

Chapter Outline: Phase Diagrams

Microstructure and Phase Transformations in Multicomponent Systems

- Definitions and basic concepts
- Phases and microstructure
- Binary isomorphous systems (complete solid solubility)
- Binary eutectic systems (limited solid solubility)
- Binary systems with intermediate phases/compounds
- The iron-carbon system (steel and cast iron)

Not tested: 8.12 The Gibbs Phase Rule

Definitions: Components and Phases

Component - chemically recognizable species (Fe and C in carbon steel, H₂O and NaCl in salted water). A **binary** alloy contains two components, a **ternary** alloy – three, etc.

Phase – a portion of a system that has uniform physical and chemical characteristics. Two distinct phases in a system have distinct physical **or** chemical characteristics (e.g. water and ice) and are separated from each other by definite **phase boundaries**. A phase may contain one or more components.

A single-phase system is called **homogeneous**, systems with two or more phases are **mixtures** or **heterogeneous** systems.

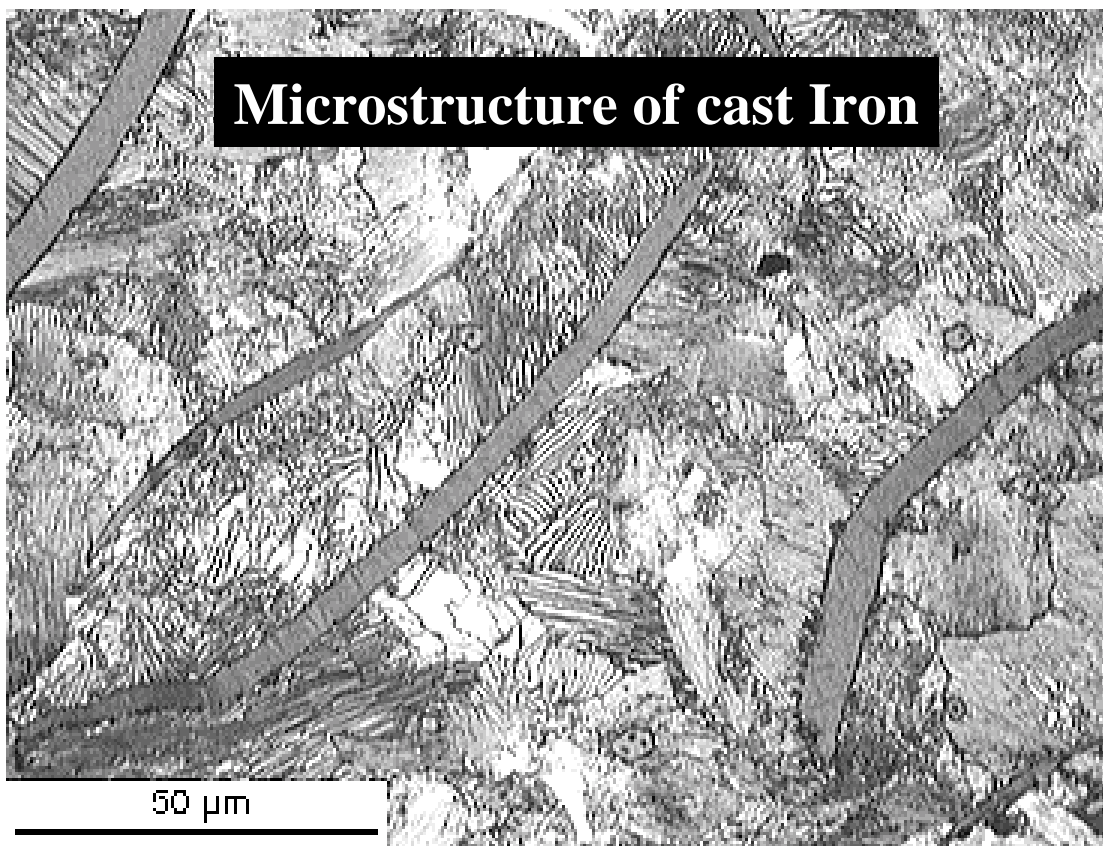
Definitions: Solubility Limit

Solvent - host or major component in solution, **solute** - minor component (Chapter 4).

Solubility Limit of a component in a phase is the maximum amount of the component that can be dissolved in it (e.g. alcohol has unlimited solubility in water, sugar has a limited solubility, oil is insoluble). The same concepts apply to solid phases: Cu and Ni are mutually soluble in any amount (unlimited solid solubility), while C has a limited solubility in Fe.

Microstructure

The properties of an alloy depend not only on proportions of the phases but also on how they are arranged structurally at the microscopic level. Thus, the microstructure is specified by the number of phases, their proportions, and their arrangement in space.



This is an alloy of Fe with 4 wt.% C. There are several phases. The long gray regions are flakes of graphite. The matrix is a fine mixture of BCC Fe and Fe₃C compound.

Phase diagrams will help us to understand and predict the microstructures like the one shown in this page

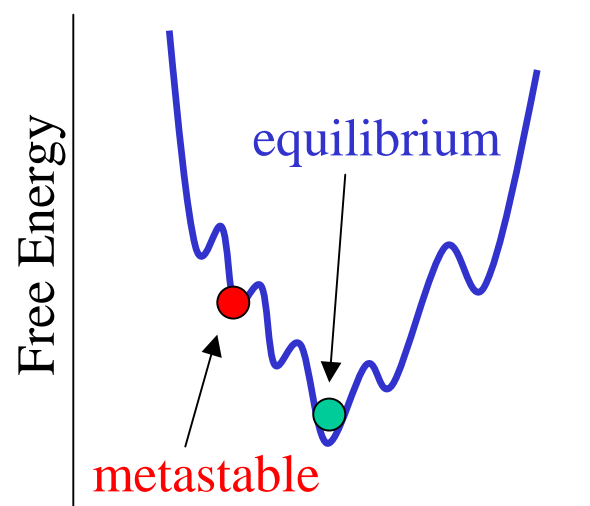
Equilibrium and Metastable States

A system is at **equilibrium** if at constant temperature, pressure and composition the system is stable, not changing with time.

Equilibrium is the state that is achieved given sufficient time. But the time to achieve equilibrium may be very long (the kinetics can be slow) that a state along the path to the equilibrium may appear to be stable. This is called a **metastable state**.

In thermodynamics the equilibrium is described as the state of system that corresponds to the minimum of thermodynamic function called the **free energy**. Thermodynamics tells us that

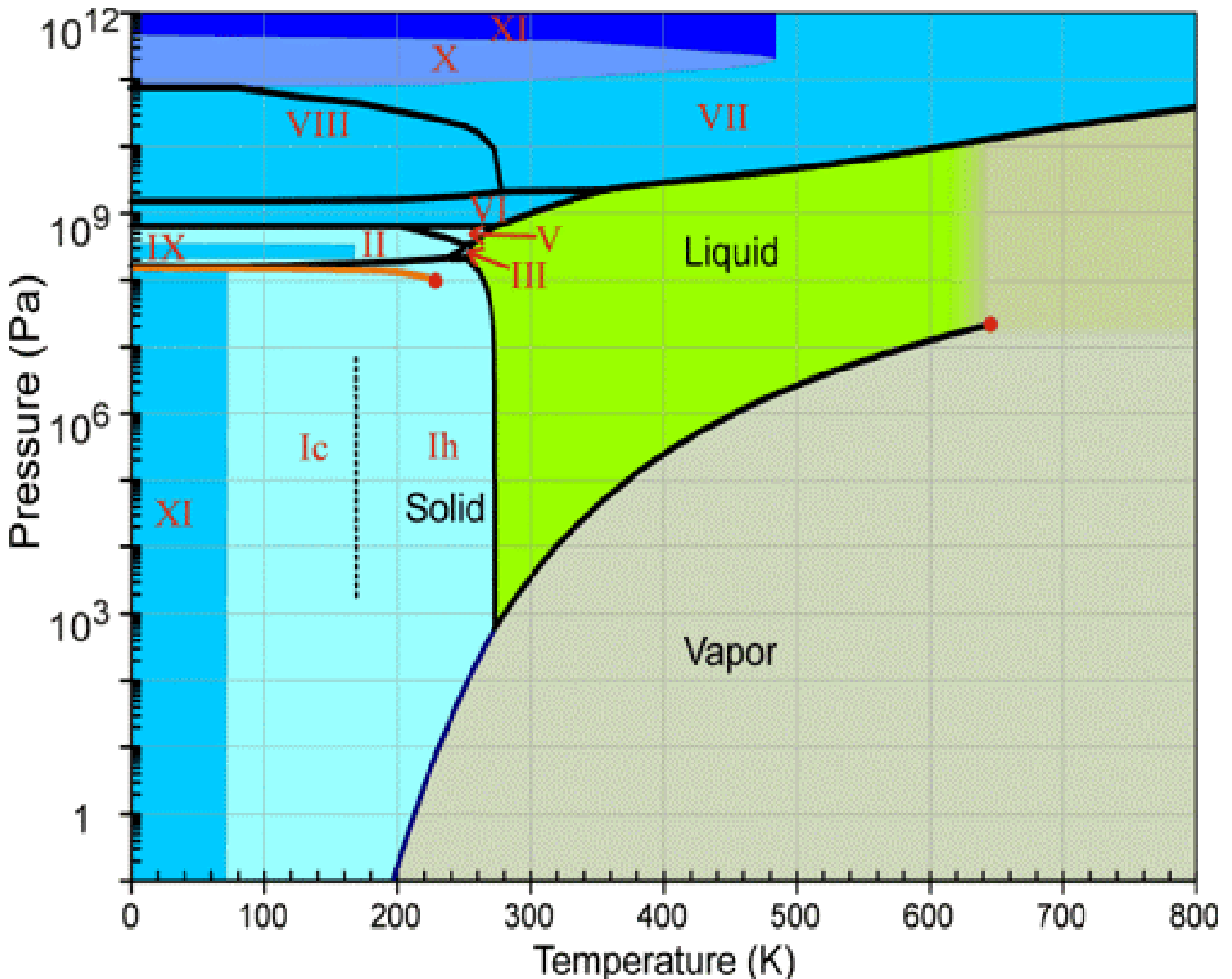
- Under conditions of a constant temperature and pressure and composition, the direction of any spontaneous change is toward a lower free energy.
- The state of stable thermodynamic equilibrium is the one with minimum free energy.
- A system at a metastable state is trapped in a local minimum of free energy that is not the global one.



Phase diagram

A **phase diagram** - graphical representation of the combinations of temperature, pressure, composition, or other variables for which specific phases exist at equilibrium.

For H_2O , a typical diagram shows the temperature and pressure at which ice (solid), water (liquid) and steam (gas) exist.



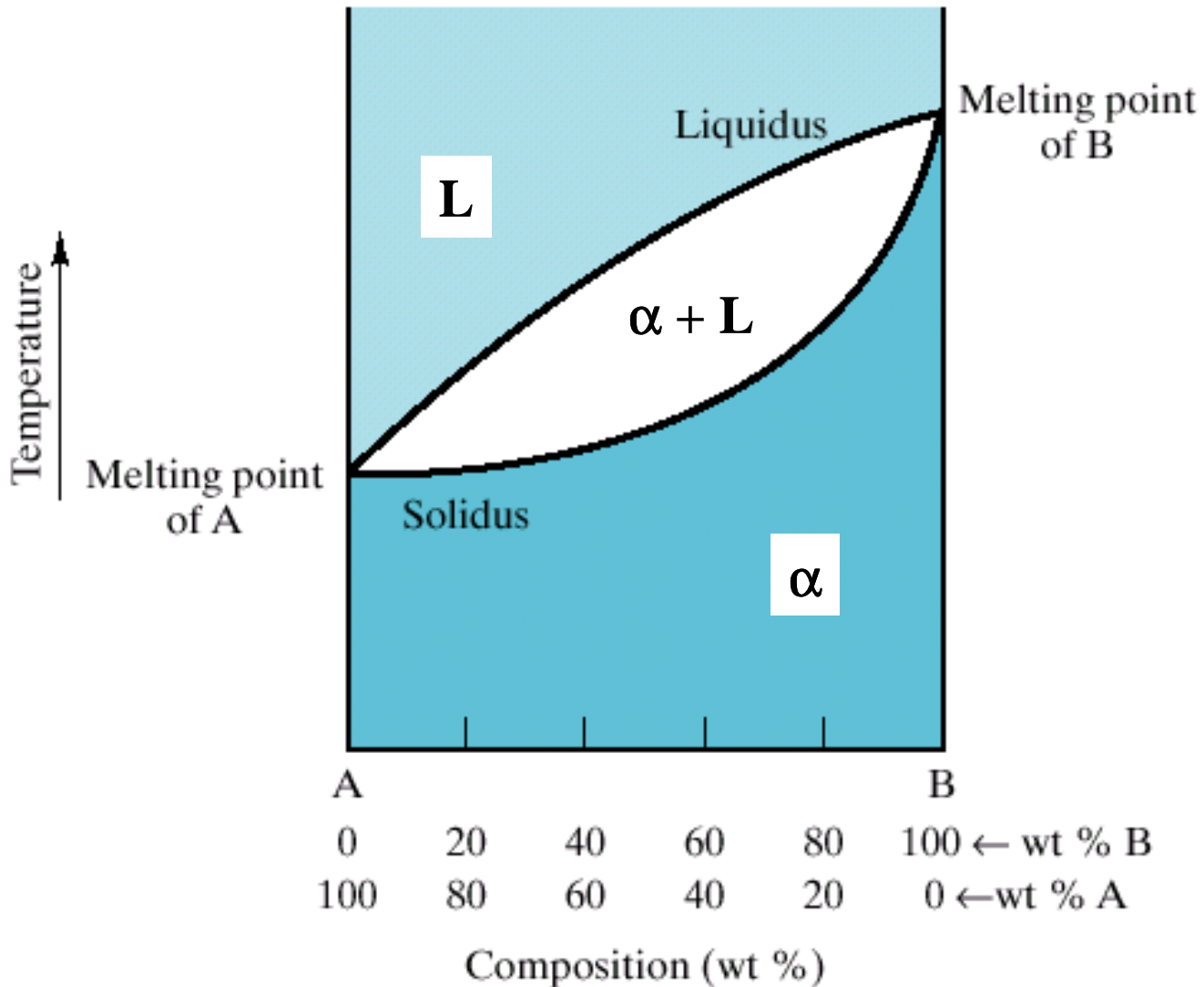
Phase diagram

A phase diagrams show what phases exist at equilibrium and what phase transformations we can expect when we change one of the parameters of the system (T, P, composition).

We will discuss phase diagrams for binary alloys only and will assume pressure to be constant at one atmosphere. Phase diagrams for materials with more than two components are complex and difficult to represent.

Binary Isomorphous Systems (I)

Isomorphous system - complete solid solubility of the two components (both in the liquid and solid phases).



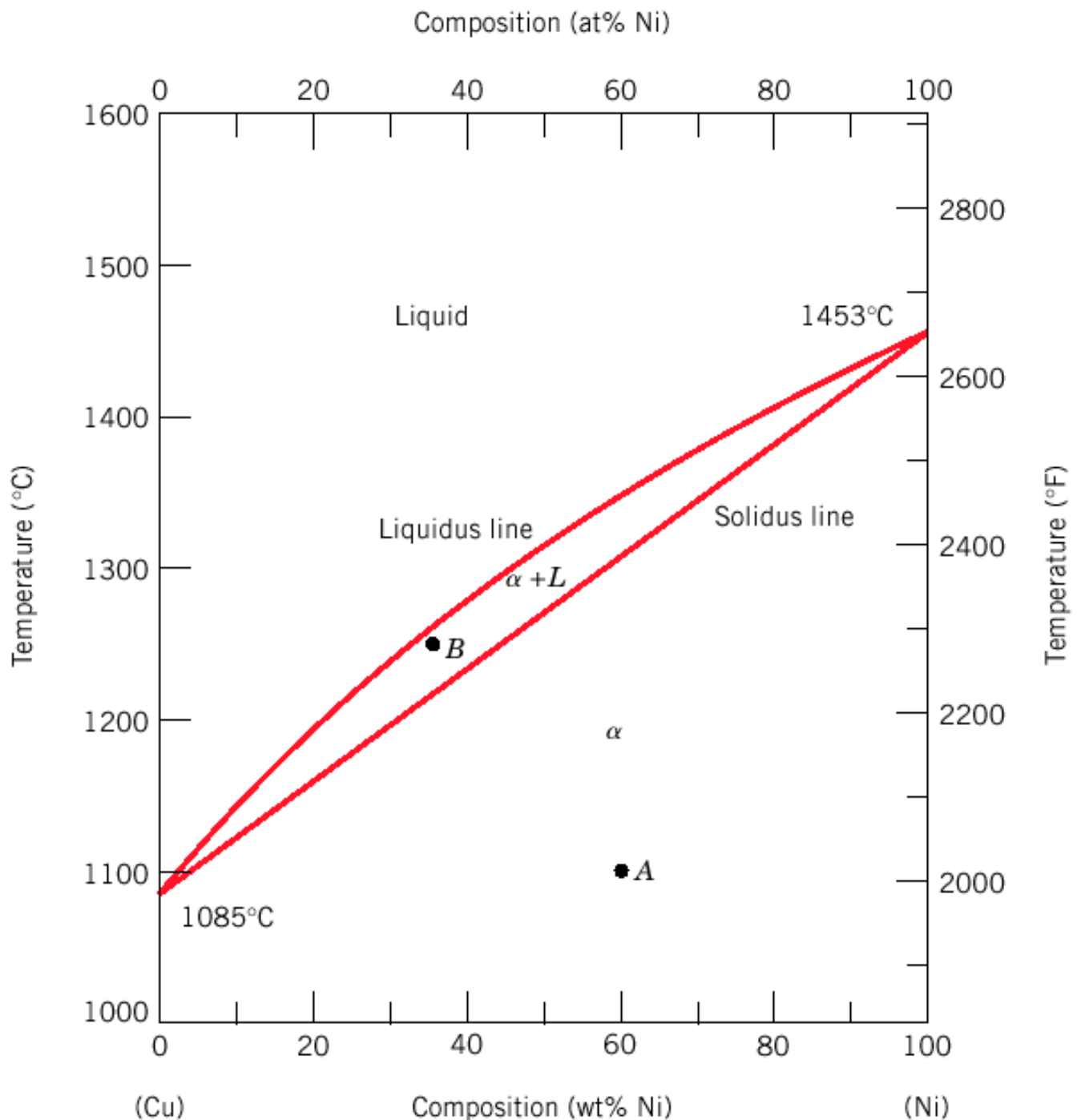
Three phase region can be identified on the phase diagram:
Liquid (L) , solid + liquid ($\alpha + L$), solid (α)

Liquidus line separates liquid from liquid + solid

Solidus line separates solid from liquid + solid

Binary Isomorphous Systems (II)

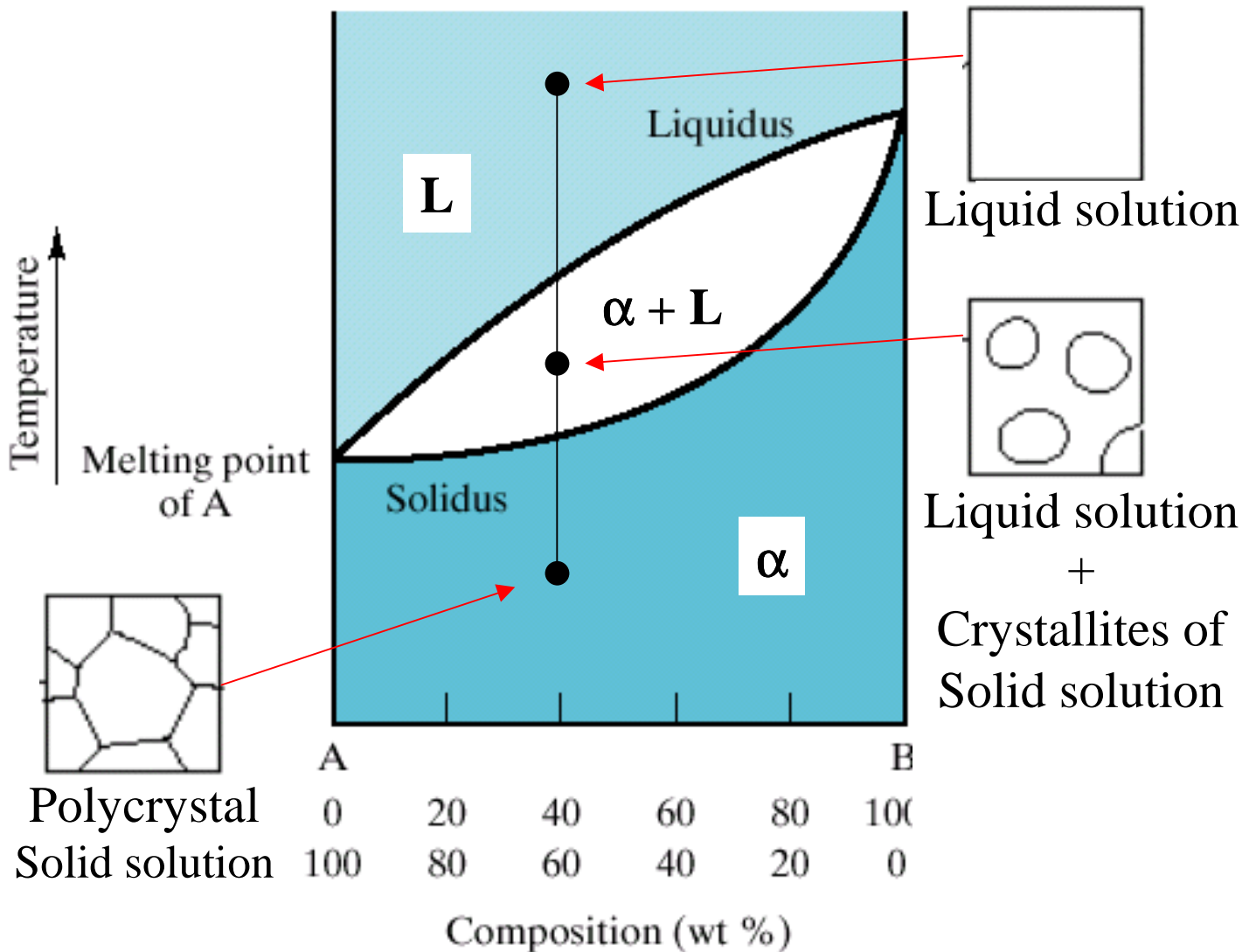
Example of isomorphous system: Cu-Ni (the complete solubility occurs because both Cu and Ni have the same crystal structure, FCC, similar radii, electronegativity and valence).



Binary Isomorphous Systems (III)

In one-component system melting occurs at a well-defined melting temperature.

In multi-component systems melting occurs over the range of temperatures, between the solidus and liquidus lines. Solid and liquid phases are in equilibrium in this temperature range.



Interpretation of Phase Diagrams

For a given temperature and composition we can use phase diagram to determine:

- 1) The phases that are present
- 2) Compositions of the phases
- 3) The relative fractions of the phases

Finding the composition in a two phase region:

1. Locate composition and temperature in diagram
2. In two phase region draw the **tie line** or isotherm
3. Note intersection with phase boundaries. Read compositions at the intersections.

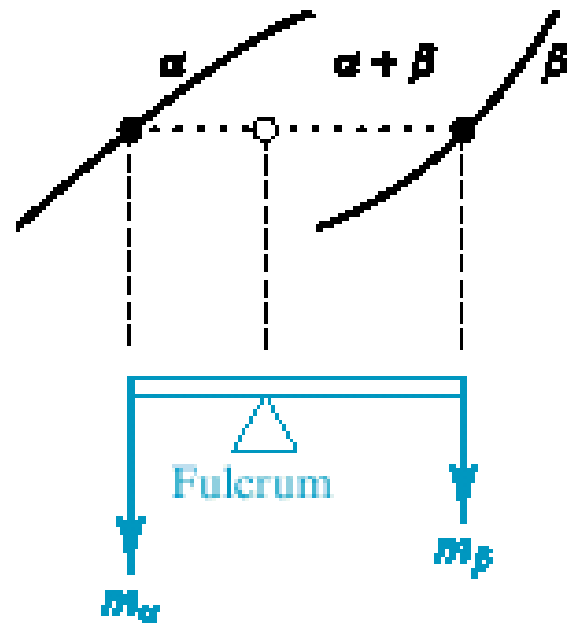
The liquid and solid phases have these compositions.

The Lever Rule

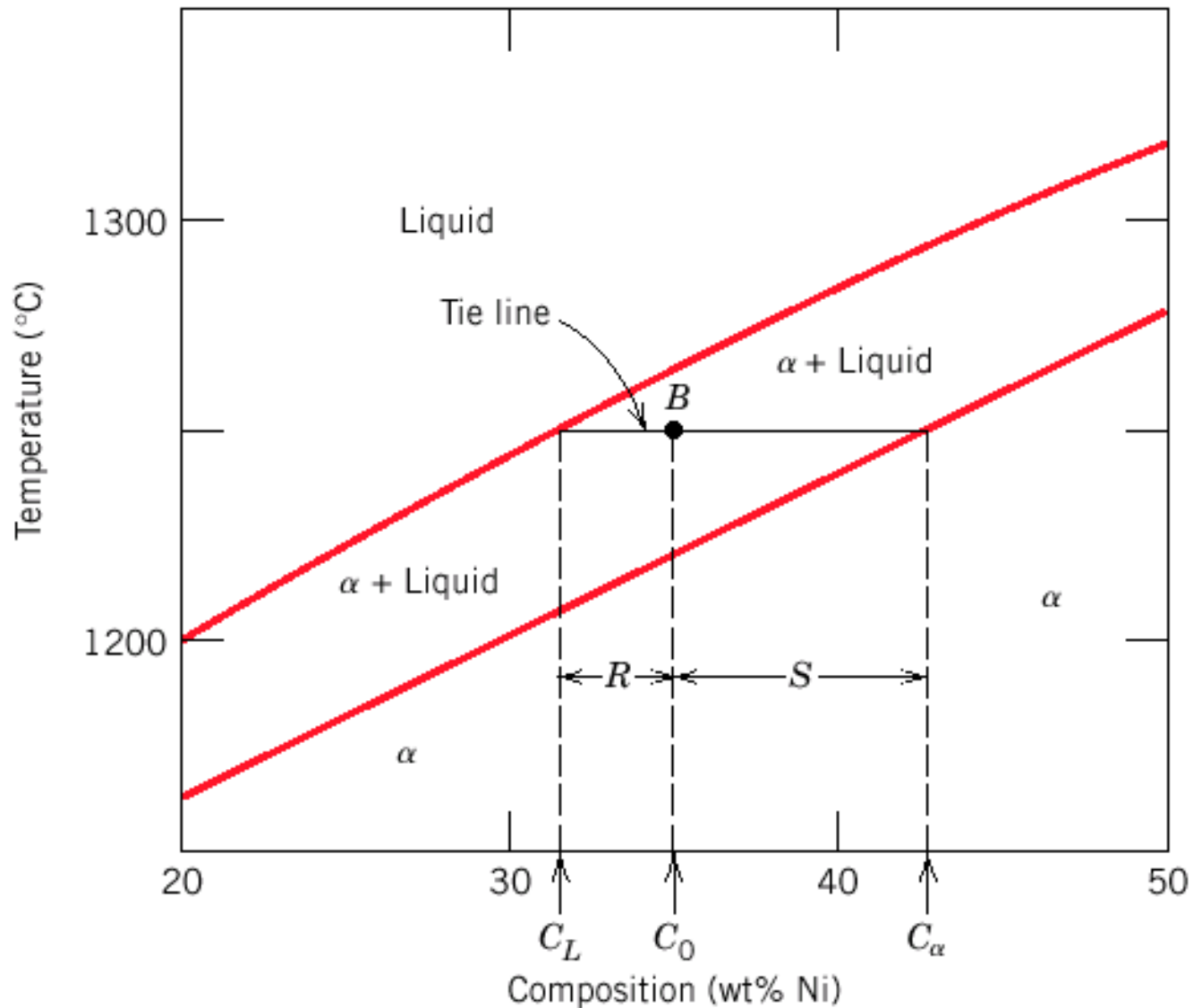
Finding the amounts of phases in a two phase region:

1. Locate composition and temperature in diagram
2. In two phase region draw the tie line or isotherm
3. Fraction of a phase is determined by taking the length of the tie line to the phase boundary for **the other phase**, and dividing by the total length of tie line

The lever rule is a mechanical analogy to the mass balance calculation. The tie line in the two-phase region is analogous to a lever balanced on a fulcrum.



The Lever Rule



Mass fractions: $W_L = S / (R+S) = (C_\alpha - C_0) / (C_\alpha - C_L)$

$W_\alpha = R / (R+S) = (C_0 - C_L) / (C_\alpha - C_L)$

Derivation of the lever rule

1) All material must be in one phase or the other:

$$W_{\alpha} + W_L = 1$$

2) Mass of a component that is present in both phases equal to the mass of the component in one phase + mass of the component in the second phase:

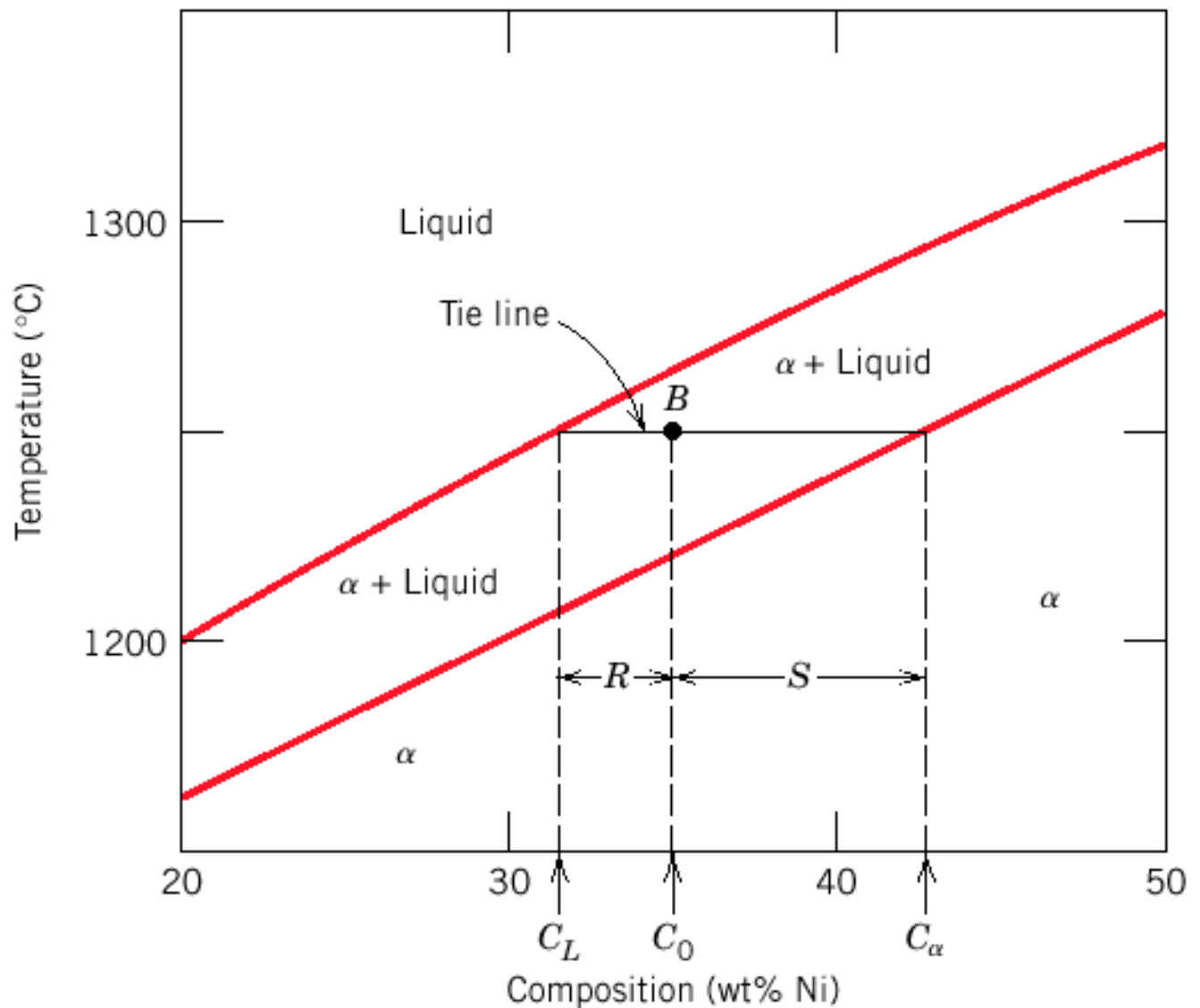
$$W_{\alpha}C_{\alpha} + W_L C_L = C_o$$

3) Solution of these equations gives us the Lever rule.

$$W_L = (C_{\alpha} - C_o) / (C_{\alpha} - C_L)$$

$$W_{\alpha} = (C_o - C_L) / (C_{\alpha} - C_L)$$

Phase compositions and amounts. An example.

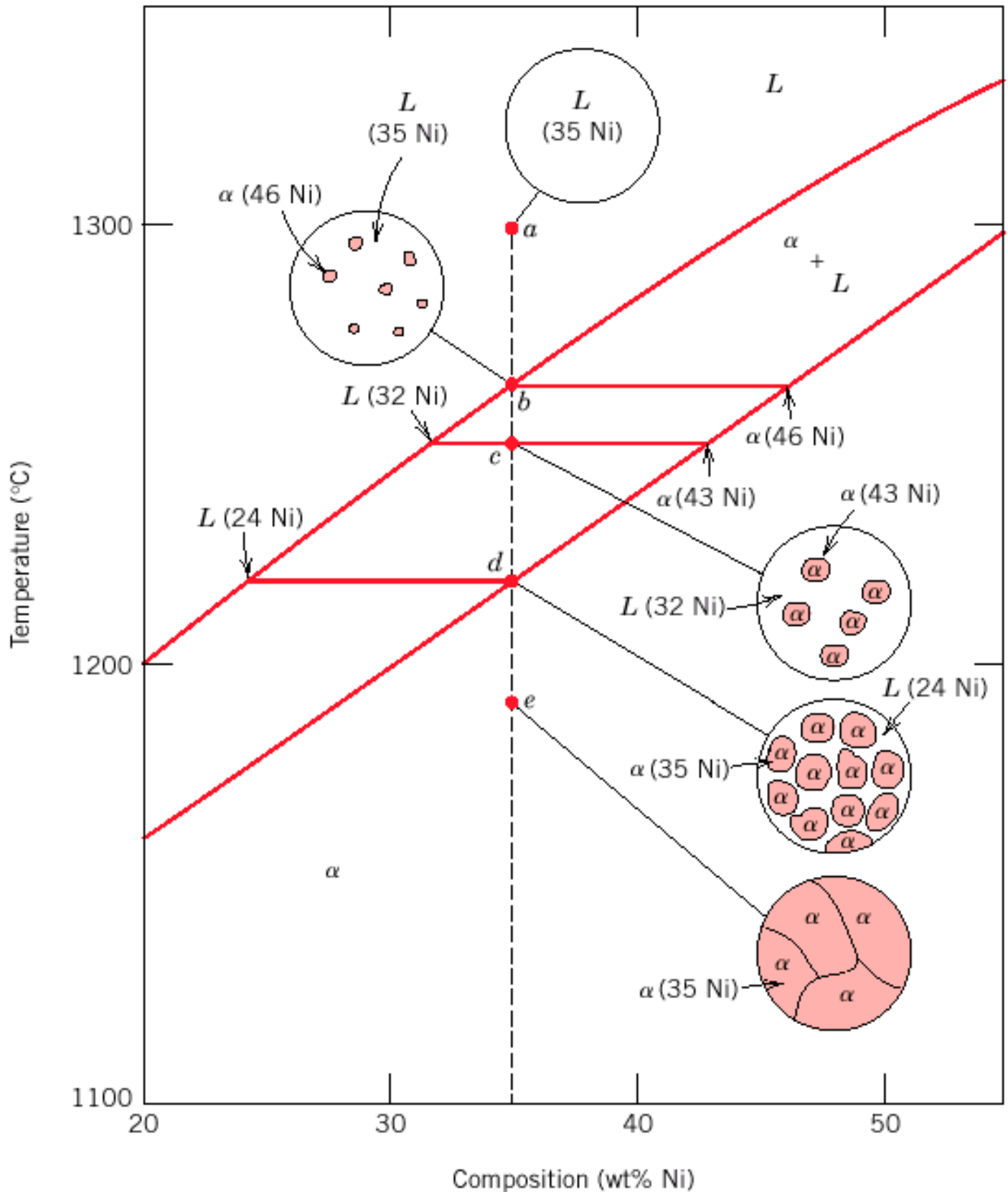


$$C_o = 35 \text{ wt. \%}, C_L = 31.5 \text{ wt. \%}, C_\alpha = 42.5 \text{ wt. \%}$$

$$\text{Mass fractions: } W_L = (C_\alpha - C_o) / (C_\alpha - C_L) = 0.68$$

$$W_\alpha = (C_o - C_L) / (C_\alpha - C_L) = 0.32$$

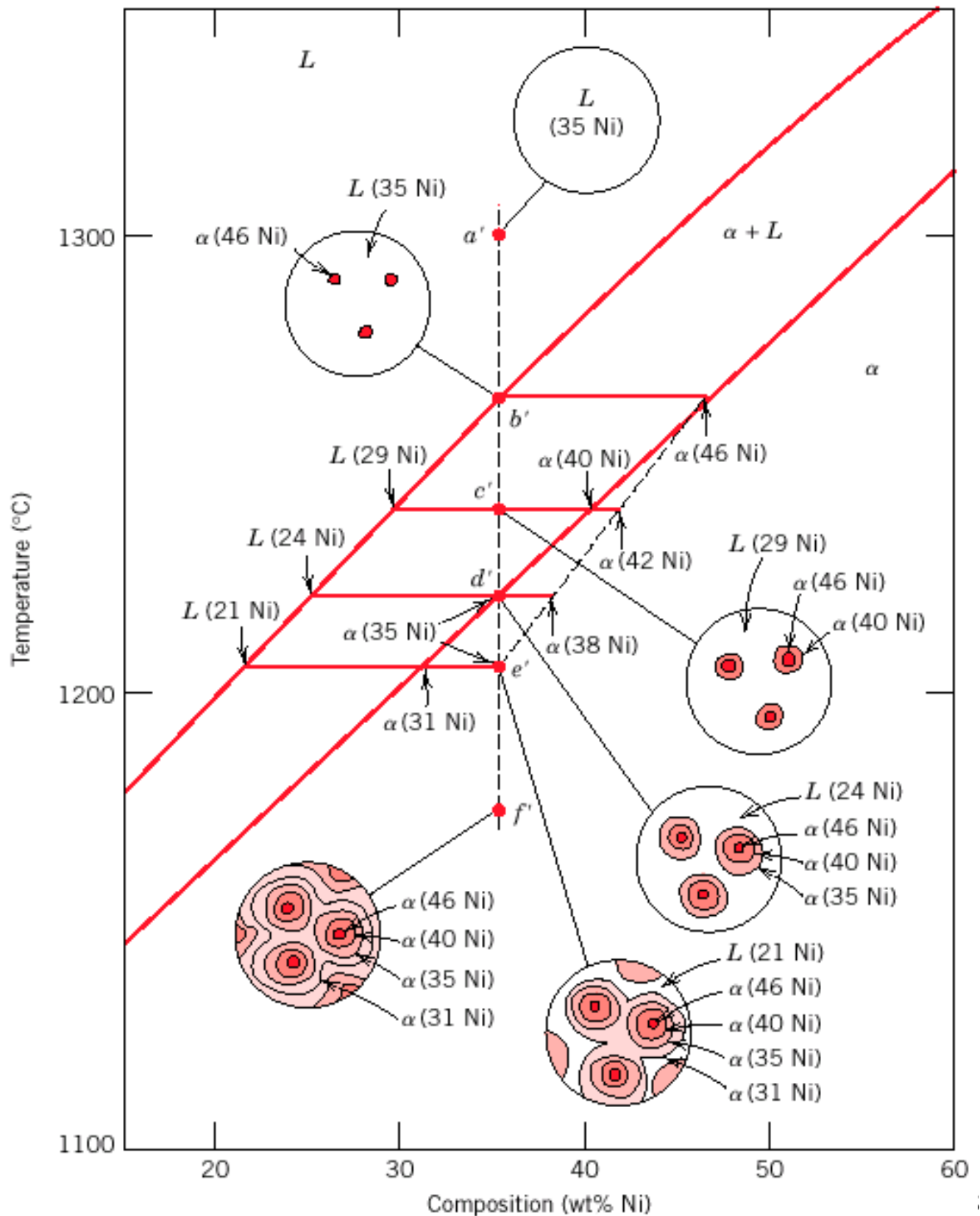
Development of microstructure in isomorphous alloys Equilibrium (very slow) cooling



Development of microstructure in isomorphous alloys Equilibrium (very slow) cooling

- Solidification in the solid + liquid phase occurs gradually upon cooling from the liquidus line.
- The composition of the solid and the liquid change gradually during cooling (as can be determined by the tie-line method.)
- Nuclei of the solid phase form and they grow to consume all the liquid at the solidus line.

Development of microstructure in isomorphous alloys Non-equilibrium cooling



Development of microstructure in isomorphous alloys

Non-equilibrium cooling

- Compositional changes require diffusion in solid and liquid phases
- Diffusion in the solid state is very slow. \Rightarrow The new layers that solidify on top of the existing grains have the equilibrium composition at that temperature but once they are solid their composition does not change. \Rightarrow Formation of layered (cored) grains and the invalidity of the tie-line method to determine the composition of the solid phase.
- The tie-line method still works for the liquid phase, where diffusion is fast. Average Ni content of solid grains is higher. \Rightarrow Application of the lever rule gives us a greater proportion of liquid phase as compared to the one for equilibrium cooling at the same T. \Rightarrow Solidus line is shifted to the right (higher Ni contents), solidification is complete at lower T, the outer part of the grains are richer in the low-melting component (Cu).
- Upon heating grain boundaries will melt first. This can lead to premature mechanical failure.

Mechanical properties of isomorphous alloys

Solid solution strengthening

