Chapter 9: Phase Diagrams

ISSUES TO ADDRESS...

- When we combine two elements... what equilibrium state do we get?
- In particular, if we specify...
 - --a composition (e.g., wt% Cu wt% Ni), and
 - --a temperature (*T*)

then...

How many phases do we get?

- What is the composition of each phase?
- How much of each phase do we get?





Phase Equilibria: Solubility Limit Introduction

- Solutions solid solutions, single phase
- Mixtures more than one phase

Adapted from Fig. 9.1, *Callister 7e.*



Components and Phases

• Components:

The elements or compounds which are present in the mixture (e.g., AI and Cu)

• Phases:

The physically and chemically distinct material regions that result (e.g., α and β).



Adapted from chapter-opening photograph, Chapter 9, *Callister 3e.*



A phase maybe defined as a homogeneous portion of a system that has uniform physical and chemical characteristics.

Effect of T & Composition (C_o)

- Changing *T* can change *#* of phases: path *A* to *B*.
- Changing C_o can change # of phases: path B to D.



Phase Equilibrium

Equilibrium: minimum energy state for a given T, P, and composition (i.e. equilibrium state will persist indefinitely for a fixed T, P and composition).

Phase Equilibrium: If there is more than 1 phase present, phase characteristics will stay constant over time.

Phase diagrams tell us about equilibrium phases as a function of T, P and composition (here, we'll always keep P constant for simplicity).



Unary Systems



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Phase Equilibria

Simple solution system (e.g., Ni-Cu solution)

| | Crystal Structure | electroneg | <i>r</i> (nm) |
|----|----------------------|------------|---------------|
| Ni | FCC | 1.9 | 0.1246 |
| Cu | FCC | 1.8 | 0.1278 |

- Both have the same crystal structure (FCC) and have similar electronegativities and atomic radii (W. Hume – Rothery rules) suggesting high mutual solubility.
- Ni and Cu are totally miscible in all proportions.

Unary Systems



Binary Isomorphous Systems

2 components

Complete liquid and solid solubility

Expect T_m of solution to lie in between T_m of two pure components



Phase Diagrams

- Indicate phases as function of *T*, *C*₀, and *P*.
- For this course:

-binary systems: just 2 components.

-independent variables: T and C_O (P = 1 atm is almost always used).



Phase Diagrams: # and types of phases

• Rule 1: If we know *T* and *C_o*, then we know: --the # and types of phases present.



Phase Diagrams: composition of phases

- Rule 2: If we know *T* and *C*₀, then we know: --the composition of each phase.
- Examples:

 $C_{O} = 35 \text{ wt\% Ni}$ At $T_{A} = 1320 \,^{\circ}\text{C}$: $C_{L} = 1320 \,^{\circ}\text{C}$ $C_{L} = C_{O} \,(= 35 \text{ wt\% Ni})$ At $T_{D} = 1190 \,^{\circ}\text{C}$: $C_{\alpha} = C_{O} \,(= 35 \text{ wt\% Ni})$ At $T_{B} = 1250 \,^{\circ}\text{C}$: $Both \,\alpha \text{ and } L$ $C_{L} = C \text{liquidus } (= 32 \text{ wt\% Ni here})$

 $C\alpha = C_{\text{solidus}}$ (= 43 wt% Ni here)



Adapted from Fig. 9.3(b), *Callister 7e.* (Fig. 9.3(b) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH, 1991.)



Determining phase composition in 2-phase region:

- 1. Draw the tie line.
- 2. Note where the tie line intersects the liquidus and solidus lines (i.e. where the tie line crosses the phase boundaries).
- 3. Read off the composition at the boundaries:

Liquid is composed of C_L amount of Ni (31.5 wt% Ni).

Solid is composed of C_{α} amount of Ni (42.5 wt% Ni).



Phase Diagrams: weight fractions of phases

- Rule 3: If we know *T* and *C_o*, then we know: --the amount of each phase (given in wt%).
- Examples:







Adapted from Fig. 9.3(b), *Callister 7e.* (Fig. 9.3(b) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH, 1991.)

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Lever Rule: Derivation

Since we have only 2 phases:

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

Conservation of mass requires that:

Amount of Ni in α -phase + amount of Ni in liquid phase = total amount of Ni or $W_{\alpha}C_{\alpha} + W_{I}C_{I} = C_{\alpha}$ (2)

From 1st condition, we have:
$$W_{\alpha} = 1 - W_{\mu}$$

Sub-in to (2): $(1 - W_L)C_{\alpha} + W_LC_L = C_o$

Solving for W_L and W_{α} gives :





The Lever Rule

• Tie line – connects the phases in equilibrium with each other - essentially an isotherm



How much of each phase? Think of it as a lever (teeter-totter)



$$M_{\alpha} \cdot S = M_{L} \cdot R$$



Ex: Cooling in a Cu-Ni Binary

- Phase diagram: Cu-Ni system.
- System is: --binary
 - *i.e.*, 2 components: Cu and Ni.
 - --isomorphous

i.e., complete solubility of one component in another; α phase field extends from 0 to 100 wt% Ni.

• Consider

 $C_0 = 35 \text{ wt\%Ni}.$



Microstructures in Isomorphous Alloys

Microstructures will vary on the cooling rate (i.e. processing conditions)

1. Equilibrium Cooling: Very slow cooling to allow phase equilibrium to be maintained during the cooling process.



Composition (wt% Ni)

Non-equilibrium cooling

Since diffusion rate is especially low in solids, consider case where:

Cooling rate >> diffusion rate in solid Cooling rate << diffusion rate in liquid (equilibrium maintained in liquids phase)



Non-equilibrium cooling

a' (T>1260°C): start as homogeneous liquid solution.

c' (T= 1250°C): solids that formed at pt **b'** remain with same composition (46wt%) and new solids with 42 wt% Ni form around the existing solids (Why around them?).

d' (T~ 1220°C): solidus line reached. Nearly complete solidification.

•Previously solidified regions maintain original composition and further solidification occurs at 35 wt% Ni.

e (T<1220°C): Non-equilibrium solidification complete (with phase segregation).



Cored vs Equilibrium Phases

- C_{α} changes as we solidify.
- Cu-Ni case: First α to solidify has $C_{\alpha} = 46$ wt% Ni. Last α to solidify has $C_{\alpha} = 35$ wt% Ni.



Mechanical Properties: Cu-Ni System

• Effect of solid solution strengthening on:



Binary-Eutectic Systems

2 components

has a special composition with a min. melting T.

- Ex.: Cu-Ag system
- 3 single phase regions
 (L, α, β)
- Limited solubility:
 α: mostly Cu
 - β: mostly Ag
- T_E : No liquid below T_E
- C_E : Min. melting T_E composition
- Eutectic transition

 $L(C_E) \implies \alpha(C_{\alpha E}) + \beta(C_{\beta E})$



Adapted from Fig. 9.7, *Callister 7e.*



Eutectic Point





Cu-Ag phase diagram

Eutectic point: Where 2 liquidus lines meet (pt. E). Sometimes also referred to as invariant point.

Eutectic Reaction:

$$-(C_{E}) \xrightarrow[heat]{cool} \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$

similar to one component (pure) system except 2 solid phases.

Eutectic Isotherm: Horizontal solidus line at $T = T_E$.

Single phase regions: α , β , L-phase 2-Phase coexistence regions: $\alpha+\beta$, $\alpha+L$ and $\beta+L$



EX: Pb-Sn Eutectic System (1)



EX: Pb-Sn Eutectic System (2)



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Microstructures in Eutectic Systems: I

• *C*₀ < 2 wt% Sn

1. One component rich composition.

a: start with homogeneous liquid.
b: α-phase solids with liquid.
Compositions and mass fractions can be found via tie lines and lever rule.

c: α -phase solid solution only.

Net result: polycrystalline α solid.

Cooling at this composition is similar to binary isomorphous systems.



Microstructures in Eutectic Systems: II

Adapted from Fig. 9.12, *Callister 7e.*

• 2 wt% Sn < *C*₀ < 18.3 wt% Sn

2. One-component rich but cooling to α + β coexistence.

d: homogeneous liquid.

e: α + L phase (same as previous but at different compositions and mass fractions). **f:** all α -phase solid solution.

g: α + β phase (passing through solvus line leads to exceeding solubility limit and β phase precipitates out).

Net result: polycrystalline α -solid with fine β crystals.



Microstructures in Eutectic Systems: III

- $C_o = C_E$
- Result: Eutectic microstructure (lamellar structure) --alternating layers (lamellae) of α and β crystals.





In order to achieve large homogeneous regions, long diffusion lengths are required.



α

Adapted from Figs. 9.14 & 9.15, Callister

Lamellar structure forms because relatively short diffusion lengths are required.

Microstructures in Eutectic Systems: IV

- 18.3 wt% Sn < C_0 < 61.9 wt% Sn
- Result: α crystals and a eutectic microstructure



Hypoeutectic & Hypereutectic



Intermediate phases

Intermediate solid solutions (intermediate phases): Solid solutions that do not extend to pure components in the phase diagram.



Terminal solid solutions: α and η .

Intermediate solid solutions: β , γ , δ and ϵ .

Tie lines and lever rule can be used to determine compositions and wt% of phases.

e.g. at 800°C with 70 wt% Zn

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 $C_L = 78 \text{ wt\% Zn}$ $C_v = 67 \text{ wt\% Zn}$



FIGURE 9.17 The copper–zinc phase diagram. [Adapted from *Binary Alloy Phase Diagrams,* 2nd edition, Vol. 2, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

Intermetallic Compounds



Note: intermetallic compound forms a discrete line - not an area - because stoichiometry (i.e. composition) is exact.

Eutectoid & Peritectic

• Eutectic - liquid in equilibrium with two solids

$$L \xrightarrow{cool} \alpha + \beta$$

Eutectoid - solid phase in equation with two solid phases

$$S_2 \iff S_1 + S_3 \qquad \qquad \begin{array}{c} \text{intermetallic compound} \\ \downarrow & - \text{ cementite} \end{array} \\ \gamma \quad \begin{array}{c} \frac{\text{cool}}{\text{heat}} \\ \end{array} \quad \alpha + \text{Fe}_3 \text{C} \end{array} \qquad (727^{\circ}\text{C}) \end{array}$$

• Peritectic - liquid + solid 1 \rightarrow solid 2 (Fig 9.21)

$$S_1 + L \implies S_2$$

$$\delta + L \stackrel{\text{cool}}{\stackrel{\text{heat}}{\stackrel{\text{heat}}{\stackrel{\text{heat}}}} \gamma \qquad (1493^{\circ}\text{C})$$



Eutectoid & Peritectic



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Congruent phase transformation

Congruent transformation: no change in composition upon phase transformation. (for example: allotropic transformation)

Incongruent transformation: phase transformation where at least one of the phases go through composition change. (for example: isomorphous, eutectic and eutectoid system)



Ceramic phase diagrams



A criterion for the number of phases that will coexist within a system at equilibrium



Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

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In the previous example of Cu-Ag phase diagram, when F = 1, only one parameter (T or C) needs to be specified to completely define the system.



e.g. (for α +L region) If T is specified to be 1000°C, compositions are already determined (C_{α} and C_{L}).

Or

If composition of the a phase is specified to be C_{α} then both T and C_{L} are already determined.

The nature of the phases is important, not the relative phase amounts.



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When F = 2, both T and C have to be specified to completely define the state of the system.



e.g.(for α region) If T is specified to be 800°C, C_{α} can be any where between 0 to ~8 wt% Ag)

If composition of the a phase is specified to be $C_{\alpha} = 3$ wt%, then T and can be any where between ~600 to 1100°C.



Where in the Cu—Ag diagram, is there a 0 degree of freedom? (i.e. T, P, and C are all fixed)---eutectic isotherm



Concept Check

• Question: For a ternary system, three components are present; temperature is also a variable. What is the maximum number of phases that may be present for a ternary system, assuming that pressure is held constant?



Iron-Carbon System structural material



TVR Tuscan Speed 6, high-performance sports car with an austempered ductile iron crankshaft.

The world's first bridge made of iron in 1779. The entire structure is made of cast iron. (near Broseley, UK)

Steel bridges







Millau Viaduct in France, the highest bridge in the world.



Golden Gate Bridge



The Akashi Kaikyo bridge, a 3-span 2hinged truss-stiffened suspension bridge. completed in 1998. It connects Kobe with Awaji Island. It is the world's longest suspension bridge, with a span between the towers of 1.9 km.

- Iron-carbon (Fe-C) system is one of the most important binary systems due to the versatile uses of the iron-based structural alloys.
- This phase diagram is so important in understanding the equilibrium structure, and in the design of heat treatment process of iron alloys.
- The most important part of the phase diagram is the region below6.7 w% carbon. All practical iron-carbon alloys contain C below 6.7 w%. This part is of the phase diagram is thus the most analyzed part of the iron carbon phase diagram.









Remarks on Fe-C system

- C is an interstitial element in Fe matrix.
- C has limited solid solubility in the alpha BCC phase (narrow region close to pure iron). Max solid solubility of C in alpha iron is 0.022 w% at 727 °C.
- Alpha iron an be made magnetic below 768 °C.
- Austenite phase is not stable below at 727 °C. Max solid solubility of C into austenite is 2.14 w% at 1147 °C, much larger that that in alpha phase.
- Austenite is a non-magnetic phase, and heat treatment of Fe-C alloys involving austenite is so important.
- Cementite phase (intermetallic, Fe₃C) forms over a large region of the Fe-C phase diagram, but it is a metastable phase (heating above 650 °C for years decomposes this phase into alpha iron and graphite). Cementite is very hard and brittle.
- δ ferrite is stable only at relatively high T, it is of no technological importance and is not discussed further.





(a) Ferrite (90x) Relatively soft Density: 7.88g/cm³



(b)

Austenite (x325)



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Classification Scheme of Ferrous Alloys

• Iron

Pure ion contains less than 0.008wt% C

Steel

0.008-2.14 wt% C, in practice,<1.0 wt% C

Cast Iron

2.14-6.70 wt% C, in practice, <4.5 wt% C







Pearl-microscope picture



Mechanically, pearlite has properties intermediate between the soft, ductile ferrite and the hard, brittle cementite.





Example: Phase Equilibria

- For a 99.6 wt% Fe-0.40 wt% C at a temperature just below the eutectoid, determine the following
- a) composition of Fe_3C and ferrite (α)
- b) the amount of carbide (cementite) in grams that forms per 100 g of steel
- c) the amount of pearlite and proeutectoid ferrite (α)



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Solution: a) composition of Fe_3C and ferrite (α)



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c. the amount of pearlite and proeutectoid ferrite (α) note: amount of pearlite = amount of γ just above T_E



Effect of alloying elements on Fe-C phase diagram

- Most iron alloys such as austenitic and ferritic steels have many other alloying elements besides carbon.
- These alloying elements result in dramatic changes in the phase boundaries of the phase diagram.
- In particular, addition of other alloying elements result in significant shifts in the eutectoid temperature and concentration.
- This most important alloying aspect is the stabilization of FCC austenite phase all the way down to room temperature by adding Ni.
- Alloying elements are added to enhance various properties. But result in many other phases being deposited in the Fe-C base system.



Alloying Steel with More Elements

• *T*_{eutectoid} changes:



Adapted from Fig. 9.34, *Callister 7e.* (Fig. 9.34 from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, American Society for Metals, 1939, p. 127.)

C_{eutectoid} changes:



Adapted from Fig. 9.35, *Callister 7e.* (Fig. 9.35 from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, American Society for Metals, 1939, p. 127.)



Summary

- Phase diagrams are useful tools to determine:
 - --the number and types of phases,
 - --the wt% of each phase,
 - --and the composition of each phase
 - for a given T and composition of the system.
- Alloying to produce a solid solution usually

 -increases the tensile strength (*TS*)
 -decreases the ductility.
- Binary eutectics and binary eutectoids allow for a range of microstructures.

