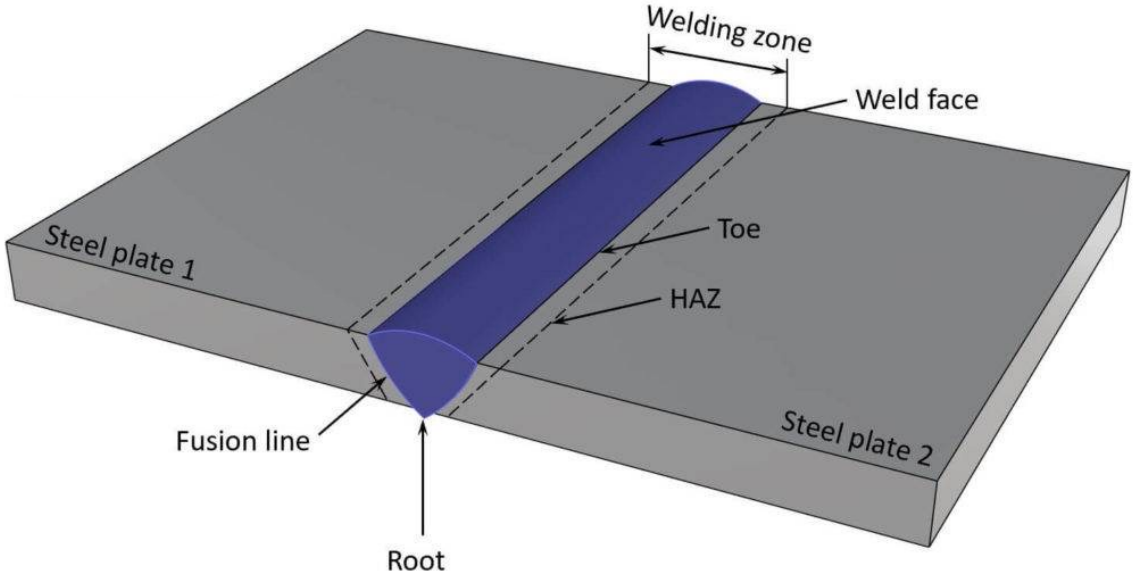
So why did the ships fail?

Reason 2: Riveting vs Welding

Rivet



Weld



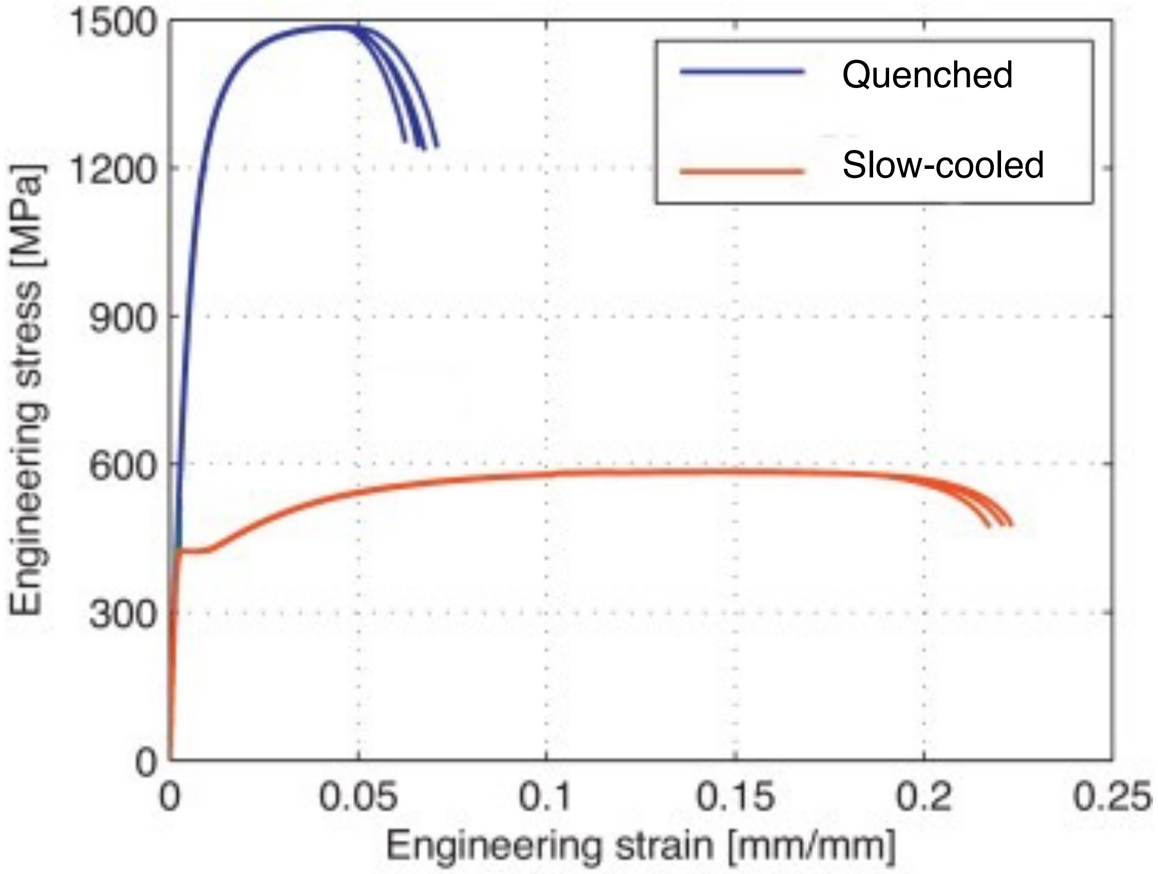
Crack in one plate would stop at the end of a panel
Riveting helped to arrest the crack from propagating

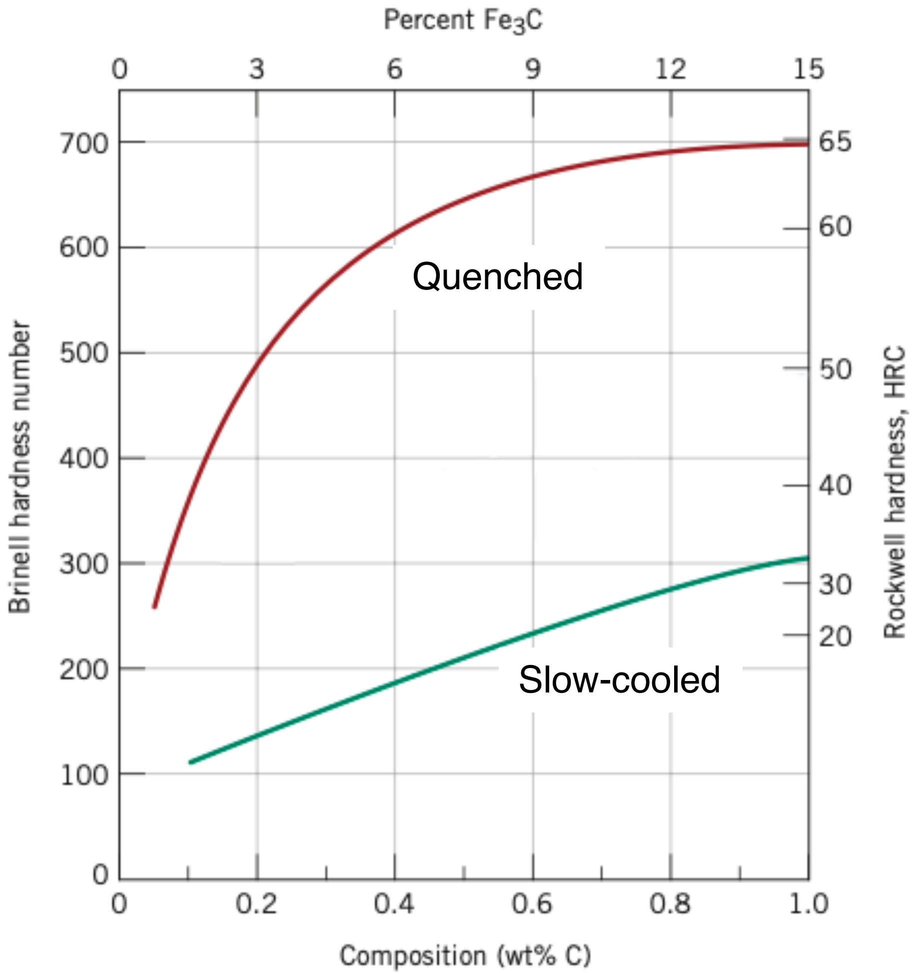
Crack in one plate can propagate unimpeded
through the weld into the other plate

Story 2: Why do we rapidly cool hot steel?

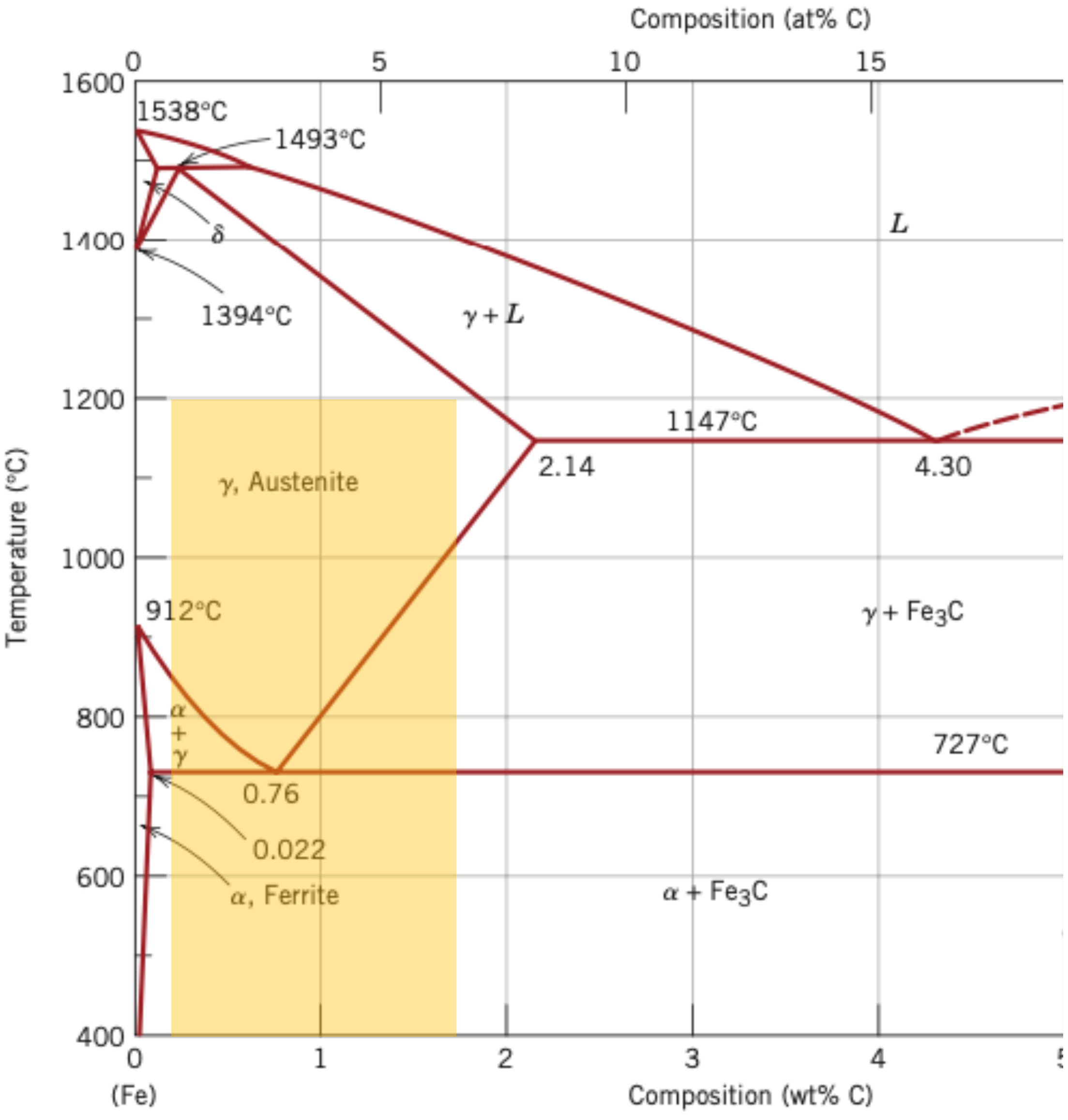
Story 2: Why do we rapidly cool hot steel?

The short answer: It makes a harder and stronger steel!





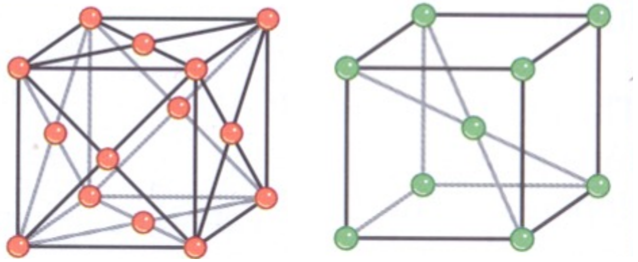
Why does rapid cooling strengthen the metal?



<u>Rapid cooling → Quench</u>

Austenite (γ) is FCC

Ferrite (α) is BCC

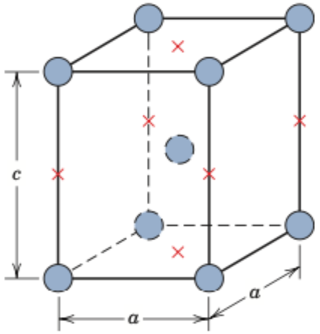


How do we rapidly transform from FCC to BCC?

You kinda can't…not enough time to rearrange the atoms!

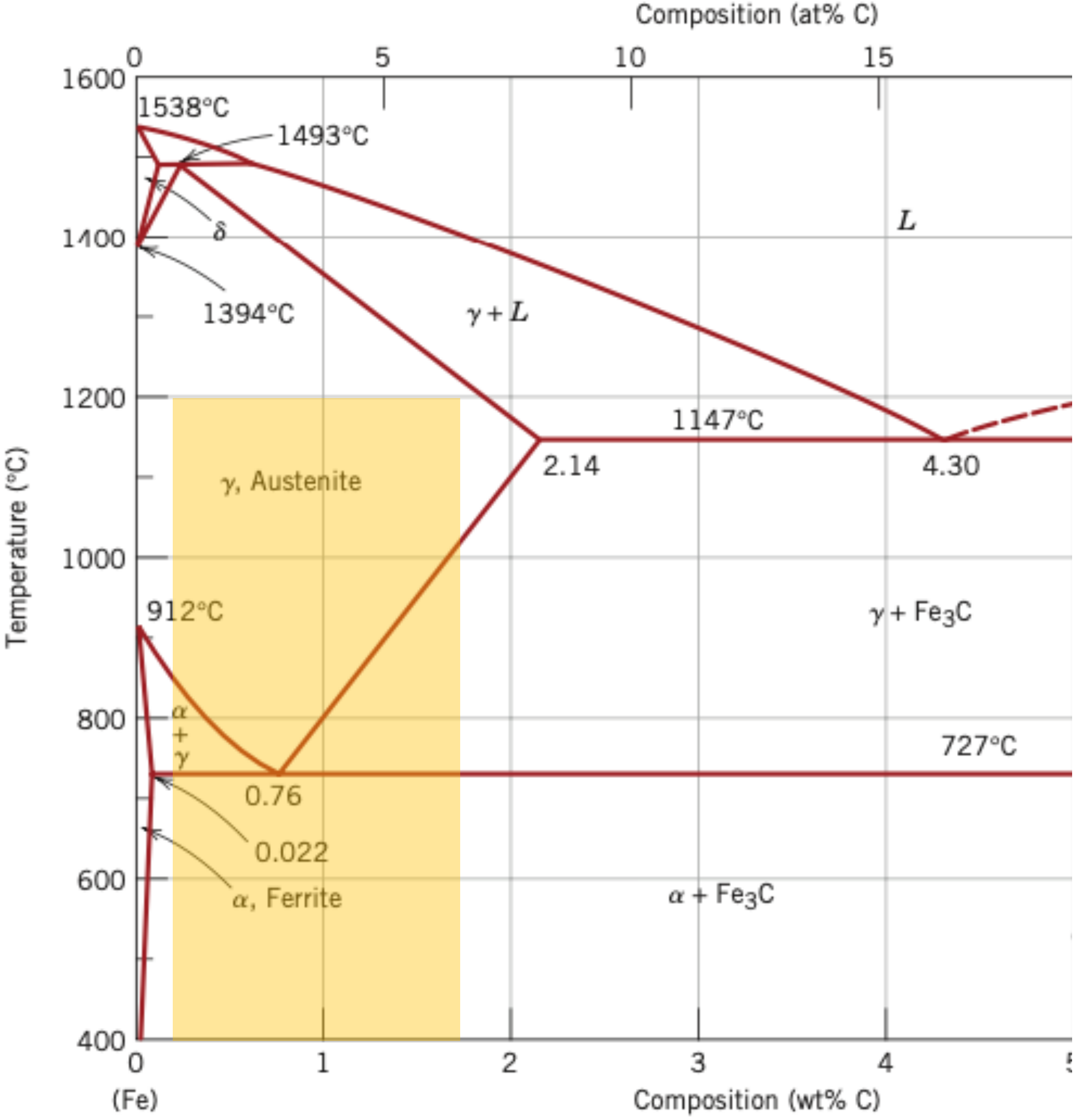
Induce the formation of a new phase → Martensite

(Body Centered Tetragonal, BCT)

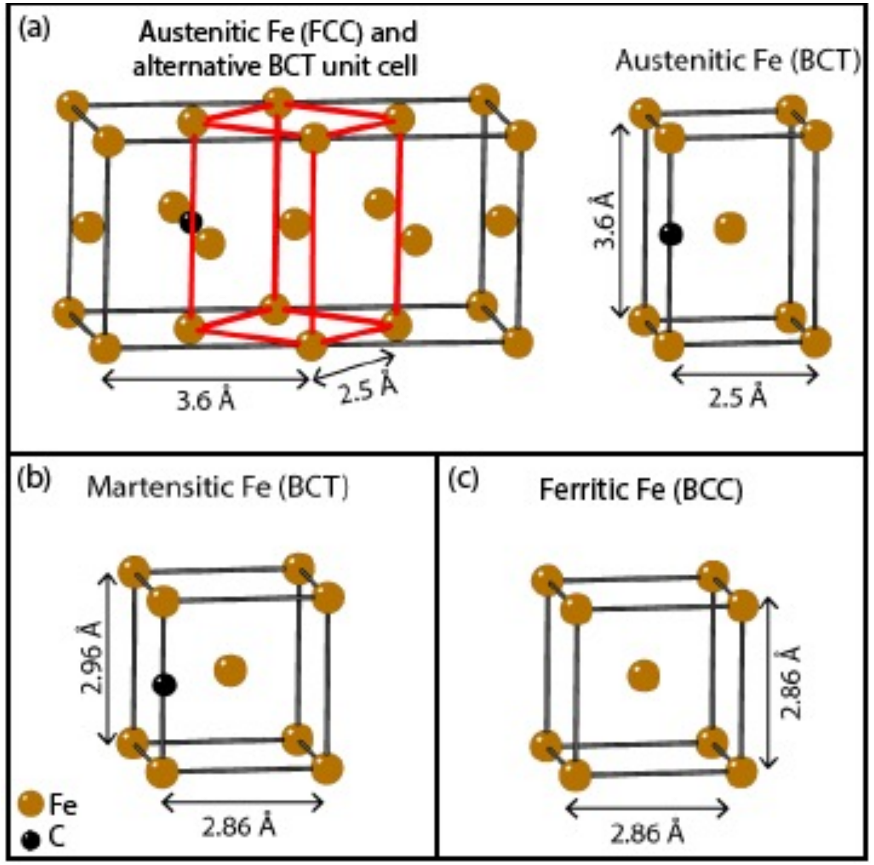


Can think of it as an elongated BCC

How does martensite form?



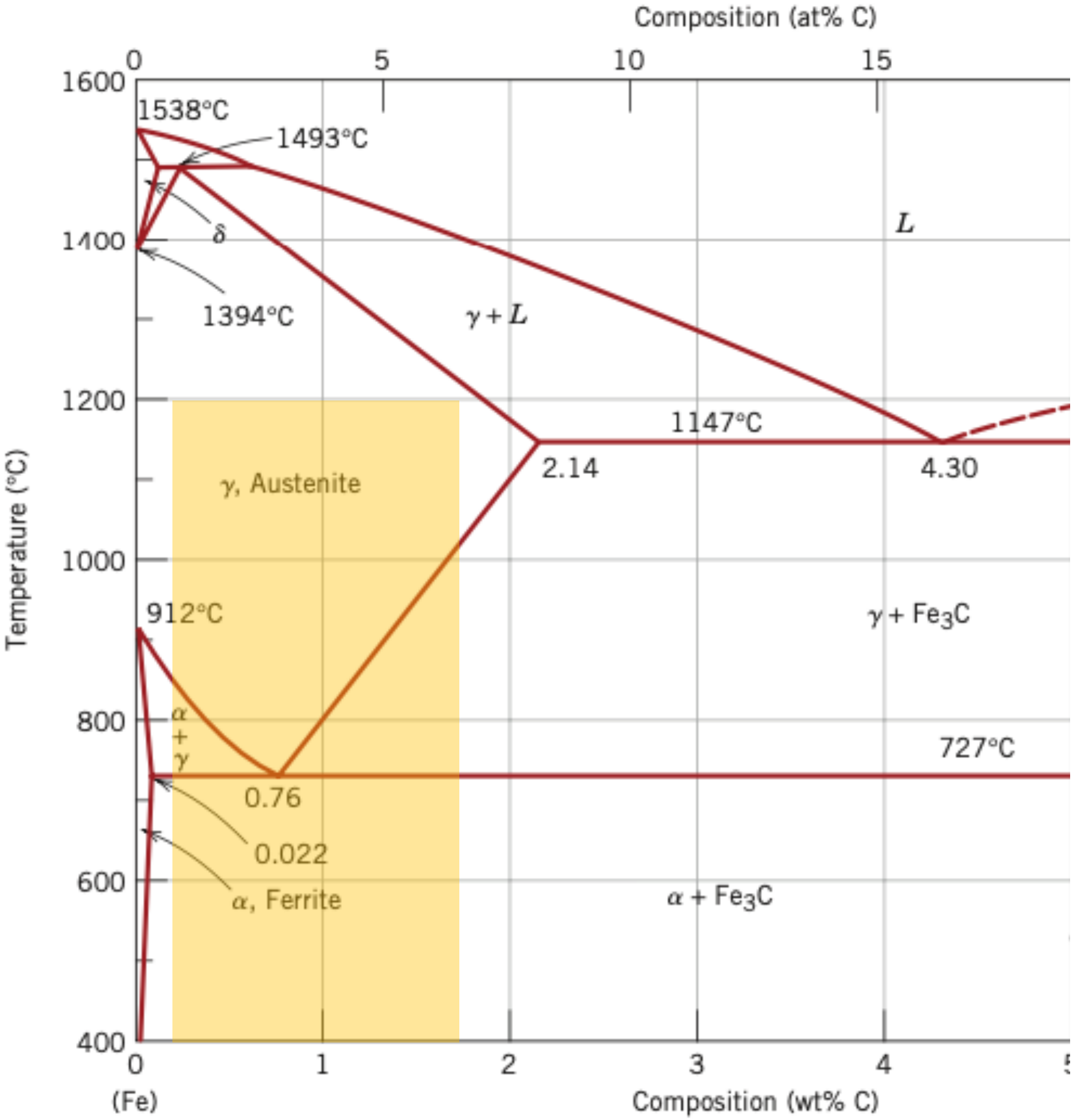
A very simplied picture of their formation



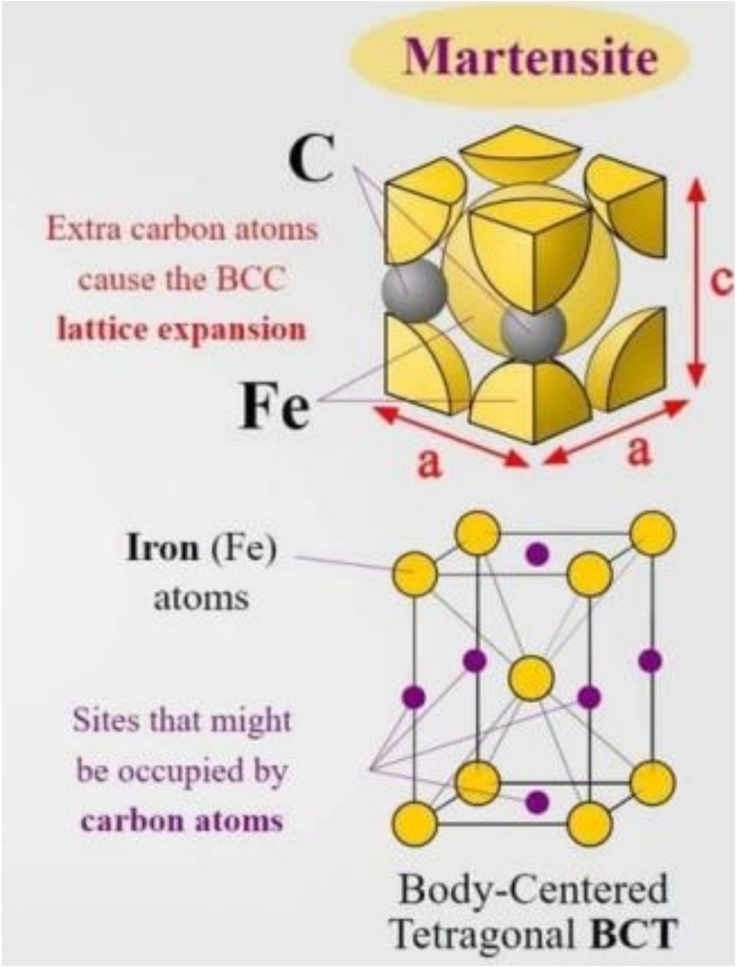
A BCT unit cell can be formed from two FCC unit cells

Diffusionless transformation occurs where the atoms collective shift to their new positions (small displacements!)

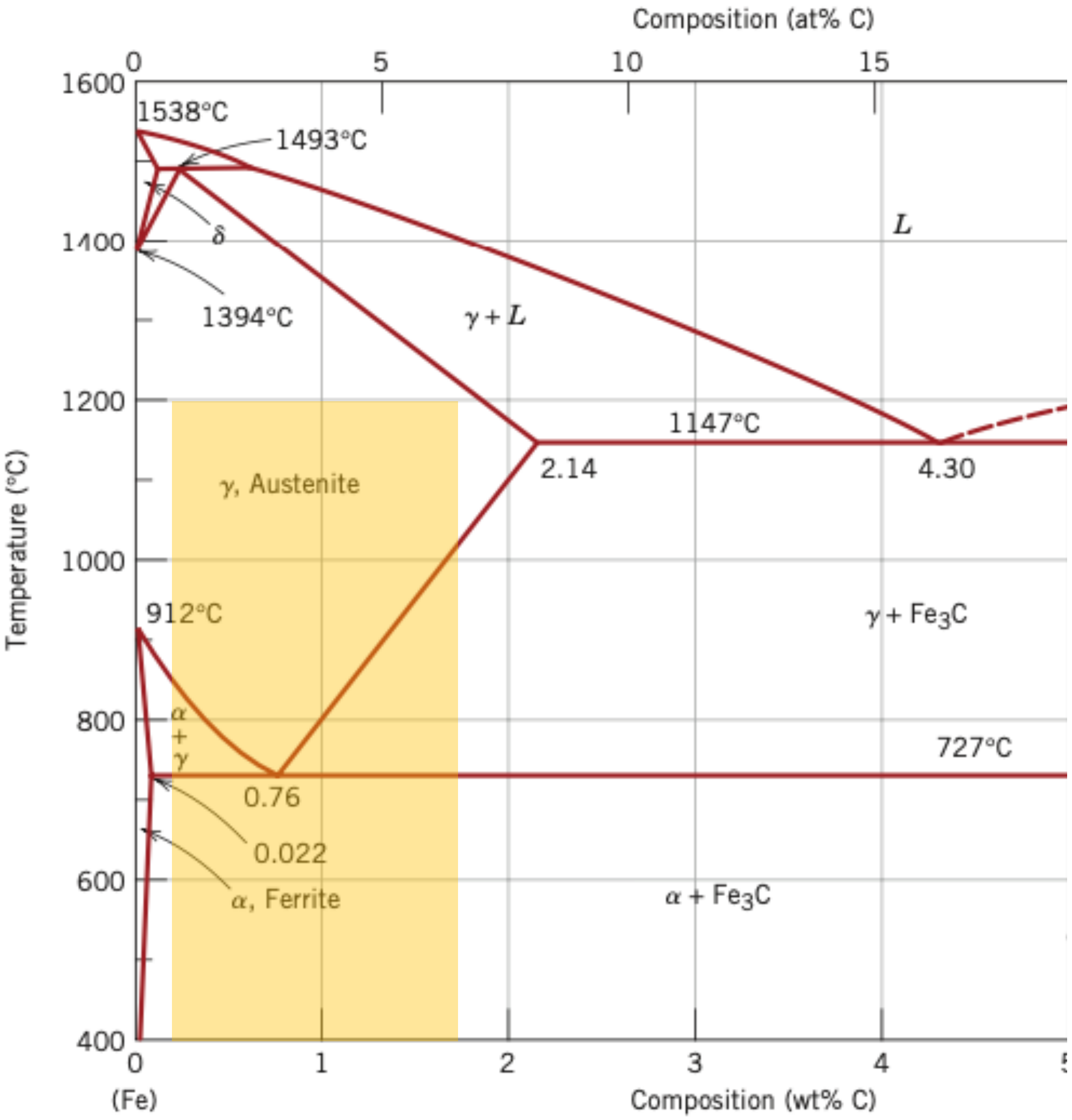
Why is martensite so hard?



Supersaturated with carbon since carbon cannot diffuse away in time. Lattice is strained / distorted due to excess carbon



Why is martensite so hard?



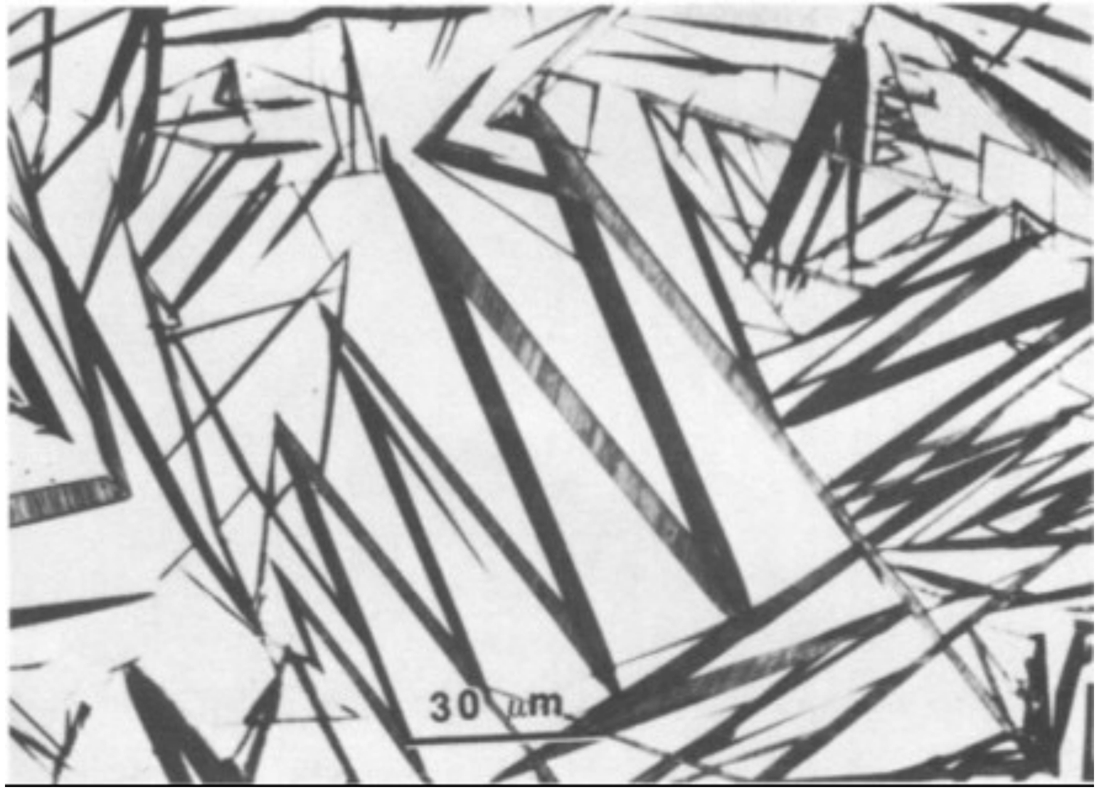
Supersaturated with carbon since carbon cannot diffuse away in time. Lattice is strained / distorted due to excess carbon

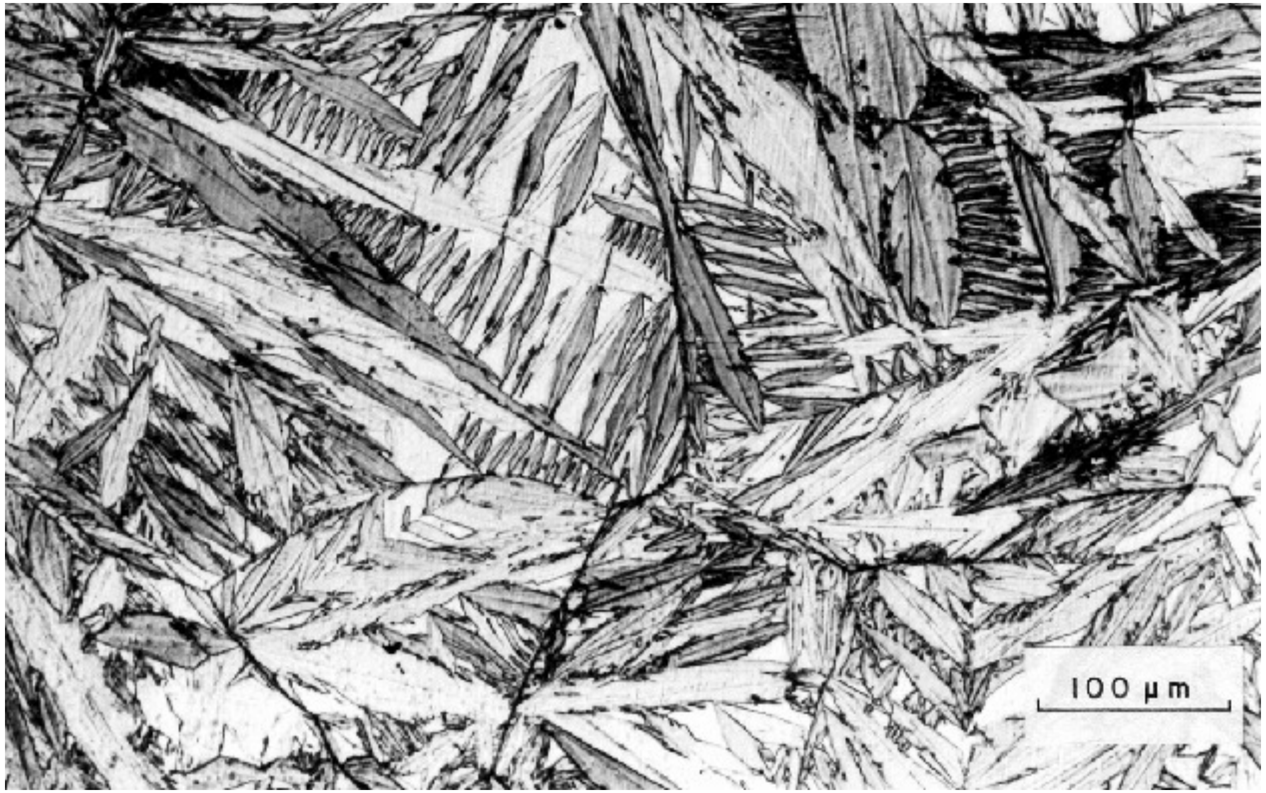
Martensite formation causes volume expansion (different densities) and shape change → Internal stresses

BCT structure has fewer active slip systems than FCC and BCC

Impede dislocation movement!

Martensite microstructure





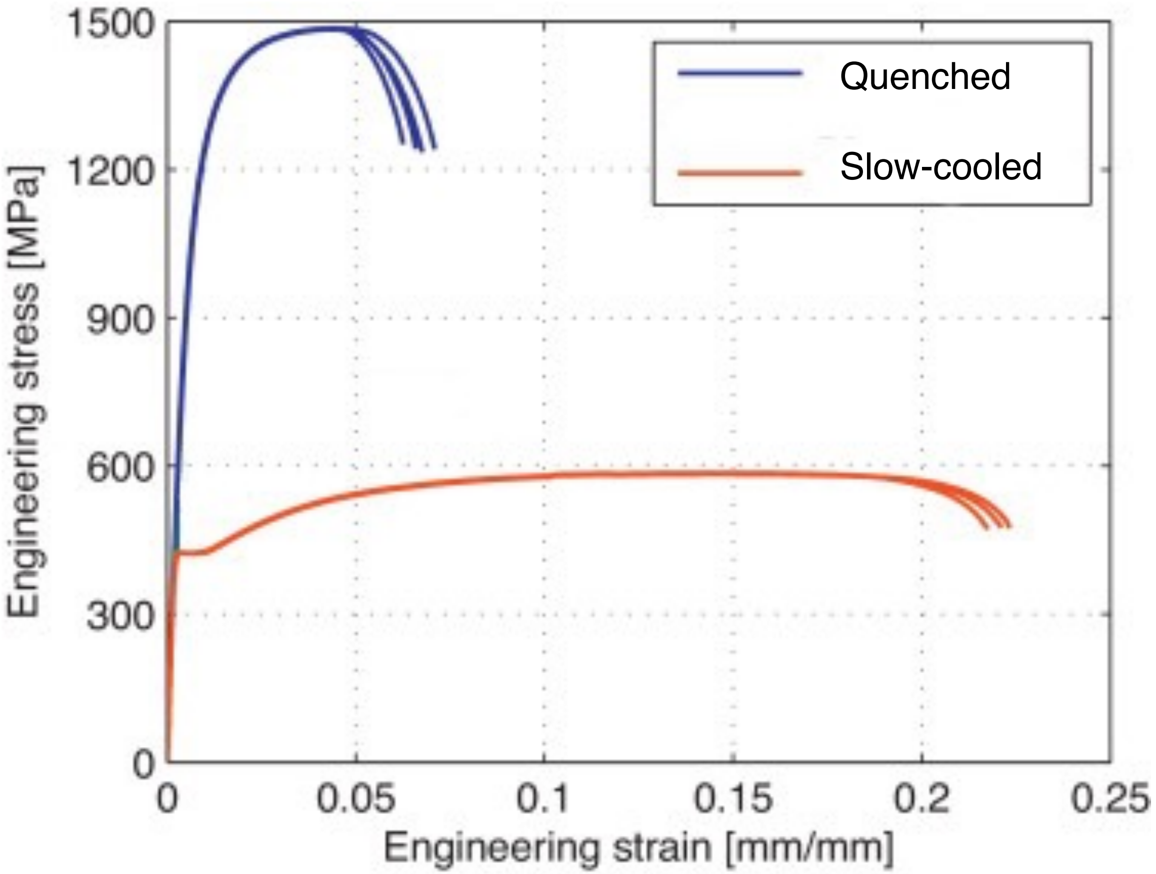
Martensite takes on a unique needle-like / lath microstructure

Needles often have a defined orientation due to crystallographic compatibility requirements*

---

*We won't go into the details why since it is not that relevant to MT

But martensite is often <u>too</u> brittle…



You need some ductility else the metal will fracture!

How do we control the mechanical properties of martensitic steels?

Method 1: Tempering

Temper = Reheat the quenched steel to change mechanical properties

Effect 1: Allows carbon supersaturated martensite to transform to equilibrium phases

Martensite (BCT, single phase)

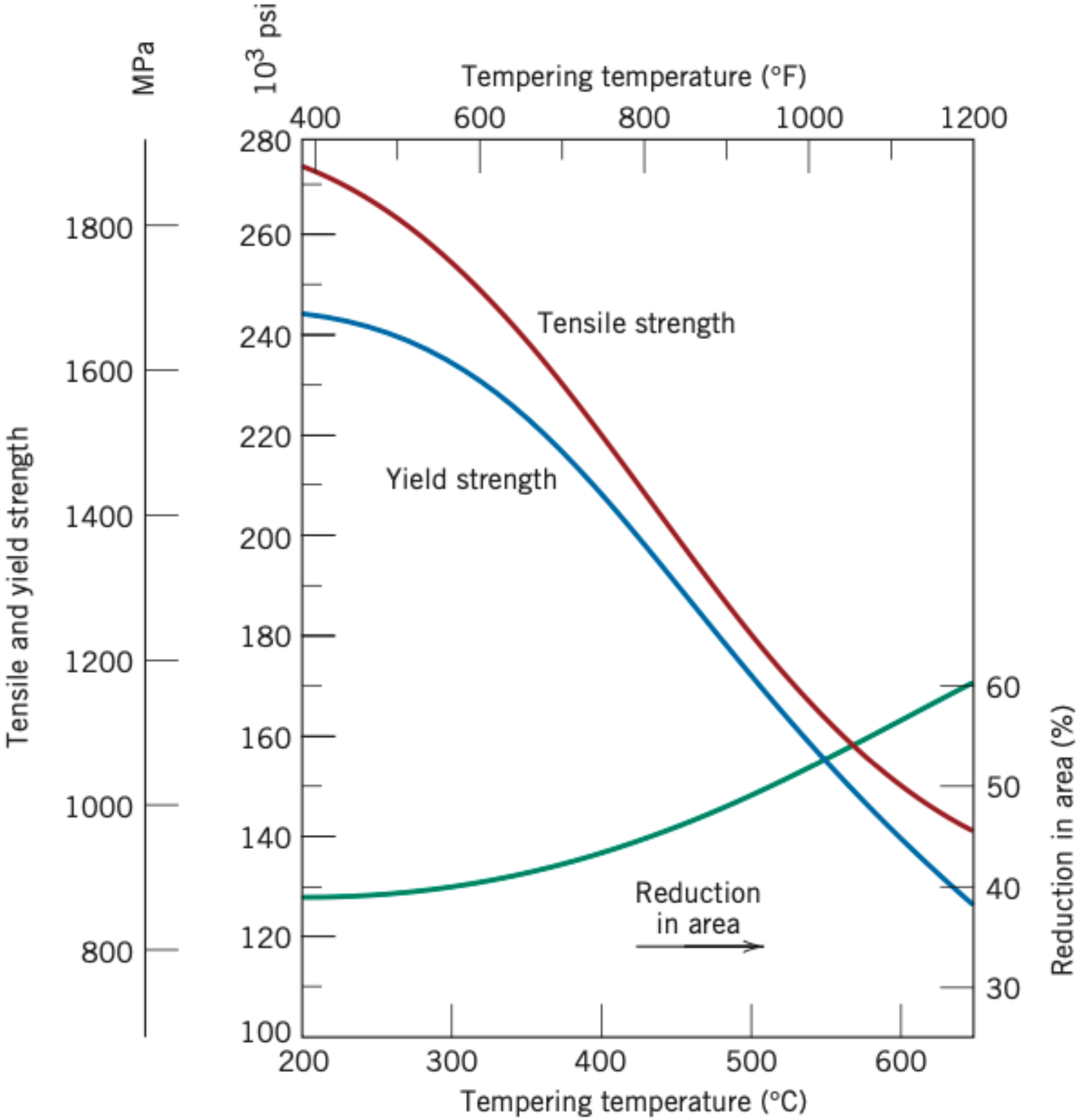
↓

Tempered martensite (α + Fe_3C phase)

This generates a new microstructure that is tougher than pure martensite

---

Effect 2: Reduce dislocation density due to increased atom mobility



EPFL

Method 1: Tempering

Temper = Reheat the quenched steel to change mechanical properties

Effect 1: Allows carbon supersaturated martensite to transform to equilibrium phases

Martensite (BCT, single phase)

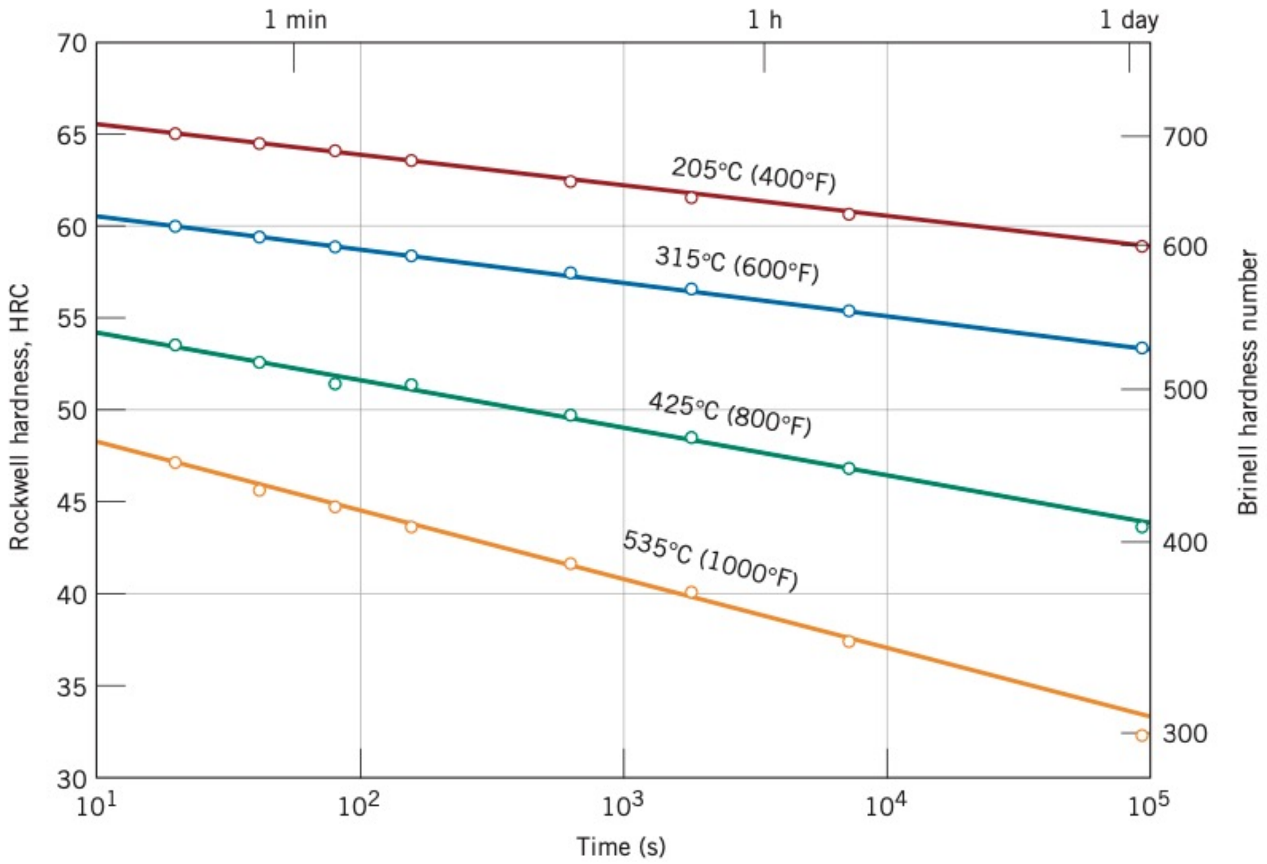
↓

Tempered martensite (α + Fe_3C phase)

This generates a new microstructure that is tougher than pure martensite

---

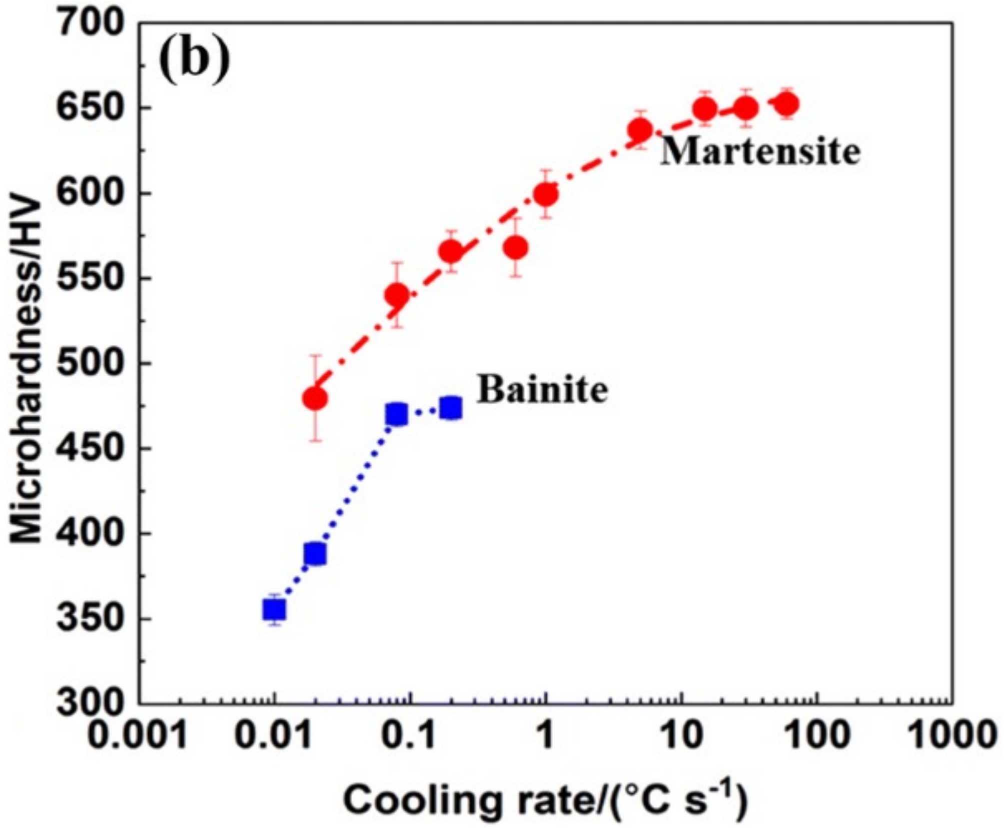
Effect 2: Reduce dislocation density due to increased atom mobility



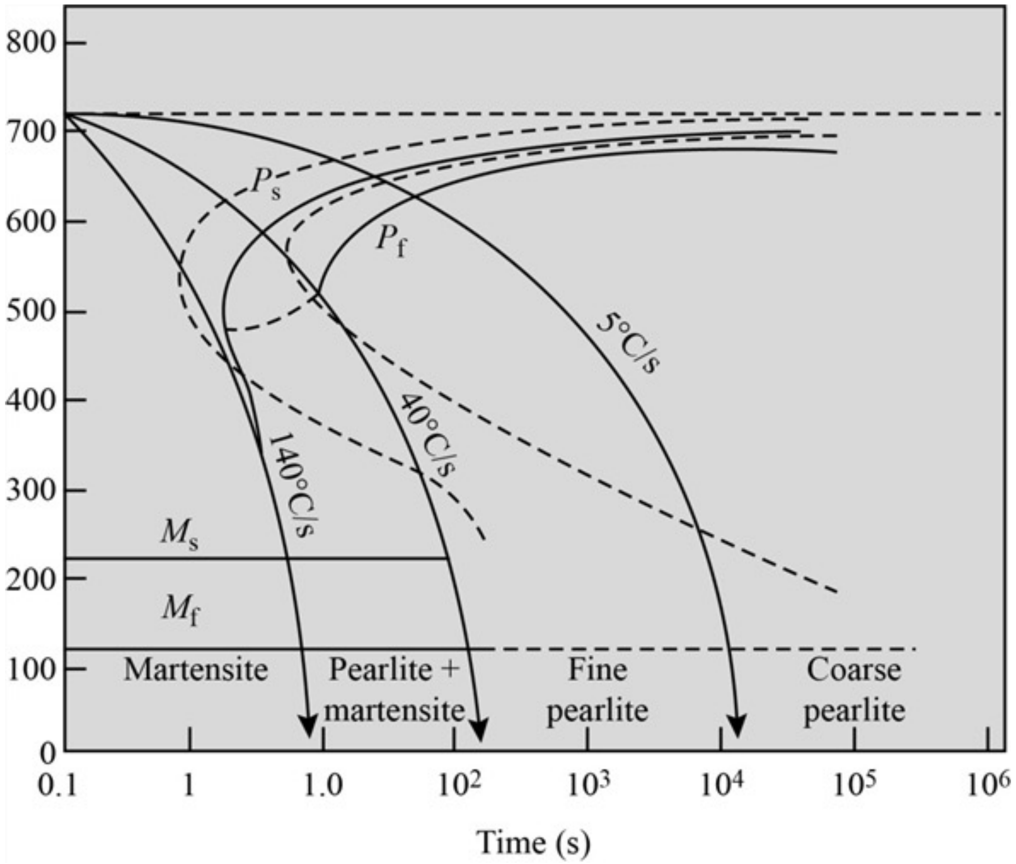
Nucleation and growth process!

Method 2: Control cooling rate

Slower cooling → Allow more diffusion to occur



Changes the microstructures and phases formed



↑ **We'll spend the rest of today understanding this plot**

Solid-state transformations

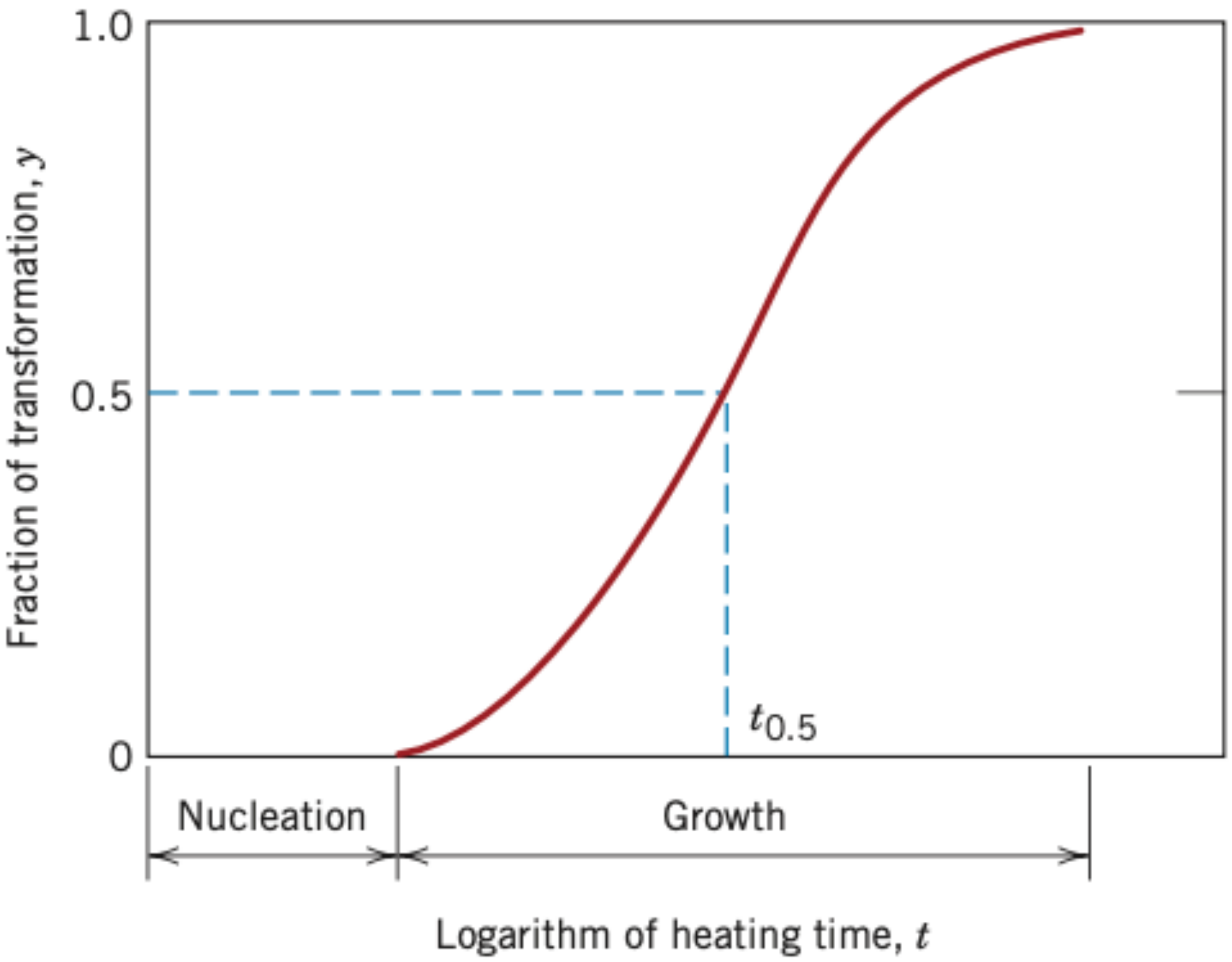
Solid-state transformation can be described by the Avrami equation:

$$y = 1 - e^{-kt^n}$$

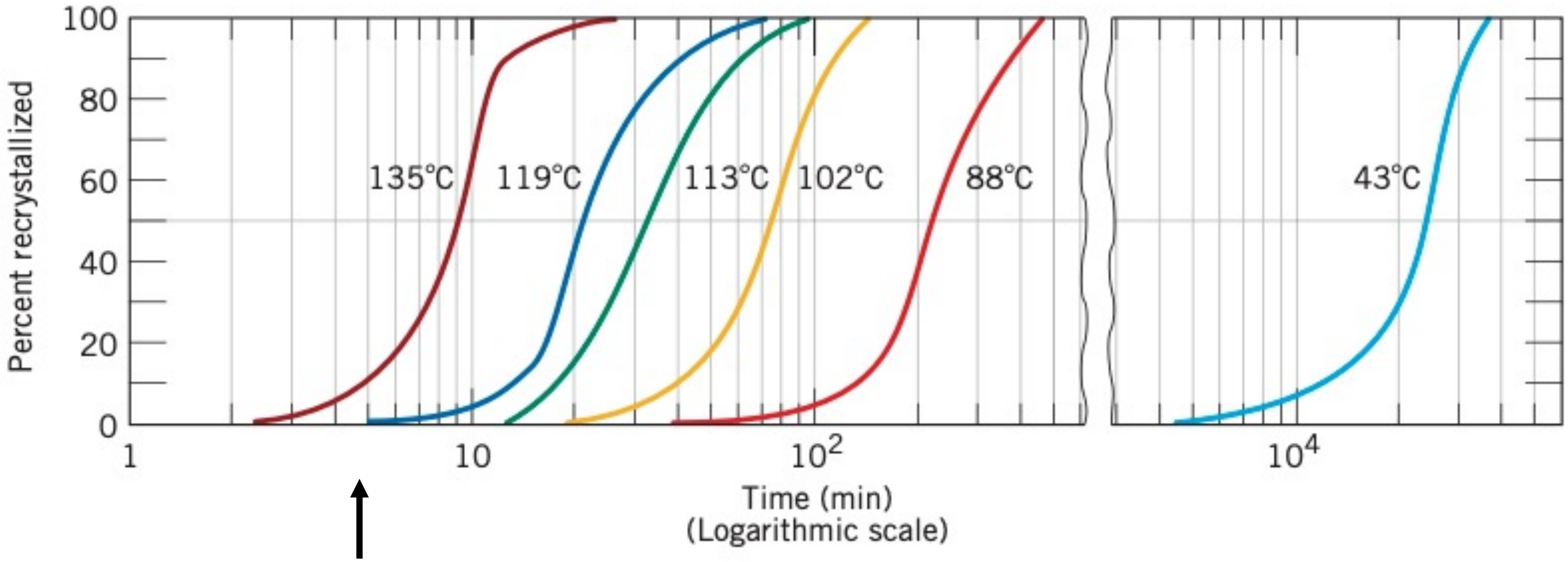
y = fraction of transformation
k, n = time independent constants for the transformation

By convention, the rate of a transformation is taken as the reciprocal of time requires for 50% transformation

$$Rate = \frac{1}{t_{0.5}}$$



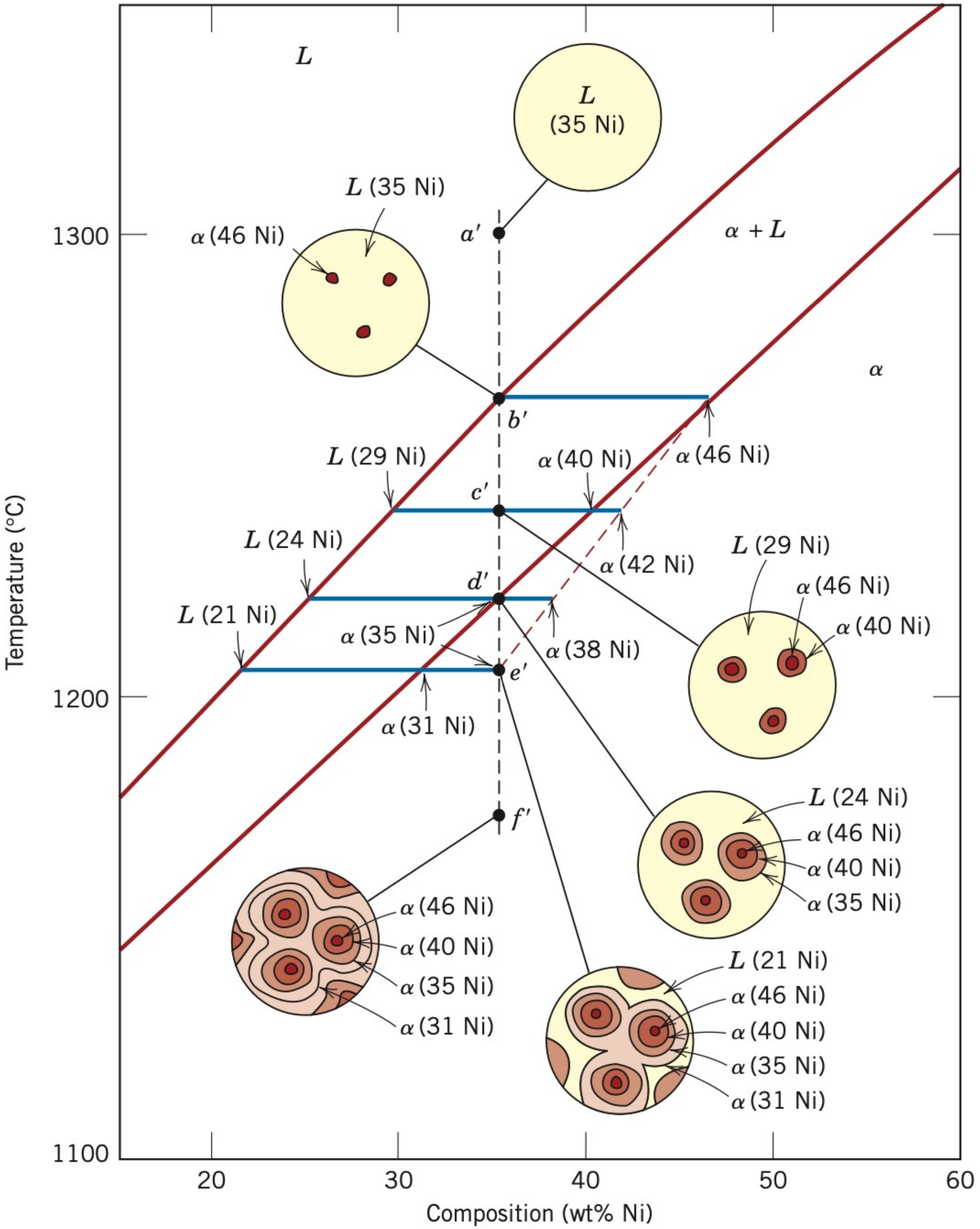
Solid-state transformations rates are affected by temperature



Recrystallization* as a function of time and temperature for pure copper

Depending on the metal, solid-state transformations can occur at MT relevant temperatures
→ Important to keep this concept in mind during material selection

*Haven't learnt this yet but it's a type of solid-state transformation



A quick clarification: What about phase diagrams?

Cannot predict solid-state transformations rates from phase diagrams

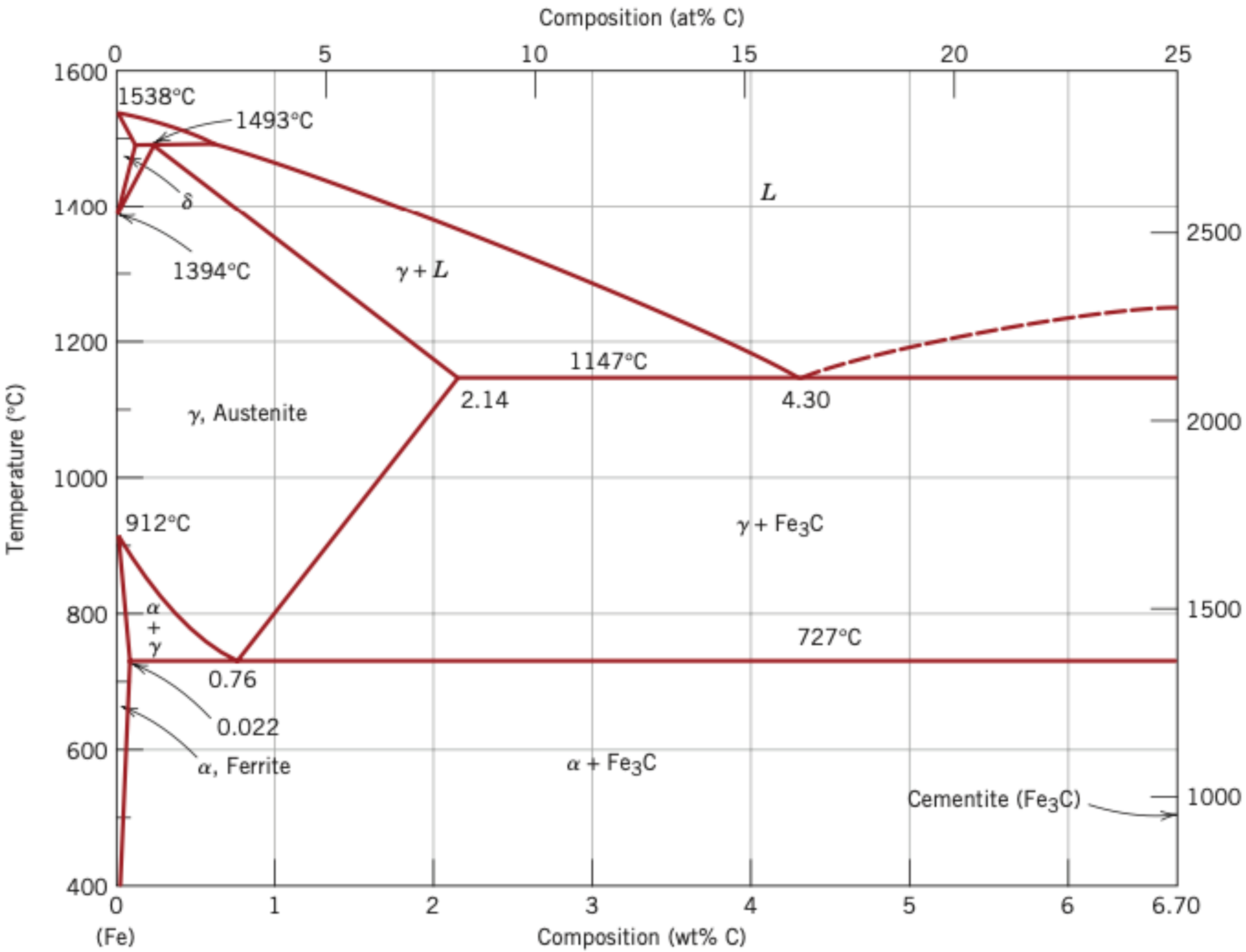
Phase diagrams give you the phase at equilibrium → No kinetic element to it

In real life, we are never at equilibrium
Metals that are made are in metastable states

Metastable states will transform to equilibrium states with enough time and energy

Metastable states are actually the most interesting! Often preferred!

How do we control what metastable states we obtain?



Fe-C phase diagram says we can only get ferrite and cementite at room temperature

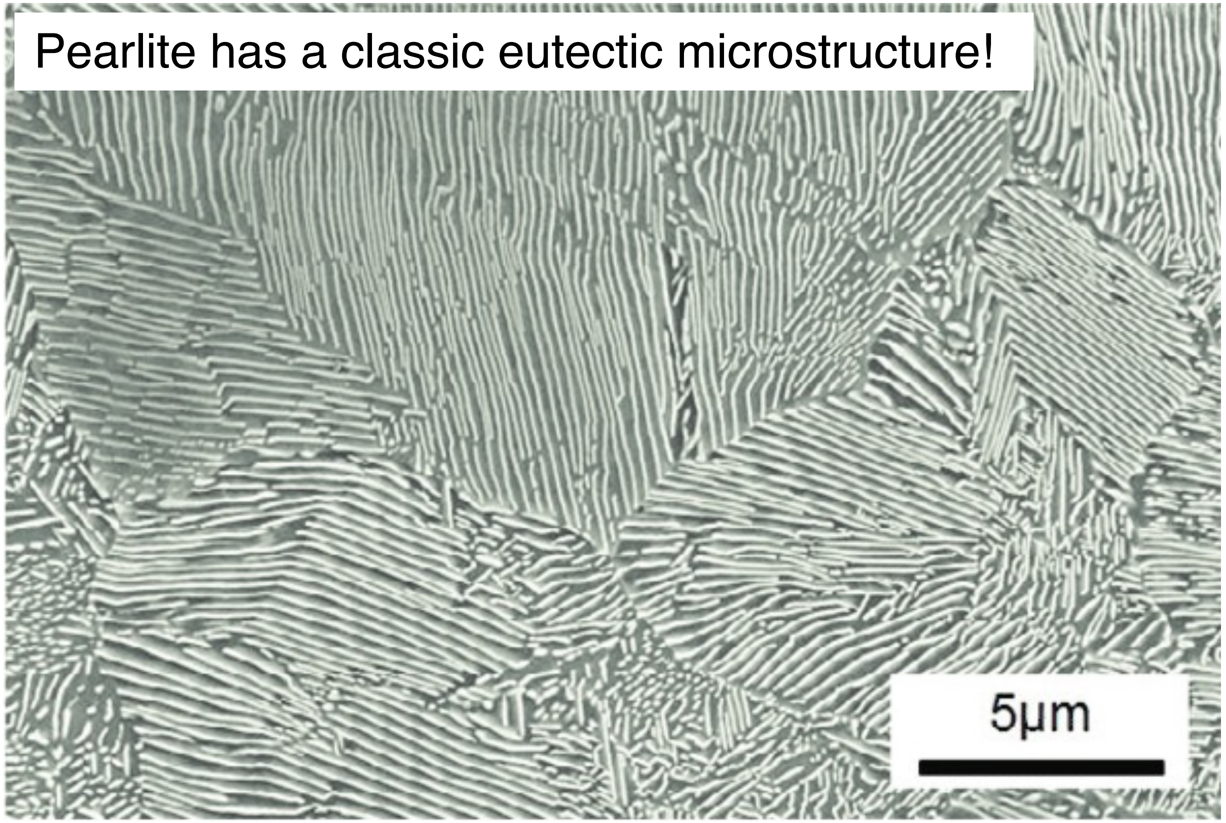
Reality: We get bainite, martensite, tempered martensite, etc.

Example: How long does the iron eutectoid take to form?

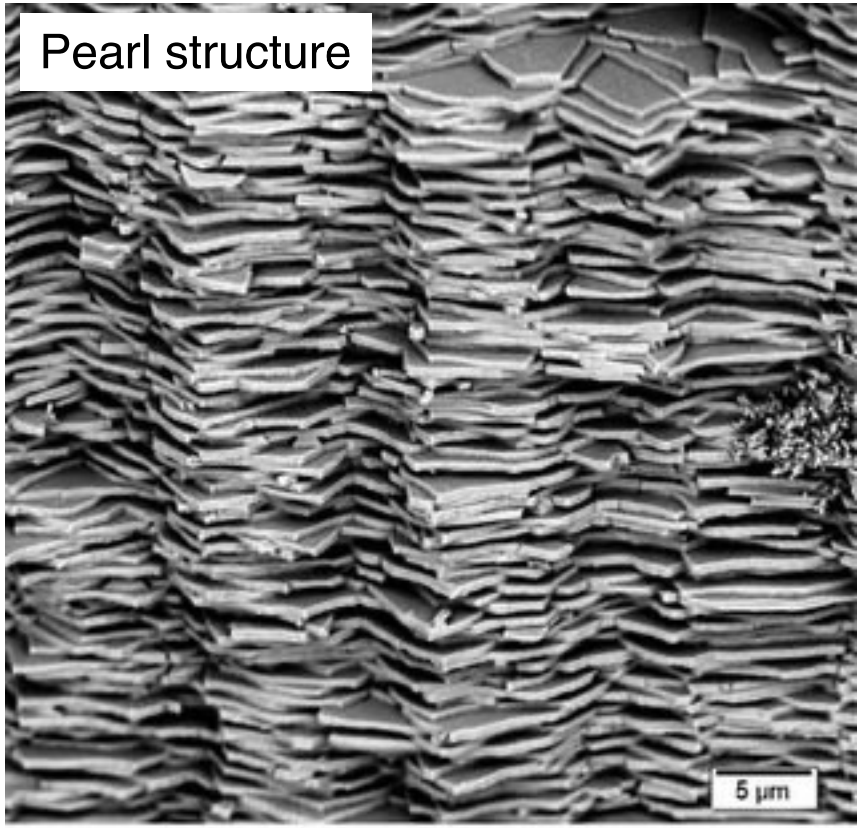
$$\gamma(0.76\,\text{wt\%}\ \text{C}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(0.022\,\text{wt\%}\ \text{C}) + \text{Fe}_3\text{C}(6.70\,\text{wt\%}\ \text{C})$$

(Austenite) (Pearlite)

Equilibrium eutectoid temperature is at 727˚C


Pearlite has a classic eutectic microstructure!

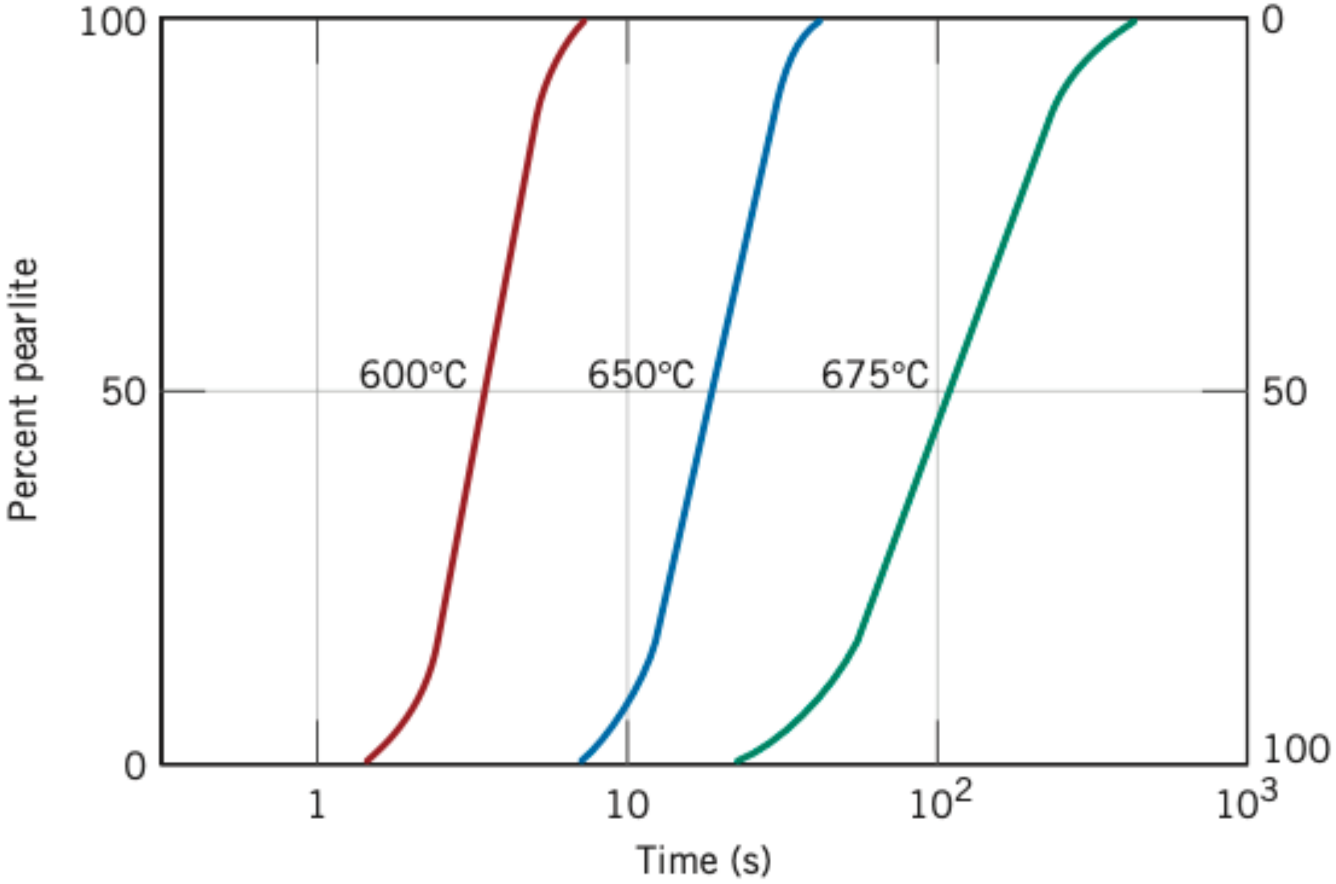
↔


Pearl structure

Example: How long does the iron eutectoid take to form?

$$\underset{\text{(Austenite)}}{\gamma(0.76\ \text{wt\%}\ \text{C})} \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \underset{\text{(Pearlite)}}{\alpha(0.022\ \text{wt\%}\ \text{C}) + \text{Fe}_3\text{C}(6.70\ \text{wt\%}\ \text{C})}$$

Equilibrium eutectoid temperature is at 727°C

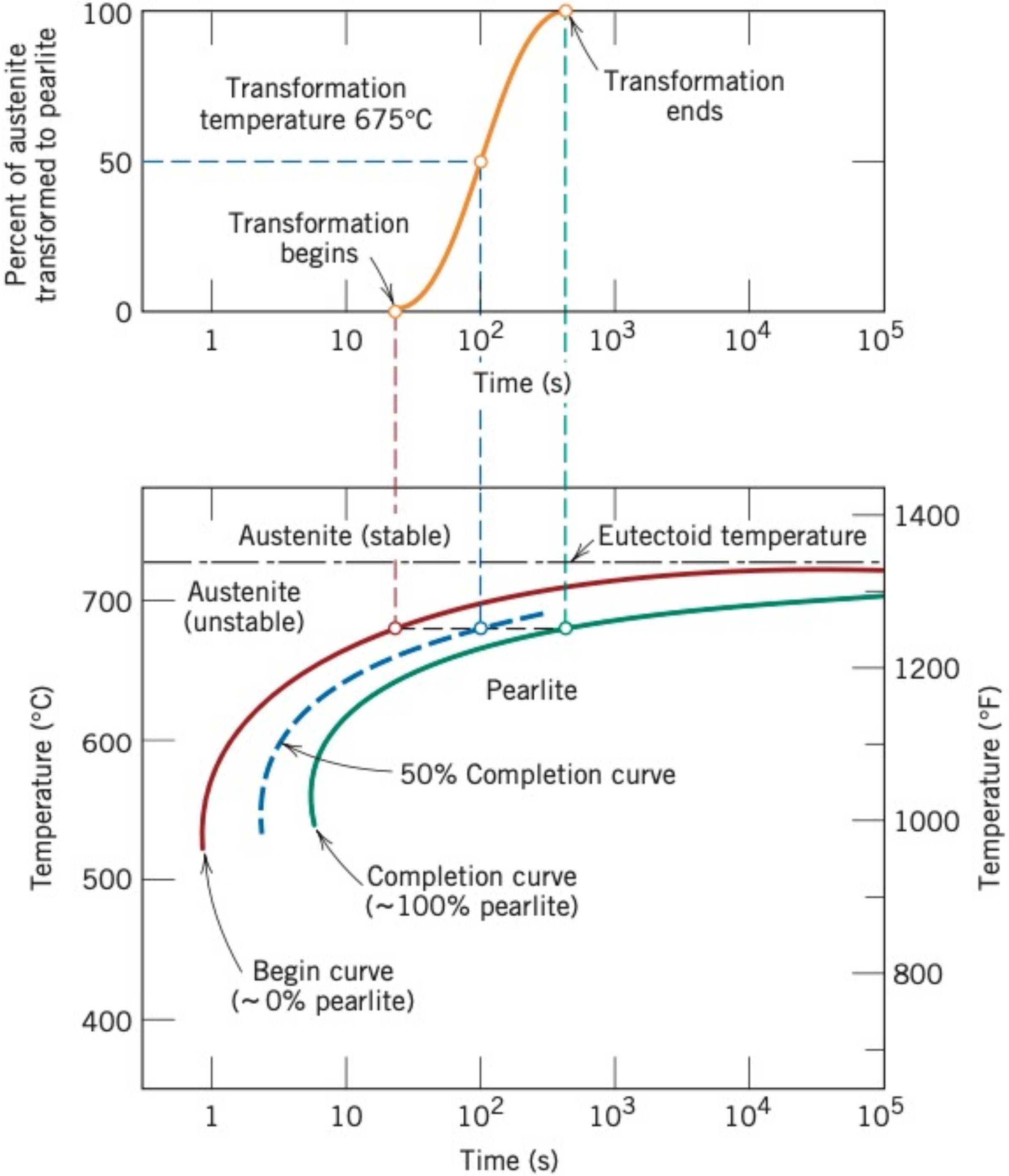


← Austenite at high temperature cooled to the temperature indicated and then maintained

Supercooling: Difference between the equilibrium transformation temperature and the hold temperature

The larger the supercooling, the larger the driving force for transformation, the faster the transformation

Time-Temperature-Transformation (TTT) diagrams*



Let's walk through this diagram:

Above the eutectoid temperature (727˚C), only stable austenite → No change over any timeframe

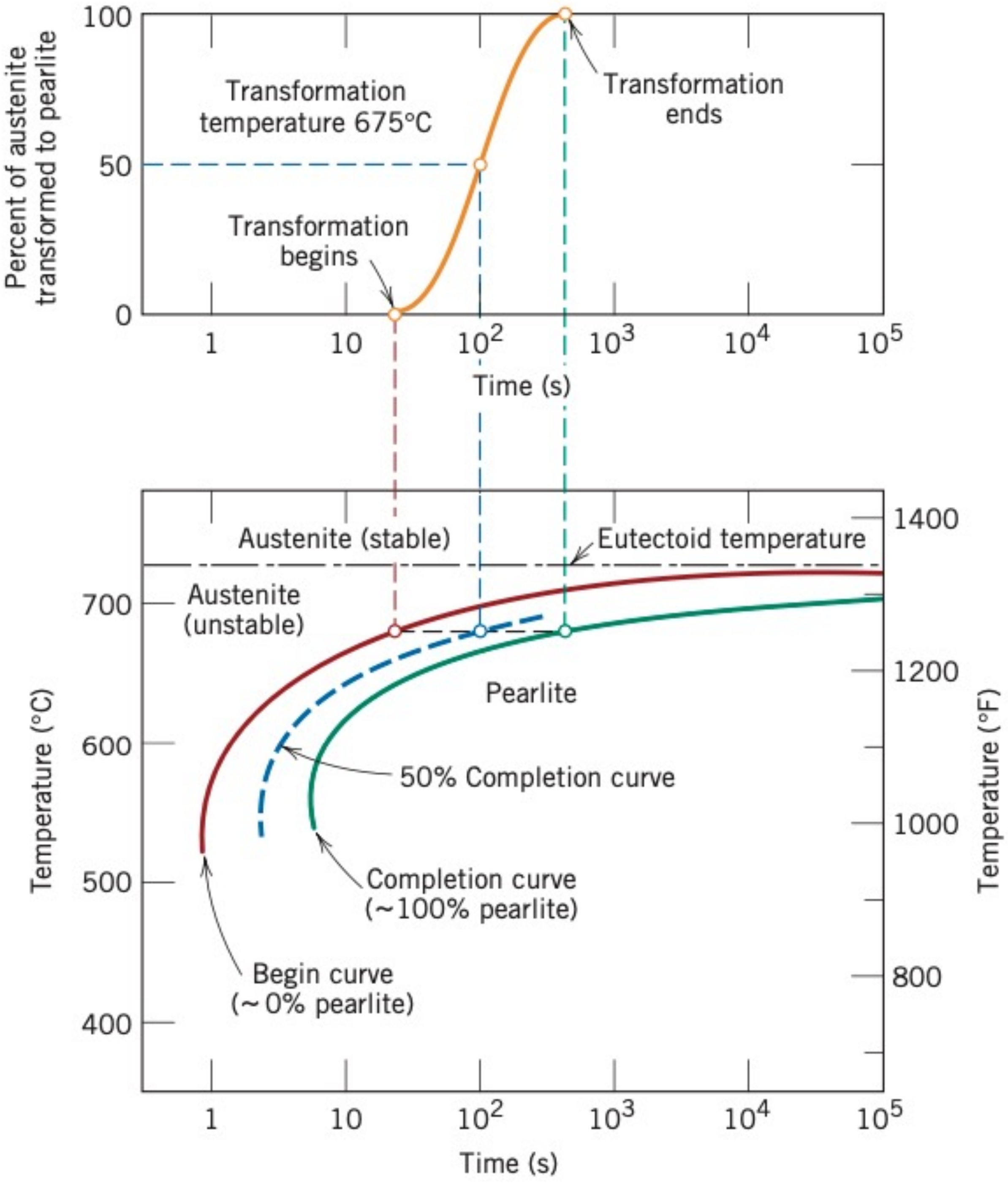
The time needed for the austentite to pearlite transformation depends on the degree of supercooling

On the left is of the red line is 100% unstable austenite. It will transform to pearlite given enough time

On the right of the green line is 100% pearlite

*Sometimes called isothermal transformation diagrams

Time-Temperature-Transformation (TTT) diagrams*



Let's walk through this diagram:

At temperatures just below the eutectoid (low supercooling) → Long times to transform (10^5 s)

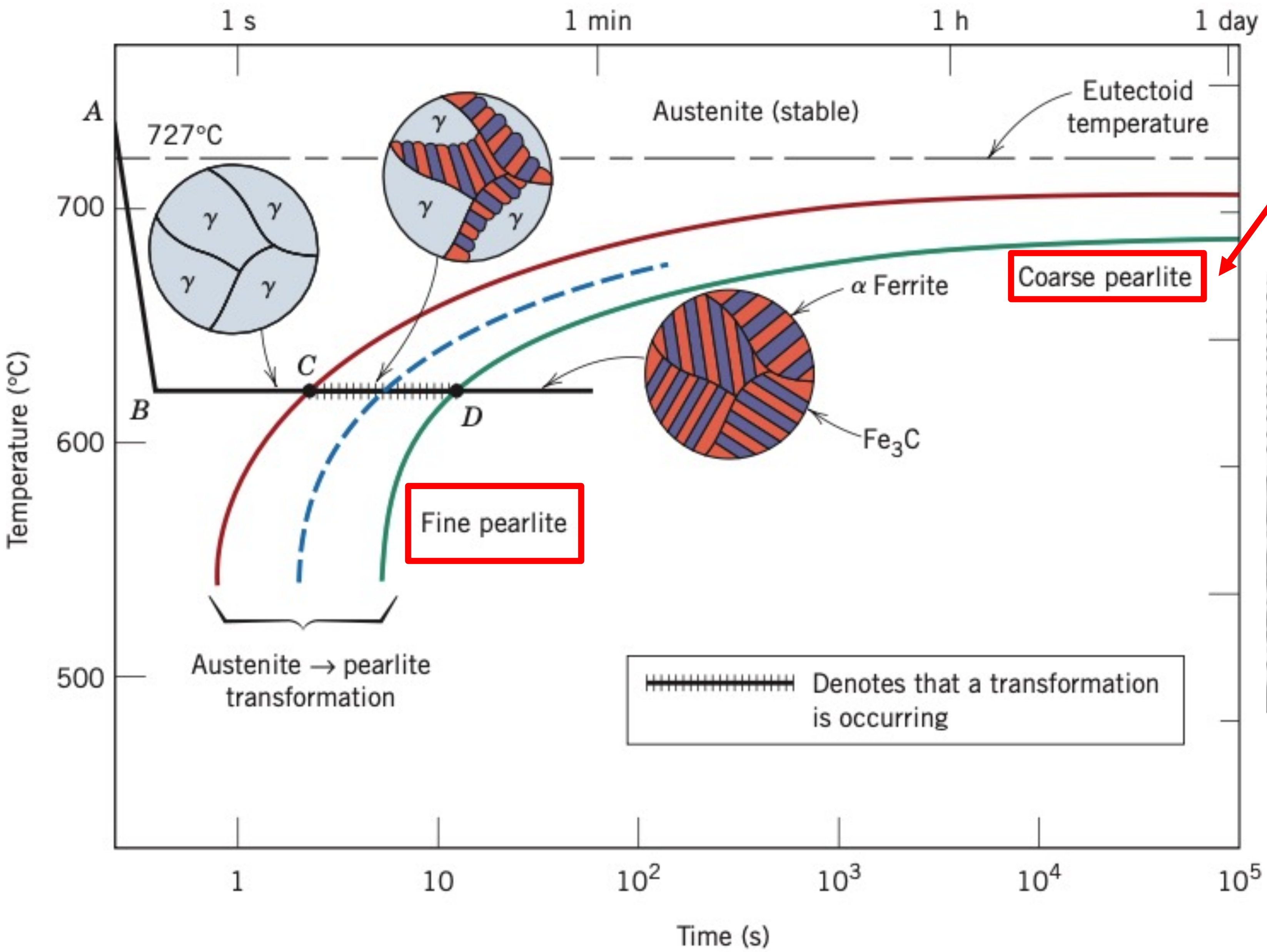
The larger the supercooling, the faster the transformation rate.

At 540˚C, ~ 3 s needed to go to 50% completion

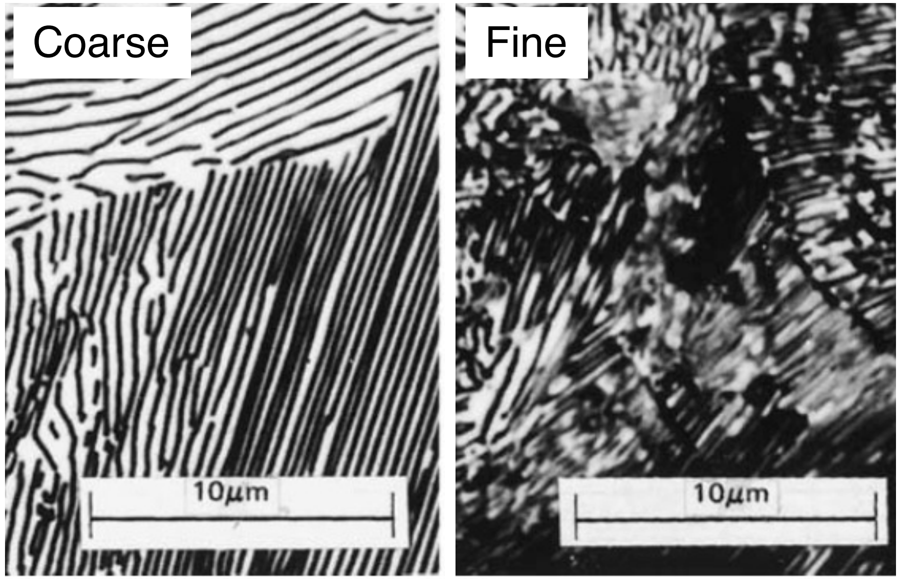
Constraint 1: A TTT diagram is only valid for a particular composition.

Constraint 2: Plots are only accurate if the temperature is held constant throughout the transformation

*Sometimes called isothermal transformation diagrams

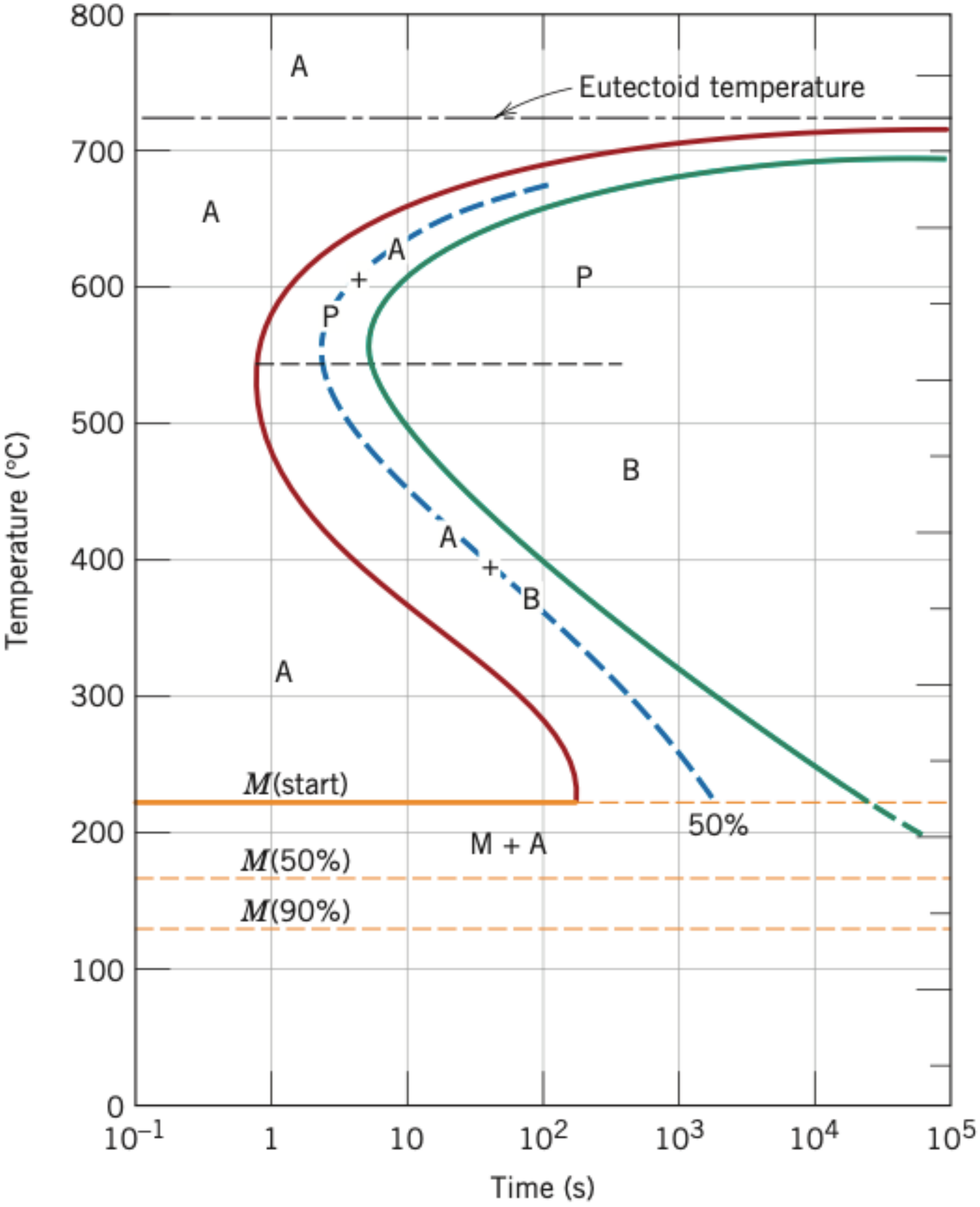


TTT diagrams can also give you information about the size of the microstructural features



Transformation temperatures impact microstructure!

Let’s look at a more realistic TTT diagram for eutectoid steel



A → Austenite
P → Pearlite
B → Bainite
M → Martensite

Note: Know that these phases exist and have different microstructures and properties

Depending on the transformation temperature, either B or P might form.

All curves are C-shaped and have a “**nose**”.
The nose represents the largest transformation rate

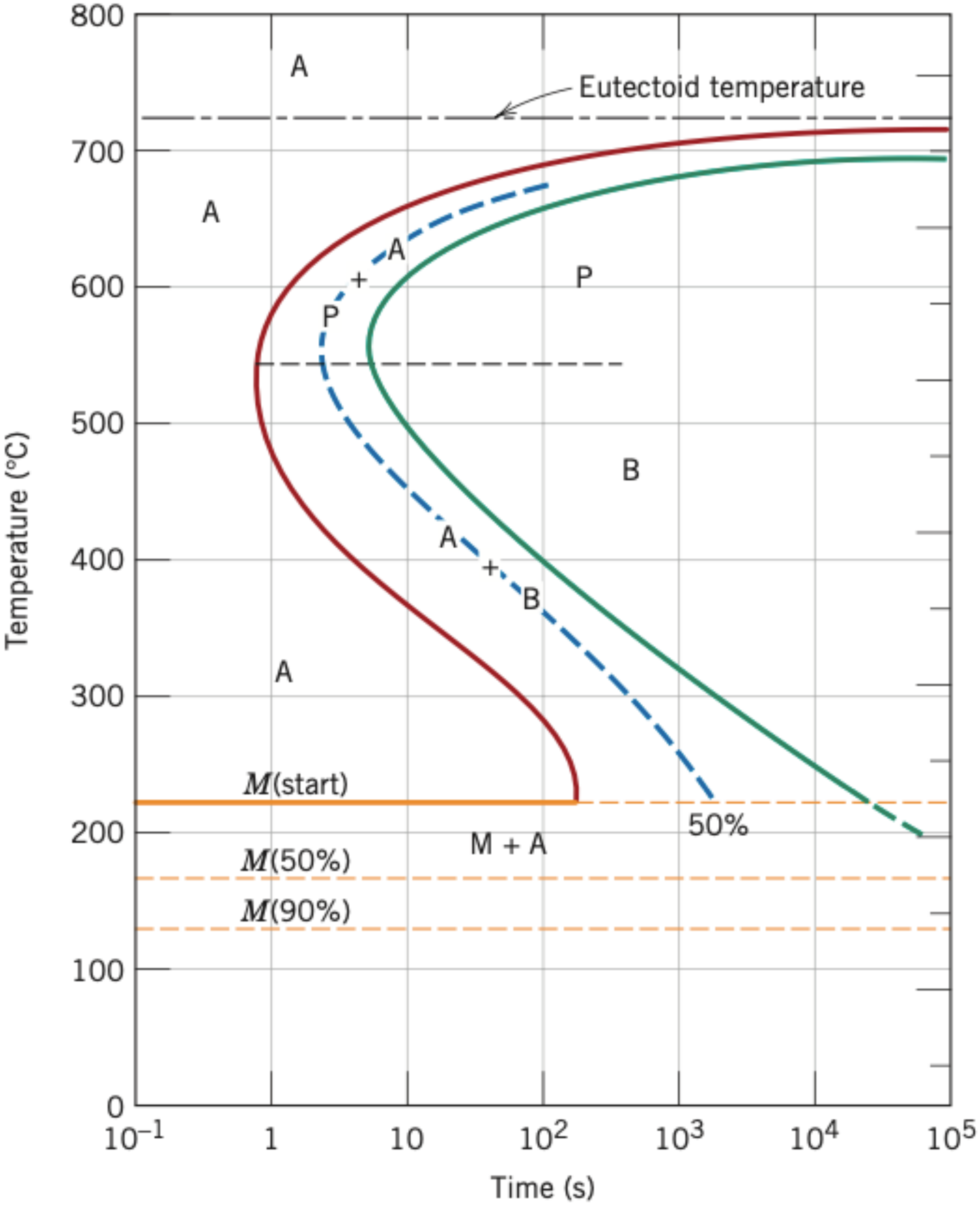
IMPORTANT: Austenite and solid-state transformations

For MSE 214, **only austenite** undergoes solid-state transformations on cooling

Allowed solid-state transformations	Not-allowed solid-state transformations
Austenite → Ferrite	Ferrite → Martenite
Austenite → Martensite	Martensite → Pearlite
Austentite → Pearlite	Pearlite → Bainite
Austenite → Bainite	Etc.

Transformations can only occur if there is some austenite left to transform

No more austenite = No more transformation = Composition is “locked-in” until room temperature



Let’s look at a more realistic TTT diagram for eutectoid steel

Since martensite formation is diffusionless and “instantaneous”, we treat it as time-independent

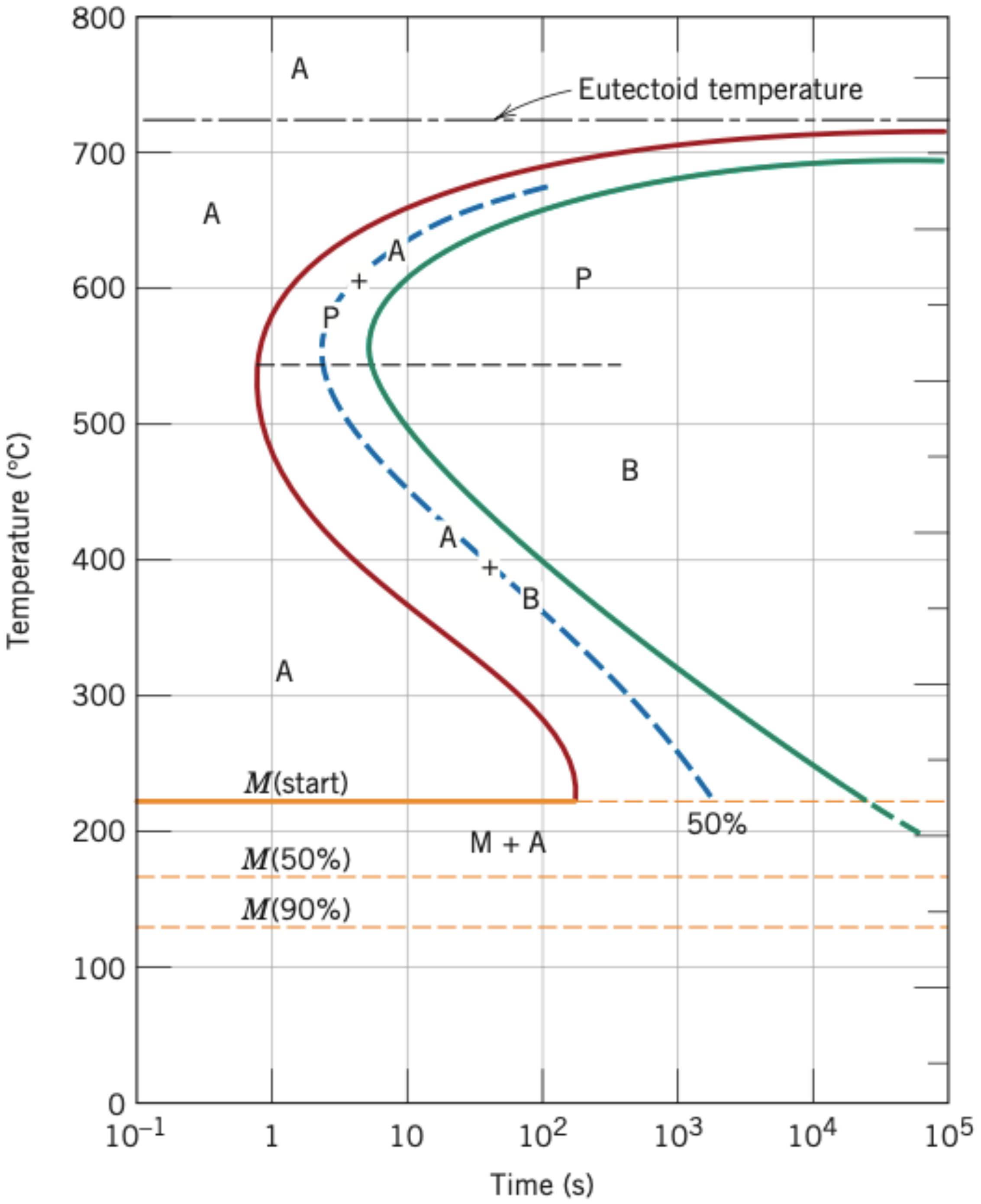
Martensite transformation lines are horizontal → martensite fraction only changes with temperature

Cooling from 727˚C to 150˚C and holding it there, we will be past the M(50%) line but before the M(90%) line.

The fraction of martensite is inbetween those values.

The remaining fraction is austenite

No change with time



Let's try to use a TTT diagram to predict metastable microstructure

Starting from 760˚C:

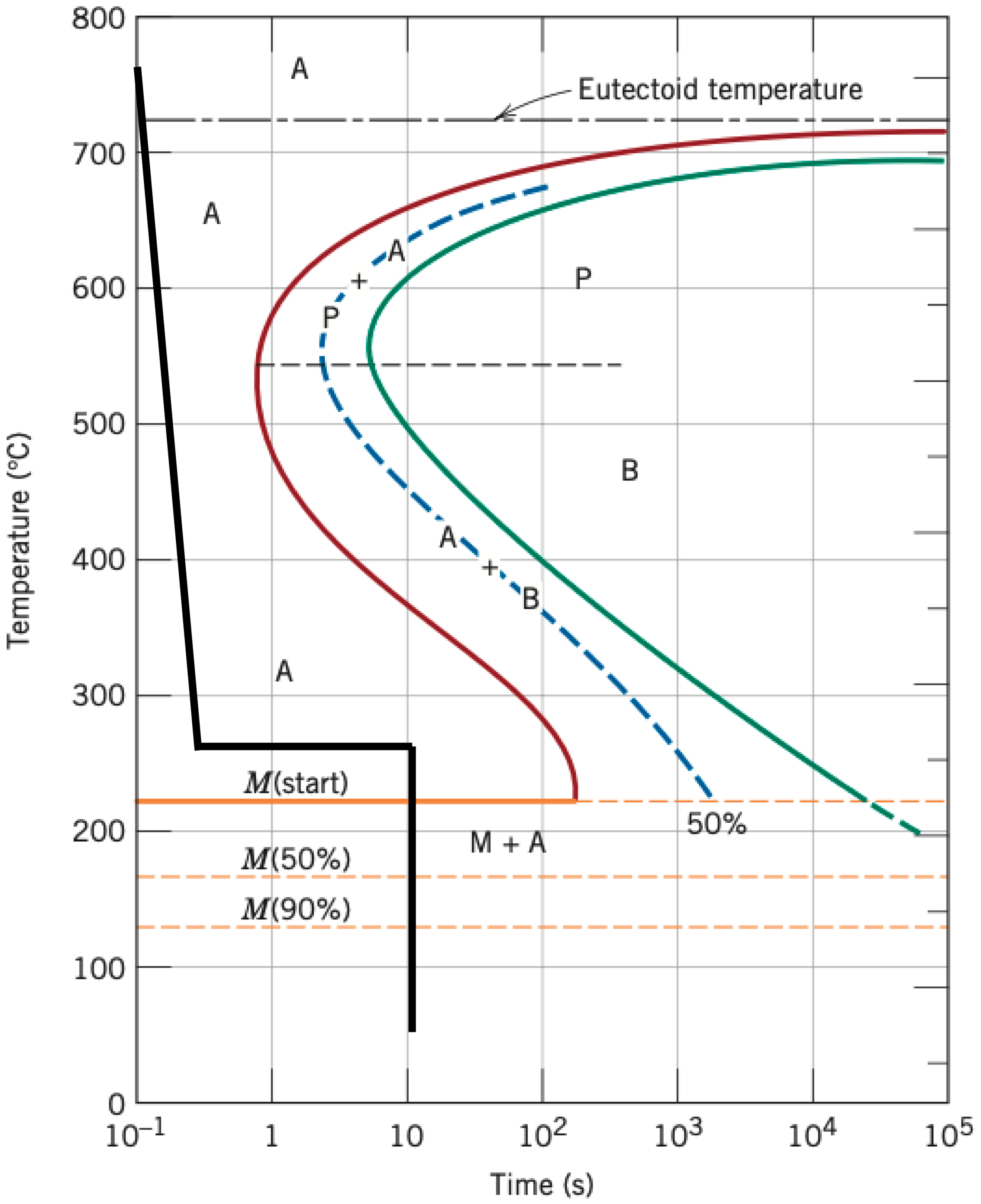
<u>**a)** Rapidly cool to 350˚C, hold for 10^4 s, quench to RT</u>

Assume initial cooling is rapid enough to prevent any transformations from happening

Austenite (A) → Bainite (B) starts ~10s and is completed after ~600 s. After 10^4s, it's 100% B

Quenching to RT does not produce any martensite even though it passes through the martensite region.

No austenite left to transform!



Let’s try to use a TTT diagram to predict metastable microstructure

Starting from 760˚C:

<u>**b)** Rapidly cool to 250˚C, hold for 10s, quench to RT</u>

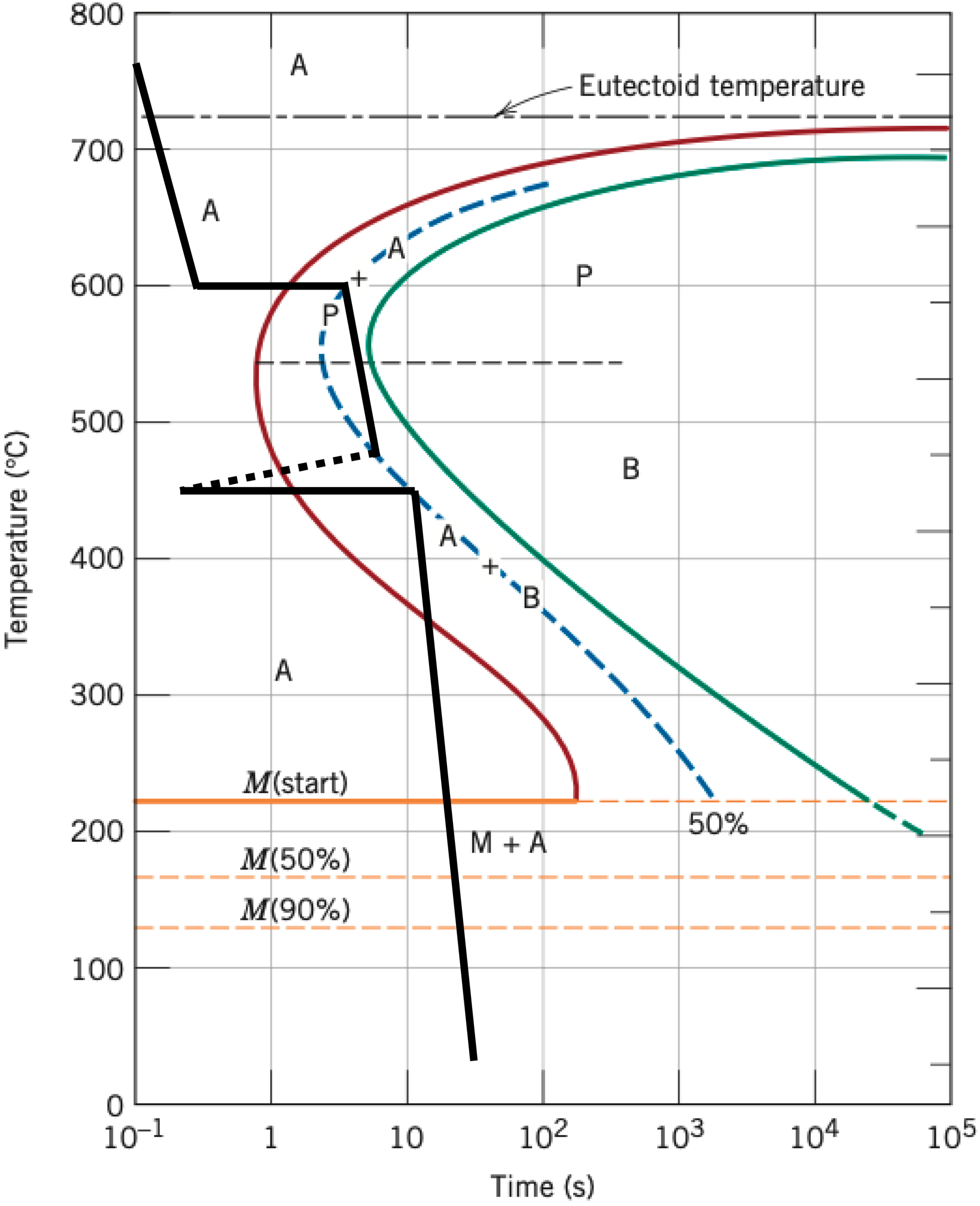
Assume initial cooling is rapid enough to prevent any transformations from happening

At 250˚C, it takes about 200s for bainite (B) transformation to begin.

At 10s, metal is still 100% austenite (A)

Quenching to RT means it crosses through the M(start) and goes through the martensite region.

Metal is 100% martensite at the end



Let’s try to use a TTT diagram to predict metastable microstructure

Starting from 760˚C:

<u>**c)** Rapidly cool to 600˚C, hold for 4s, rapidly cool to 450˚C, hold for 10s, then quench to RT</u>

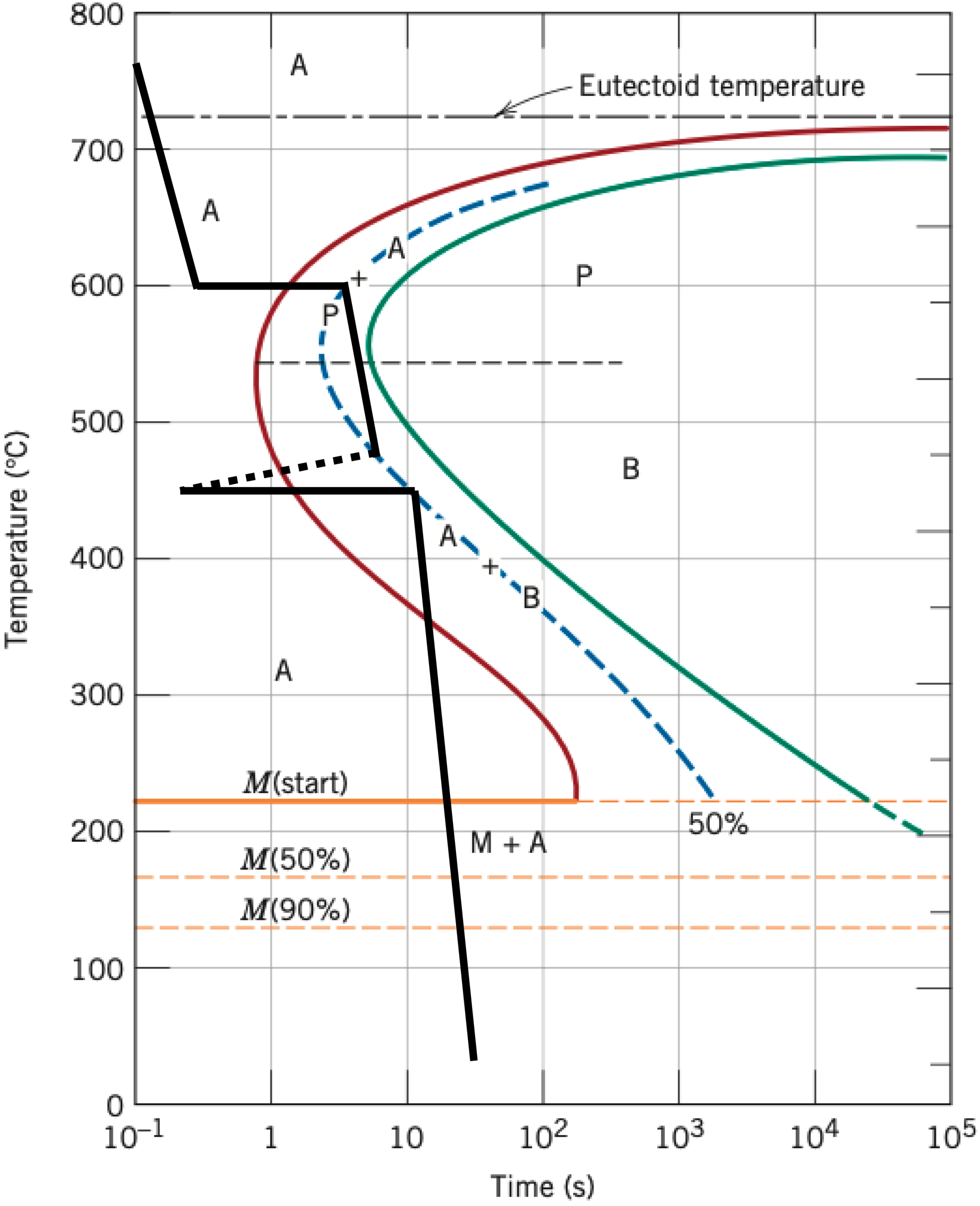
Holding at 600˚C for 4s → ~50% A + P

Assume during rapid cooling to 450˚C, nothing happens

At 450˚C, we start timing from 0 again to see what happens to the unstable austenite.

Holding at 450˚C for 10s → 50% of remaining A till transform into B (25% of original sample is B)

Quenching to RT transforms the remaining A to M.



Limitations of TTT diagrams

TTT diagrams: Only valid for conditions of constant temperature

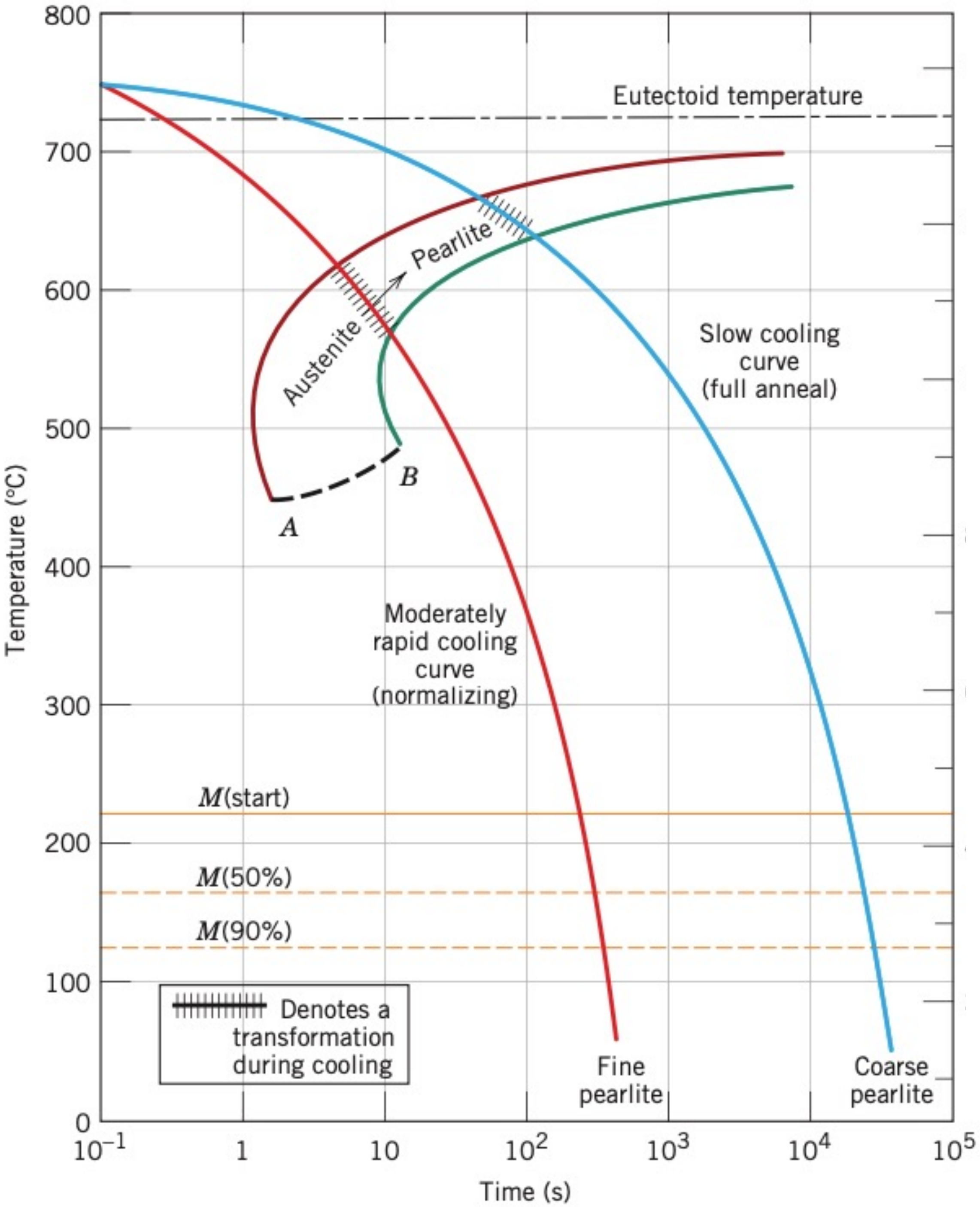
In real life, not practical to rapidly cool a metal to a set temperature and then hold it there for time.

Instead, we cool the metal continuously over time

TTT
(Time-Temperature-Transformation)

↓

CCT
(Continuous cooling transformation)



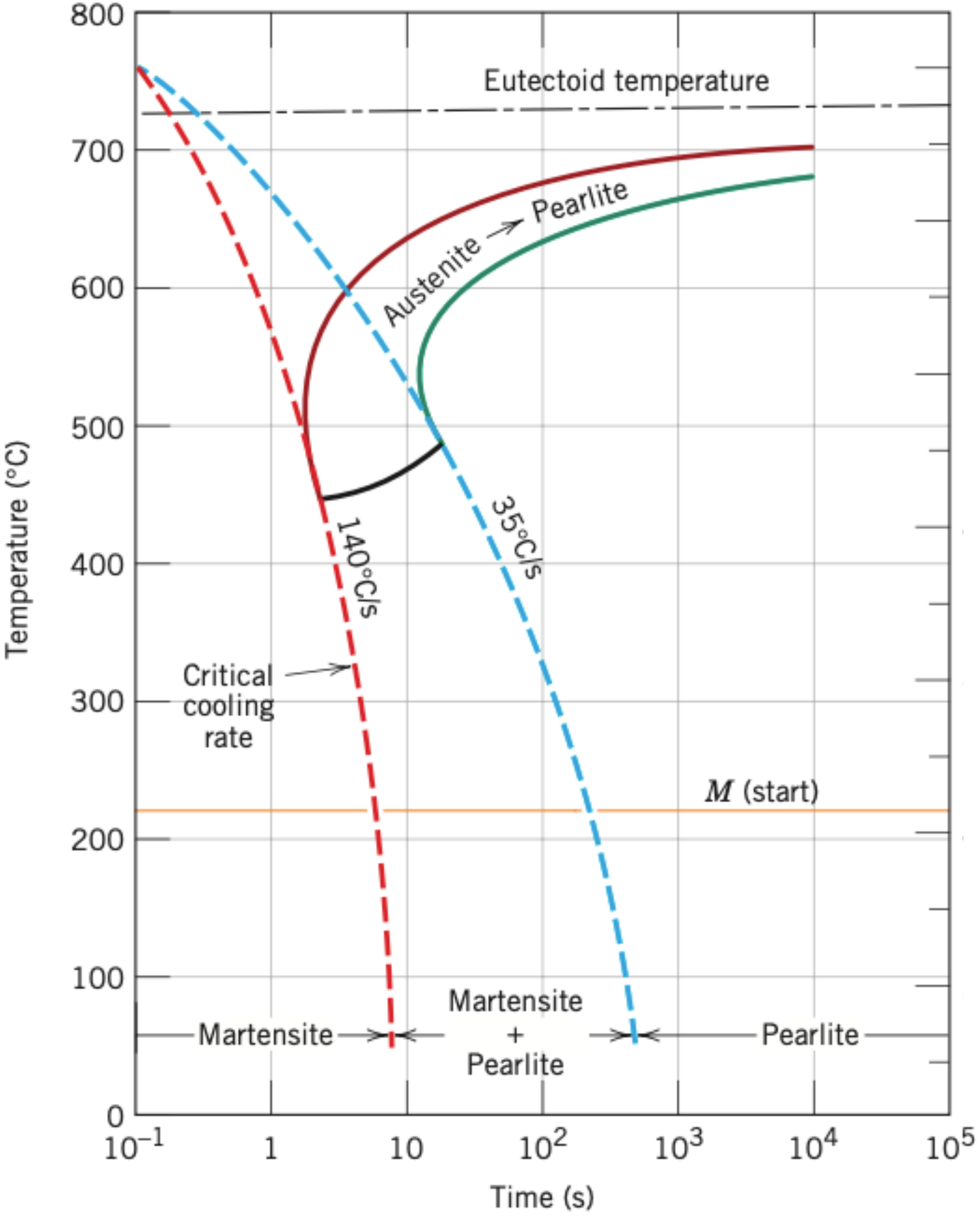
← CCT diagram

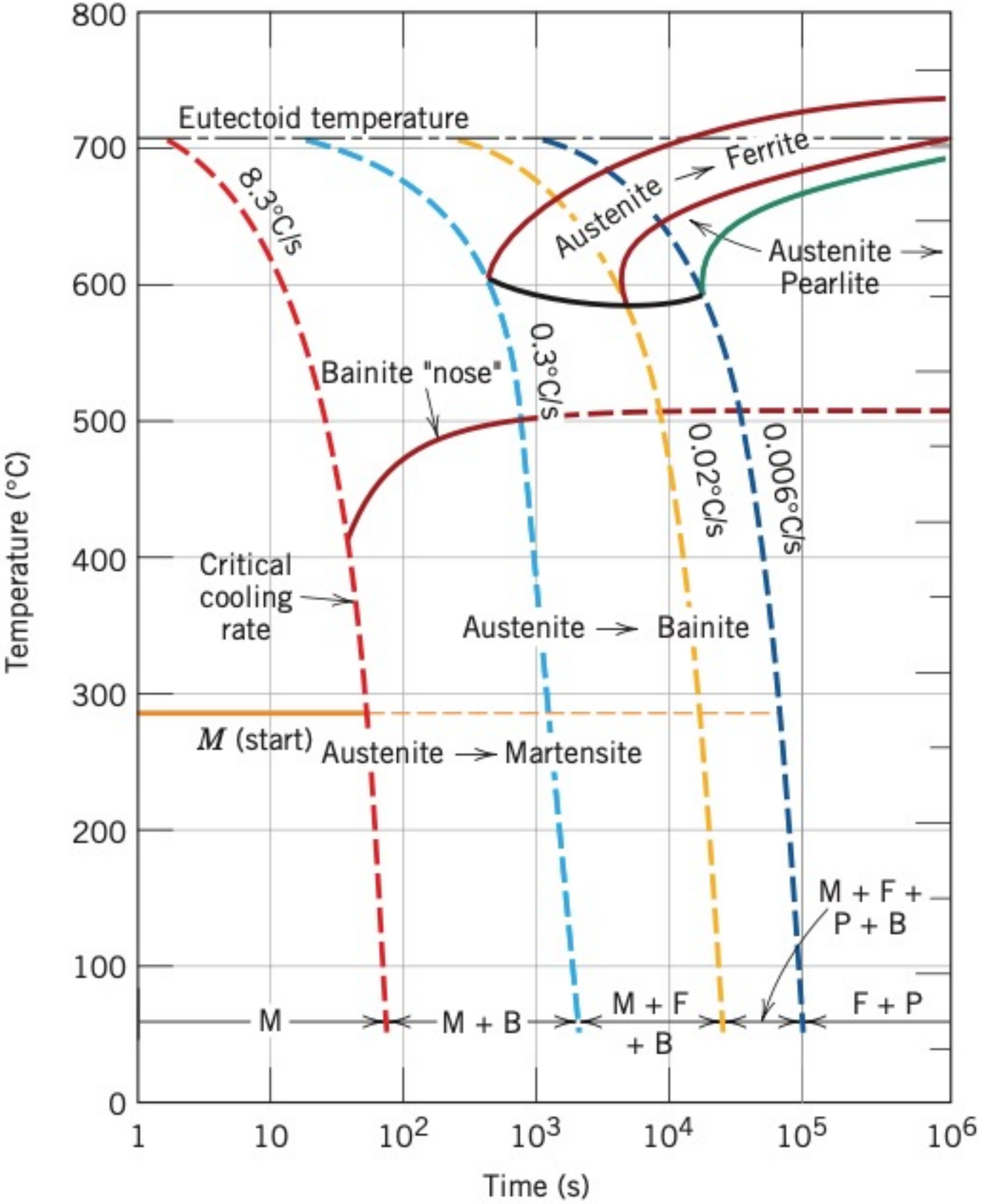
CCT diagrams can look similar to TTT diagrams!

Cooling curves (cooling at different rates) superimposed onto CCT diagrams

Transformation starts when the cooling curve intersects the beginning reaction curve and is completed when it crosses the completion curve.

If the cooling curve exits the region before crossing the completion curve, only some fraction of the metal transformed


800
700
600
500
400
300
200
100
0
Temperature (°C)
Eutectoid temperature
Austenite → Pearlite
140°C/s
35°C/s
Critical cooling rate
M (start)
Martensite
Martensite + Pearlite
Pearlite
10^{-1}
1
10
10^2
10^3
10^4
10^5
Time (s)


800
700
600
500
400
300
200
100
0
Temperature (°C)
Eutectoid temperature
Austenite → Ferrite
Austenite → Pearlite
8.3°C/s
0.3°C/s
0.02°C/s
0.006°C/s
Bainite "nose"
Critical cooling rate
Austenite → Bainite
M (start)
Austenite → Martensite
M + F + P + B
M
M + B
M + F + B
F + P
1
10
10^2
10^3
10^4
10^5
10^6
Time (s)

Week 9 Learning Objectives

- **Understand how to calculate phase fractions in hypo/hypereutectic metals**
- **Understand what a slip system is**
- **Understand why BCC metals have a ductile to brittle transition temperature**
- **Understand what martensite is and why it is strong and brittle**
- **Understand what a TTT diagram is and how to use it**
- **Understand what a CCT diagram is and how to use it**