



Granta EduPack White Paper

Teach Yourself Unit 2: Phase diagrams and phase transformations

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Teach Yourself Unit 2: Phase diagrams and phase transformations

Introduction and synopsis

Phases and phase transformations are more familiar in everyday life than you may realize. Rain and snow signify the products of phase transformations in the sky succumbing to gravity – the word “precipitation” is used in phase transformation theory, and this is no coincidence. We make roads safer in the ice and snow by spreading salt – lowering the melting point of the water by changing its composition, and causing a phase change. Bubbles rising in a glass of beer signify gases dissolved in the beer forming a separate phase, while in a boiling pan of water the bubbles of steam are formed by the water itself changing phase from liquid to vapor.

Phase diagrams and phase transformations are central to understanding microstructure evolution (and hence properties) in relation to processing. Manufacturing involves shaping and assembling engineering products and devices, while simultaneously providing the material properties required by the design. Most material processing operations involve a *thermal history* (e.g. cooling from a high temperature shaping or deposition process, or producing a controlled diffusional change in a solid product). The details of the thermal history govern the way phase transformations take place, generating the microstructure. Our mantra for this topic is thus:

Composition + Processing → Microstructure + Properties

Phase *diagrams* provide some fundamental knowledge of what the *equilibrium* structure of a metallic (or ceramic) alloy is, as a function of temperature and composition. The real structure may not be the equilibrium one, but equilibrium gives a starting point from which other (non-equilibrium) structures can often be inferred.

This Teach Yourself Unit aims to provide a working knowledge of:

- what a phase diagram is;
- how to read it;
- how phases change on heating and cooling;
- the resulting microstructures.

When you have worked through this unit you should be able to do the following:

- (1) Interpret the equilibrium phases at any point on binary phase diagrams.
- (2) Predict the microstructures which may result from simple processing histories relating to solidification and heat treatment of important engineering alloys.
- (3) Understand how equilibrium and non-equilibrium microstructure evolution in alloy heat treatment relate to the form of time-temperature-transformation (TTT) diagrams.

Key definitions are marked “DEF” as they appear, and Exercises are provided throughout on each topic – do these as you go along to build up your knowledge systematically. Full solutions are provided at the end of each section – use these to check your answers, not as a short-cut!

Part 1 contains some essential terminology and definitions;

Parts 2-4 show you how to read and interpret simple phase diagrams, describe the important iron-carbon phase diagram, and give examples of some more complex phase diagrams;

Parts 5-7 introduce phase transformations and show how phase diagrams can be used to predict microstructure evolution during slow cooling (for example in solidification, and in the solid state during cooling to room temperature);

Part 8 extends the theory of phase transformations to examples of non-equilibrium cooling in heat treatment of steels and other alloys, relating this to the TTT (time-temperature-transformation) diagram.

Further reading and exercises are provided at the end. The Unit fits best with Chapter 19 in two installments:

Parts 1-4, dealing with phase diagrams; Parts 5-8, covering microstructure evolution in relation to phase diagrams.

PART 1: Key terminology

Alloys and Components

DEF. A *metallic alloy* is a mixture of a metal with other metals or non-metals. Ceramics too can be mixed to form *ceramic alloys*.

For example:

Brass: a mixture of Copper (Cu) and Zinc (Zn).

Carbon steel: based on Iron (Fe) and Carbon (C).

Spinel: a ceramic alloy made of Magnesia (MgO) and Alumina (Al₂O₃).

DEF. The *components* are the chemical elements that make up alloys.

Components are given capital letters: A, B, C or the element symbols Cu, Zn, C. In *brass* the main components are Cu and Zn. In *carbon steel* the main components are Fe and C.

DEF. A *binary alloy* contains two components. A *ternary alloy* contains three; a *quaternary alloy*, four, etc.

Concentration

Alloys are defined by stating the components and their concentrations, in weight or atom %.

DEF.

The *weight %* of component A:

$$W_A = (\text{weight of component A} / \Sigma \text{ weights of all components}) \times 100$$

The *atom (or mol) %* of component A:

$$X_A = (\text{number of atoms (or mols) of component A} / \Sigma \text{ number of atoms (or mols) of all components}) \times 100$$

To convert between weight and mols:

(Weight in grams)/(atomic or molecular wt in grams/mol) = number of mols.

(Number of mols) x (atomic or molecular wt in grams/mol) = weight in grams (g).

Phases

For pure substances, the idea of a phase is familiar: ice, water and steam are the solid, liquid and gaseous states of pure H_2O – each is a distinct phase. Processing of metallic alloys leads to microstructures in which the component elements are distributed in a number of ways. In the liquid state for metals, more or less everything dissolves completely. But in the solid state, things are more complex – for example, in a binary alloy the solid microstructure usually takes one of three forms (examples later):

- (a) a single solid solution;
- (b) two separated solid solutions;
- (c) a chemical compound, with a separated solid solution.

Recall that a *solid solution* is a solid in which one (or more) elements are “dissolved” in another so that they are homogeneously dispersed, at an atomic scale. Some solid solutions may be so dilute that they are effectively the pure component.

A region of a material which has a homogeneous atomic structure is called a phase. A phase can be identified as a cluster of as few as 10 or so atoms, but it is usually much more. In the three types of solid microstructures listed above, each solid solution or chemical compound would be an identifiable phase.

DEF. All parts of an alloy microstructure with the same atomic structure are a single *phase*.

Exercises

E.1 A 1.5 kg sample of α -brass contains 0.45 kg of Zn, and the rest is Cu. The atomic weight of copper is 63.5 and zinc 65.4. Write down the concentration of copper in α -brass, in wt%, W_{Cu} . Find the concentrations of copper and zinc in the α -brass, in at%, X_{Cu} and X_{Zn} .

E.2 A special brazing alloy contains 63 wt% gold (Au) and 37wt% nickel (Ni) (which is written Au-37wt% Ni). The atomic weight of Au (197.0) is more than three times that of Ni (58.7). At a glance, which of the two compositions, in at %, is more likely to be correct?

- (a) $X_{Au} = 0.34$, $X_{Ni} = 0.66$
- (b) $X_{Au} = 0.66$, $X_{Ni} = 0.34$

E.3 An alloy consists of X_A at% of A with an atomic weight a_A , and X_B at% of B with an atomic weight a_B . Derive an equation for the concentration of A in wt%. By symmetry, write down the equation for the concentration of B in wt%.

E.4 On heating, pure copper starts to melt at 1083°C. While it is melting, solid and liquid copper co-exist. Using the definition of a phase, are one or two phases present? Explain why.

E.5 Three components A, B and C of an alloy dissolve completely when liquid but have no mutual solubility when solid. They do not form any chemical compounds. How many phases, and of what compositions, do you think would appear in the solid state?

Constitution, equilibrium, and thermodynamics

DEF. The *constitution* of an alloy is described by:

- (a) the phases present;
- (b) the weight fraction of each phase;
- (c) the composition of each phase.

At *thermodynamic equilibrium*, the constitution is stable: there is no further tendency for it to change. The independent *state variables* determining the constitution are temperature, pressure and composition. Hence, the *equilibrium constitution* is defined at constant temperature and pressure, for a given alloy composition.

Thermodynamics controls the phases in which mixtures of elements can exist as a function of the state variables – this is discussed in *Thermodynamics of Phases* in Section 19.4 of the text. In summary, for a given composition held at fixed temperature T and pressure p , the Gibbs free energy, G , is defined as:

$$G = U + pV - TS = H - TS$$

where U is the *internal energy*, V is the volume, H is the enthalpy ($U + pV$), and S is the entropy. The internal energy U is the sum of the atomic vibration and the bond energies between the atoms. For the liquid and solid states most relevant to materials processing, U dominates the enthalpy (pV is small), so $H \approx U$. Entropy S is a measure of the disorder in the system – when an alloy solidifies there is a decrease in entropy because the solid has a regular lattice, whereas the liquid does not.

Each possible state – liquid solution, solid solution, mixtures of phases and so on – has an associated free energy, and that with the lowest free energy is the state at thermodynamic equilibrium.

DEF. The *equilibrium constitution* is the state of lowest Gibbs free energy G , for a given composition, temperature and pressure. An alloy in this state shows no tendency to change – it is thermodynamically stable.

Phase diagrams

As noted above, pressure has a limited influence on material processing, as this primarily involves the liquid and solid states. From now on, we will therefore consider these material states to be controlled by the remaining two state variables: temperature and composition. Two-dimensional maps with these state variables as axes are called *phase diagrams*.

DEF. A *phase diagram* (or equilibrium diagram) is a diagram with T and composition as axes, showing the equilibrium constitution.

The phase diagram of an alloy made of components A and B, for all combinations of T and X_B , defines the *A-B system*. Binary systems have two components, ternary systems three, and so on. Commercial alloys may contain 10 or more elements, but in all cases there is one principal element (copper alloys, aluminum alloys and so on) to which other elements are added. The starting point for understanding the essential behavior of any alloy is therefore to consider the binary systems for the principal component element and one or more alloying elements in turn.

Answers to Exercises, Part 1:

E.1

$$W_{\text{Cu}} = (1.5 - 0.45)/1.5 = 70\%$$

No. mols Cu = $1050/63.5 = 16.535$; No. mols Zn = $450/65.4 = 6.881$;

Atomic fraction of Cu: $X_{\text{Cu}} = 16.535/(16.535+6.881) = 71\%$; hence $X_{\text{Zn}} = (100 - 71)\% = 29\%$

E.2 (a) is correct. If (b) were true, 2/3 of the atoms would be the much heavier gold atoms, giving a wt% well above 66%, whereas it is 63 wt%.

E.3 Consider 100 atoms: mass of A atoms = $a_A X_A$ and mass of B atoms = $a_B X_B$.

Hence

$$W_A = a_A X_A / (a_A X_A + a_B X_B)$$

and by inspection,

$$W_B = a_B X_B / (a_A X_A + a_B X_B)$$

E.4 Two phases: liquid and solid. These are separate phases as one has a regular crystal lattice, the other a random atomic arrangement without regular packing.

E.5 Three phases: pure A, pure B and pure C.

PART 2: Simple phase diagrams, and how to read them

Melting point, liquidus and solidus

Consider first a pure material A heated from the solid state. The *melting temperature* is the unique temperature at which the phase change to the liquid state occurs, and solid and liquid can co-exist – see Fig. P1(a). Similarly, liquid changes to vapor at a unique (higher) temperature, the boiling point. In practical phase diagrams boiling is of little interest, so the diagram is usually limited to liquid and solid states. Now if we consider the binary A-B system and add a second axis for composition, the behavior illustrated in Fig. P1(b) is commonly observed.

This figure shows that the upper limit of 100% solid, and lower limit of 100% liquid separate, and there is not a unique melting point - this is known as *partition*. In the region between the two *phase boundaries* on the figure, liquid (L) and solid (S) are stable together, in proportions that depend on the temperature (see later) These boundaries have special names, defined below.

DEF. The phase boundary which limits the bottom of the *liquid* field is called the *liquidus line*; the line giving the upper limit of the single phase *solid* field is called the *solidus line*.

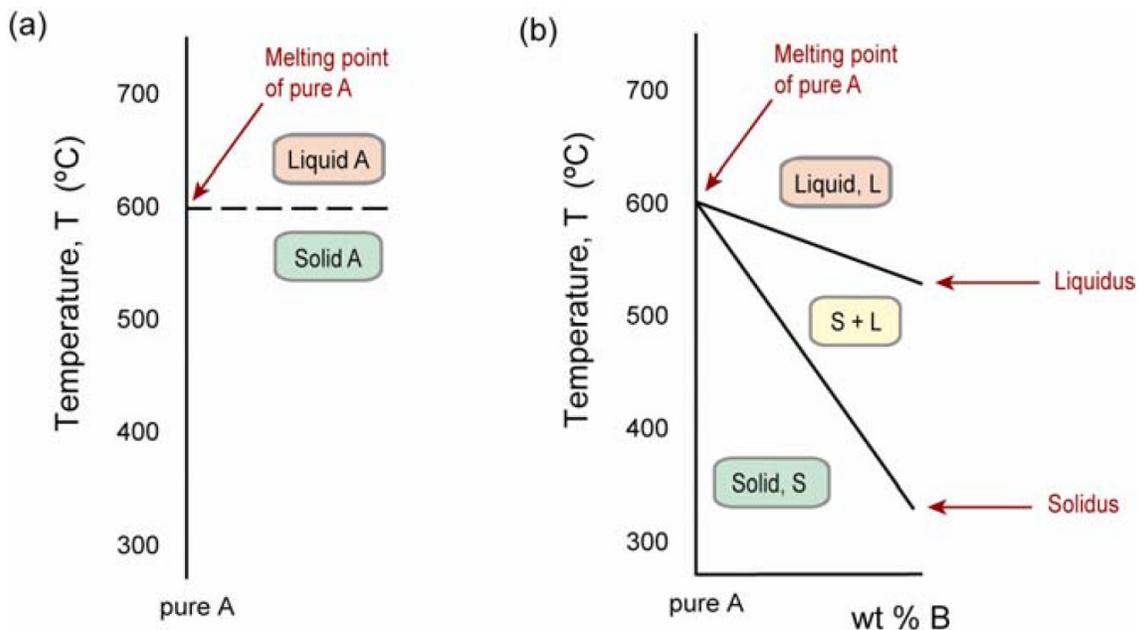


Figure P1: (a) one-dimensional phase diagram for a pure substance: a temperature scale showing the phase boundary between solid and liquid – the melting point; (b) the A-rich end of a binary A-B phase diagram, illustrating partition of the melting point between solidus and liquidus boundaries.

Had we considered pure B first, it too would have a unique melting point and shown partition as we added some A. So what happens as we cover all possible compositions between pure A and pure B? One possible outcome is illustrated in Figure P2, the phase diagram for the Cu-Ni system (the basis of several alloys used for coinage, explaining the terminology “coppers” in the UK, and “nickels” in the USA). This *isomorphous phase diagram* is the simplest possible example: “isomorphous” meaning “single-structured”. Here the solid state is a solid solution for all compositions, all the way from pure A to pure B. Since the atomic structure of this solid solution is the same at all compositions (with only the proportions of Cu and Ni atoms varying), it is a single phase.

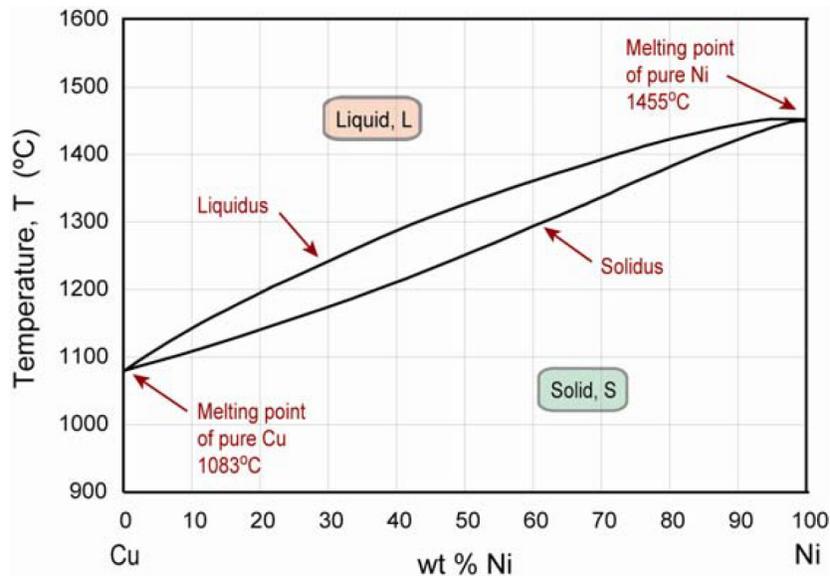


Figure P2: Isomorphous phase diagram for the Cu-Ni system.

It turns out that in the solid state this behavior is very unusual – in virtually every other atomic mixture, there is a limit to the amount of an element that can be dissolved in another. We will explore this *solubility limit* with an everyday example: a cup of tea.

Solubility limits

For the purposes of illustration, we will think of tea as hot water, and sugar as a component (albeit molecular). Add a spoonful of sugar to hot tea, and it dissolves – the sugar disperses into solution. Those with a very sweet tooth may keep spooning until there is solid sugar sitting on the bottom of the cup. The tea has reached its *solubility limit* at this temperature and has become *saturated*: it will not dissolve any more sugar. This saturated tea now co-exists with a second phase – wet sugar. This too is a saturated solution, as the sugar absorbs as much tea as it can. This is characteristic of mixtures of two equilibrium phases, both of which are solutions – both phases are saturated (i.e. both are as impure as possible). If we add sugar to cold tea, we find less sugar will dissolve – the saturation limit (in wt% sugar) rises with temperature. Harder to observe, but equally true, the sugar too will absorb more water as it is heated. Conducting this experiment quantitatively over a range of temperatures would lead to the partial phase diagram shown in Figure P3. The boundaries between the single and two-phase regions are known as *solvus boundaries*.

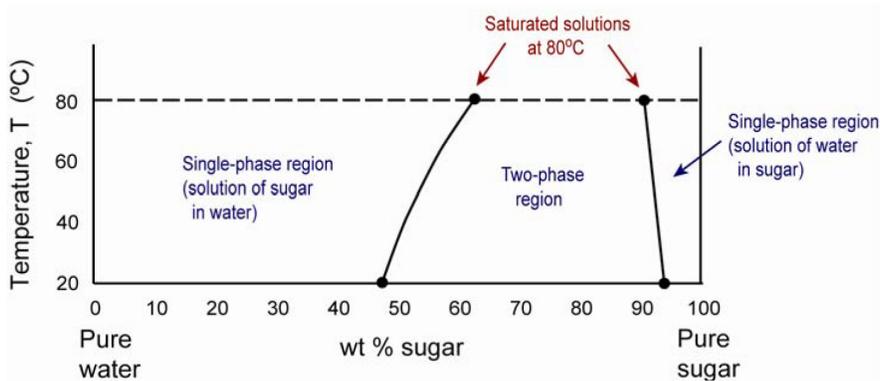


Figure P3: schematic phase diagram for sugar and tea (water) – the saturation level of both solutions increase with temperature.

What happens at a given temperature and composition is determined by the thermodynamics of mixing sugar and water. Minimizing free energy dictates whether there are one or two phases, and in the two-phase regions fixes the proportions and compositions of the phases.

Building a simple binary diagram, and the eutectic point

The picture in Figure P3 is also found in many metallic mixtures. As an exemplar binary alloy we will consider the Pb-Sn system, the basis for many years of solders used for electronic joints (but rapidly falling out of favor due to environmental health concerns). Figure P4 shows a partially complete Pb-Sn phase diagram. The lower part replicates the sugar-tea behavior: the solubility of Pb in Sn (and of Sn in Pb) increases with temperature. Note that the solubilities of these elements in one another is low, especially Pb in Sn on the right of the diagram. The upper part of the diagram shows the partition behavior from the melting points of the pure elements, as in Figure P1(b).

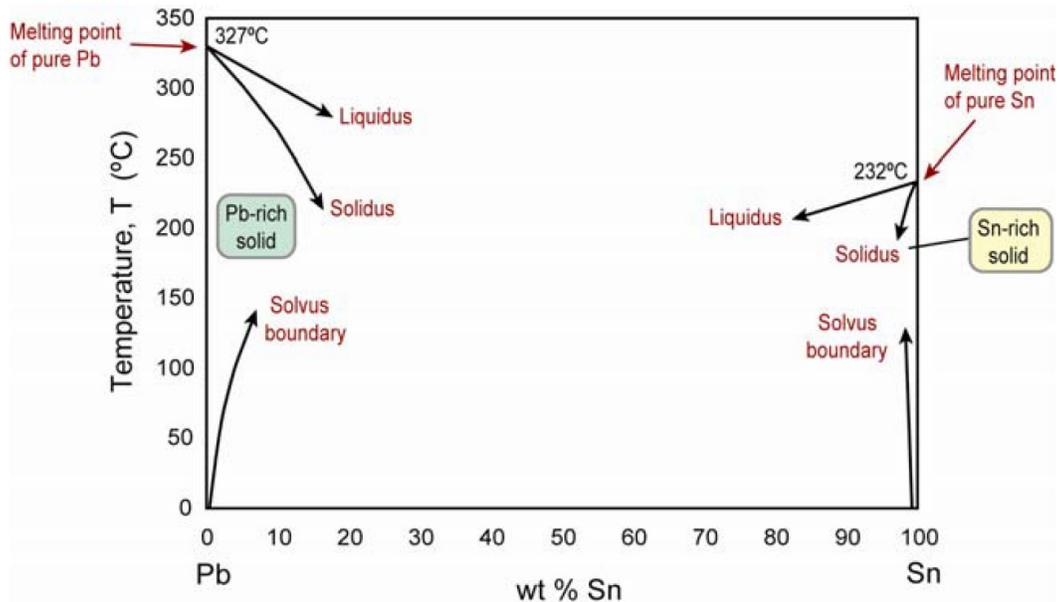


Figure P4: partial phase diagram for the Pb-Sn system, showing the limiting behavior at high and low temperatures.

To complete the diagram, first consider where the falling solidus boundaries meet the rising solvus boundaries. Figure P5 shows that the point where they intersect represents the point of maximum solubility (highest saturation) in the single phase solid. This closes the region representing single phase solid solutions – a region in which the phases present is called a *field*. Note also the nomenclature adopted: (Pb) for a Pb-rich single solid phase, and (Sn) for Sn-rich single solid phase. For good thermodynamic reasons, which will not be elaborated here, peak saturation of (Pb) occurs at the same temperature as that for (Sn). It is essentially a corollary of the fact that in a two-phase region, both phases are as impure as possible. Below this temperature we have a mixture of solid solutions; above it we have mixtures of solids and liquids. Hence there is a horizontal boundary linking the two, as shown in Figure P5, closing the two-phase field, (Pb) + (Sn).

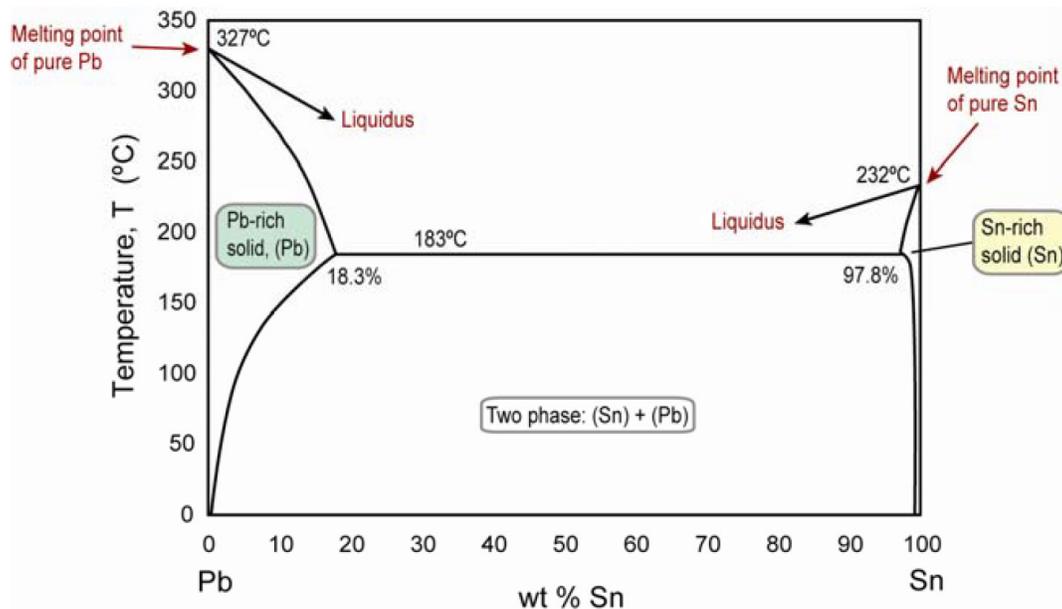


Figure P5: partial phase diagram for the Pb-Sn system, showing the completed single phase solid and two phase solid fields.

Finally: what happens to the two liquidus boundaries? Again, thermodynamics dictates that these meet the horizontal line at a single point, and the liquid field closes in a shallow “V”. At this special temperature and composition, two solid phases and liquid of that composition can co-exist. This point on the diagram is very important, and is known as a *eutectic point*.

DEF. The lower limit of the single-phase liquid field formed by the intersection of two liquidus lines is called the *eutectic point*.

Figure P6 shows the completed Pb-Sn phase diagram. For the Pb-Sn system the eutectic point is at the composition $W_{Sn} = 64 \text{ wt\%}$, and temperature $T = 183^\circ\text{C}$. Eutectics will be discussed again later in relation to the microstructures which form when a eutectic composition solidifies. For the time-being we simply note that the eutectic composition gives the lowest temperature for which 100% liquid is stable. For this reason, brazing and soldering alloys are often eutectic or near-eutectic in composition.

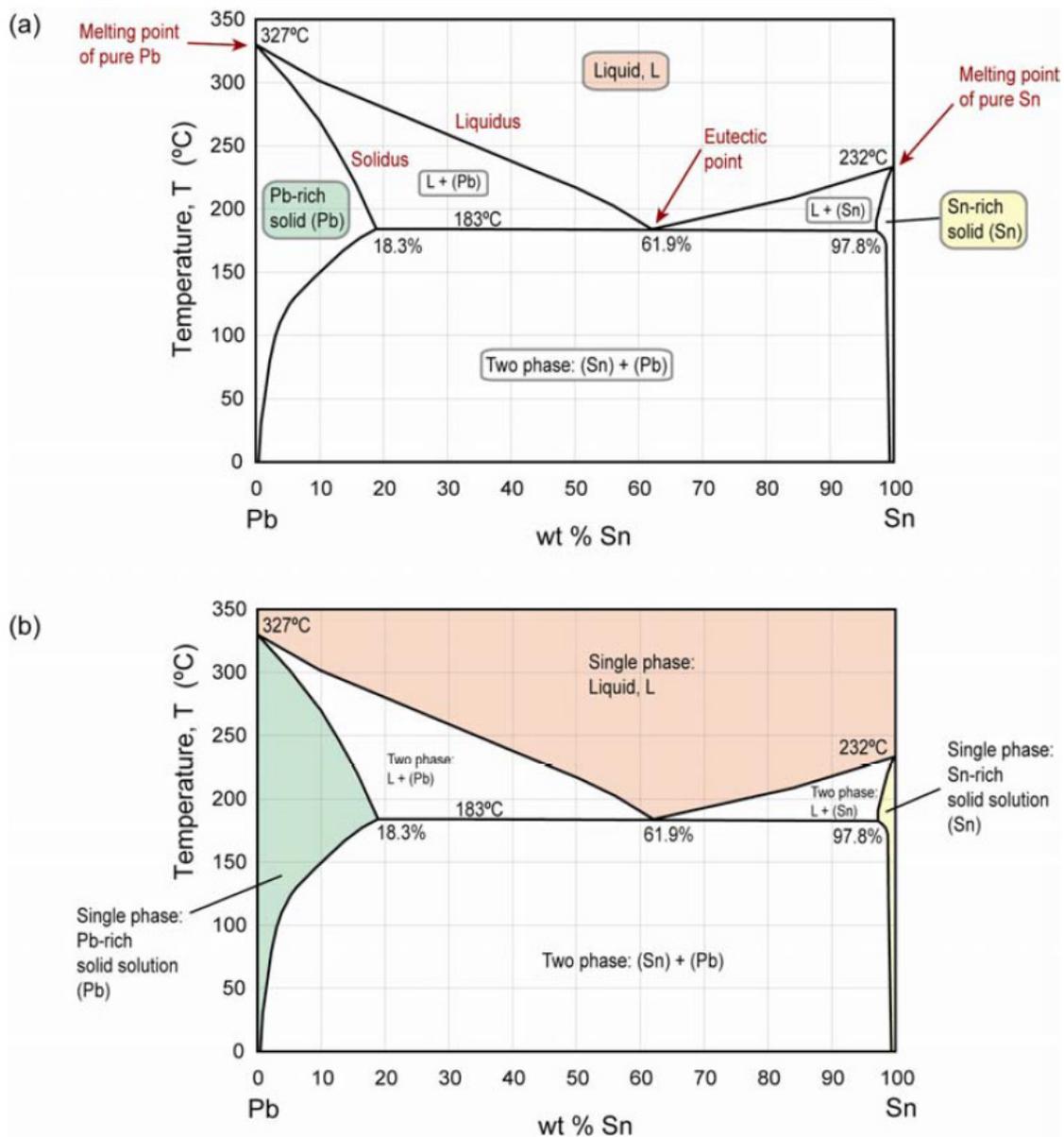


Figure P6: the completed phase diagram for the Pb-Sn system, showing (a) the eutectic point closing the liquid field; (b) the single phase fields (shaded), separated by two-phase fields.

Reading a binary phase diagram: phase compositions

The state variables (temperature and composition) define a point on the phase diagram: the *constitution point*. The first thing to establish at a constitution point is the number of phases present, one or two (in a binary system). Single phase regions are always labeled, either with the notation in Figure P6, with (Pb) for Pb-rich solid and so on, or with a Greek character (α , β , γ etc). When a phase diagram is traversed at a given temperature, crossing phase boundaries takes us from a one-phase field to a two-phase field (or vice versa) (Figure P6b). In the two-phase regions, a horizontal line through the constitution point ending at the adjacent phase boundaries identifies the phases present: they are the single phases beyond those boundaries. This line is called a *tie-line* (Figure P7).

At a constitution point in a single-phase region, the *phase composition* is simply the composition of the alloy itself (point A in Figure P7). In two-phase regions, the phase compositions are given by the values

on the phase boundaries at the ends of the tie-line through the constitution point (point B in Figure P7). Recall that these are the saturation limits of the single-phase fields on the other sides of the boundaries.

DEF. In a single-phase region, phase and alloy compositions coincide. In a two-phase region the phase compositions lie on the phase boundaries at either end of a horizontal tie-line through the constitution point.

Consider points A and B on the Pb-Sn phase diagram in Figure P7. Constitution point A (temperature 250°C, alloy composition Pb-30wt% Sn) lies in the single-phase liquid field; the phase composition is also Pb-30wt% Sn. Constitution point B (temperature 130°C, alloy composition Pb-40wt% Sn) lies in a two-phase field with two solid phases identified from the ends of the tie-line: (Pb) and (Sn); the phase compositions are Pb-7wt% Sn and Pb-98wt% Sn respectively.

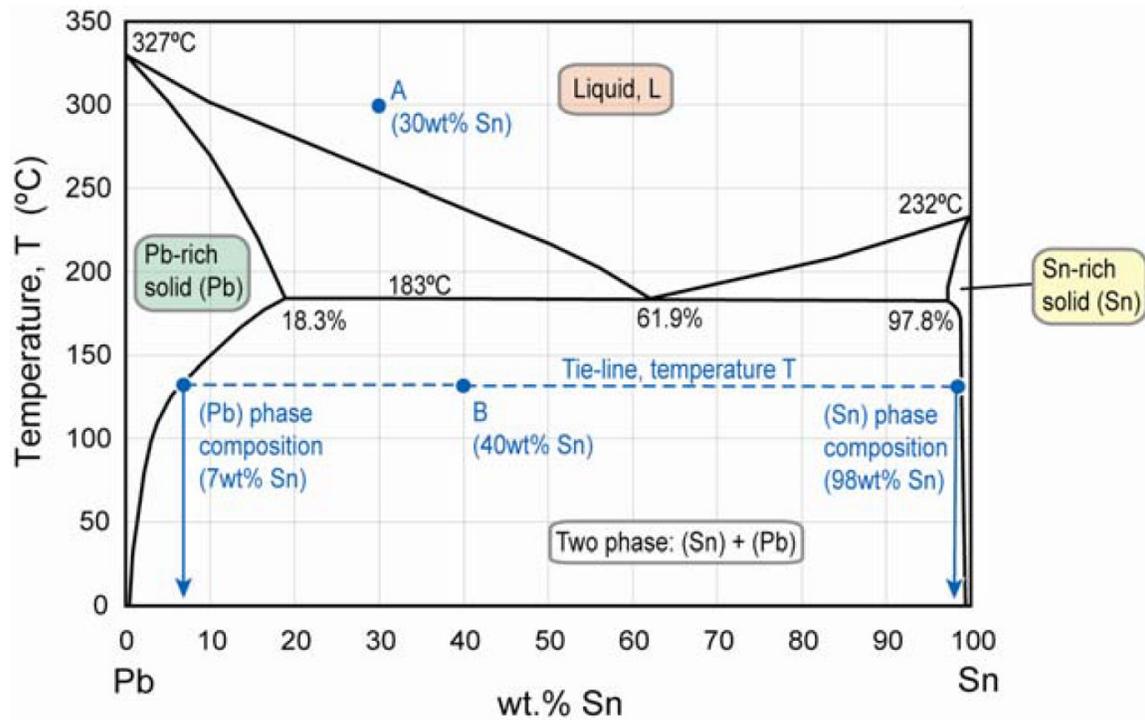


Figure P7: Phase diagram for the Pb-Sn system, illustrating constitution points in single and two-phase fields, and the tie-line defining the phases and compositions in the two-phase field.

Exercises

E.6 Use the Pb-Sn diagram below to answer the following questions.

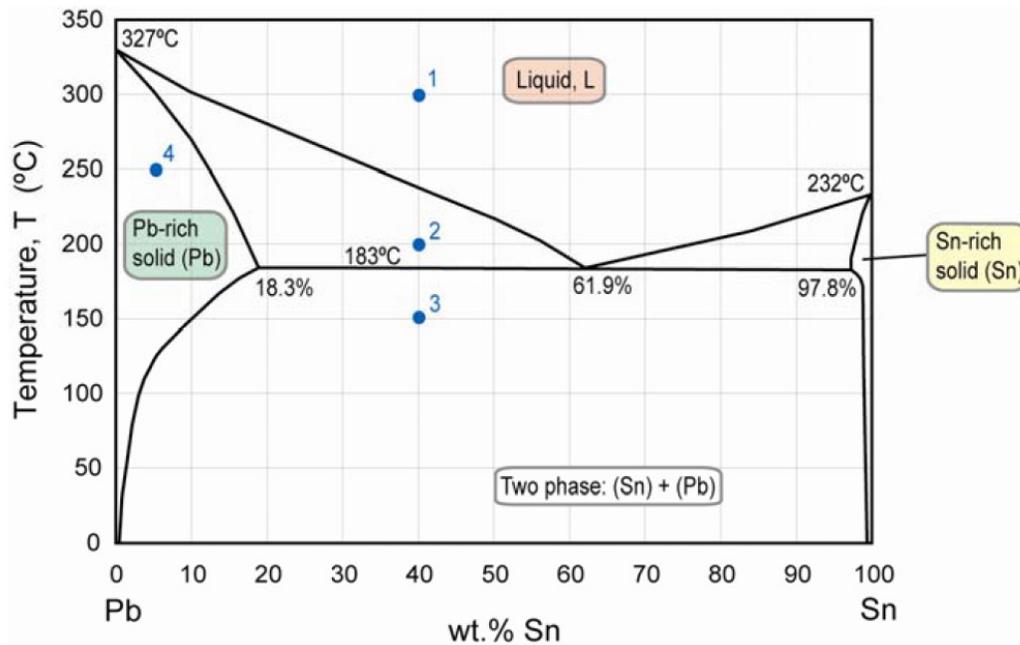


Figure E6: Pb-Sn phase diagram

- (a) What are the values of the state variables (composition and temperature) at constitution point 1?
- (b) Mark the constitution points for Pb-60wt% Sn and Pb-20wt% Sn alloys at 250°C. What phases are present in each case?
- (c) The alloy at constitution point 1 is cooled very slowly to room temperature, maintaining equilibrium. At which temperatures do changes in the number or type of phases occur? What phases are present at constitution points 2 and 3?
- (d) The alloy at constitution point 4 is cooled slowly to room temperature. Identify the following:
- the initial composition, temperature and phase(s);
 - the temperature at which a phase change occurs, and the final phase(s).

E.7 Use the Pb-Sn diagram below to answer the following questions.

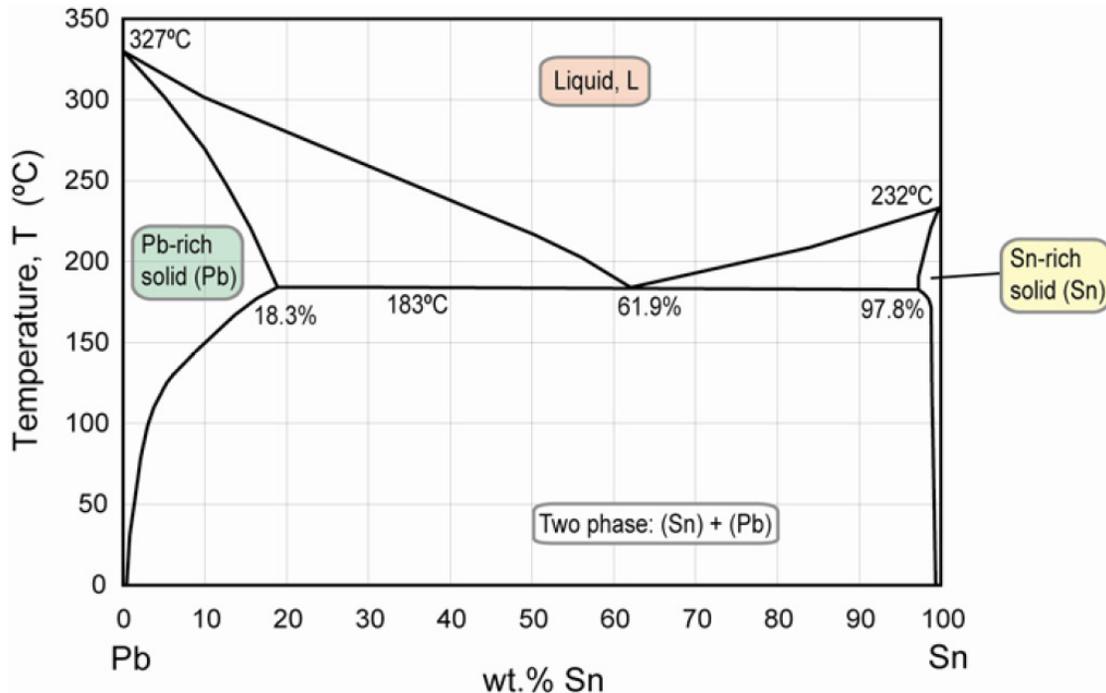


Figure E7: Pb-Sn phase diagram

- The constitution point for a Pb-25wt% Sn alloy at 250°C lies in a two-phase field. Construct a tie-line on the figure and read off the two phases and their compositions.
- The alloy is slowly cooled to 200°C. At this temperature, identify the phases and their compositions.
- The alloy is cooled further to 150°C. At this temperature, identify the phases and their compositions.
- Indicate with arrows on the figure the lines along which the compositions of phase 1 and phase 2 move during slow cooling from 250°C to 200°C.

The overall composition of the alloy stays the same, of course. How can this be maintained when the compositions of the phases change?

Reading a binary phase diagram: proportions of phases

In a two-phase field at constant temperature, the compositions of the phases are fixed at the saturation limits – the values on the boundaries at the ends of the tie-line. So different compositions at this temperature will contain different *proportions* of each phase, in such a way as to conserve the overall fractions of the two elements. The proportions of each phase (by weight) in a two-phase region can be found from the phase diagram using the *lever rule*. These weight fractions are fixed by the requirement that matter is conserved – the derivation is given as an exercise below.

Consider Pb-20wt% Sn at 250°C in Figure P8, a constitution point in the two-phase field: liquid plus Pb-rich solid. To find the proportions of each phase, first construct a tie-line through the constitution point and read off the compositions of the phases:

Pb-rich solid with $W_{Sn}^{SOL} = 12\%$; Liquid with $W_{Sn}^{LIQ} = 34\%$.

The tie-line is of length l , while the lengths of the segments to either side of the constitution point are a and b respectively. For the example alloy of composition $W_{Sn} = 20\%$:

$$l = W_{Sn}^{LIQ} - W_{Sn}^{SOL} = 34 - 12 = 22\%$$

$$a = W_{Sn} - W_{Sn}^{SOL} = 20 - 12 = 8\%$$

$$b = W_{Sn}^{LIQ} - W_{Sn} = 34 - 20 = 14\%$$

The weight fractions of liquid and solid in the alloy are: $W^{LIQ} = a/l$ and $W^{SOL} = b/l$. Hence:

$$W^{LIQ} = 8/22 = 36\%$$

$$W^{SOL} = 14/22 = 64\%$$

This illustrates why the name is the lever rule – it is analogous to balancing two weights on either side of a pivot, with the shorter distance being to the greater weight (for moment equilibrium).

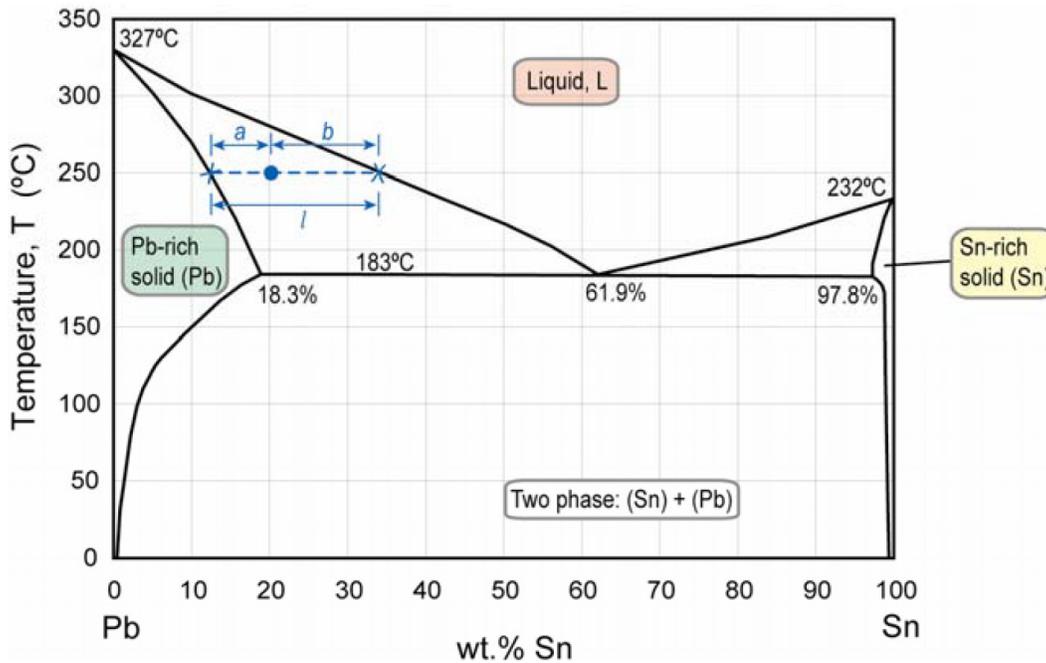


Figure P8: Phase diagram for the Pb-Sn system, illustrating the lever rule for finding the weight fractions of the phases in a two-phase field.

Note the following:

- $W^{SOL} + W^{LIQ} = a/l + b/l = (a + b)/l = 1$ (as expected, the two fractions sum to unity)
- at the left-hand end of the tie-line, $W^{SOL} = 1$ ($a = 0, b = l$)
- at the right-hand end of the tie-line, $W^{LIQ} = 1$ ($a = l, b = 0$)

To summarize: to find the weight fractions of the phases in any two-phase region (liquid-solid, or two solid phases):

- construct the tie-line through the constitution point;
- read off the three compositions (for the alloy, and the two ends of the tie-line);
- apply the lever rule.

Alternatively, and more approximately, the lengths can be measured directly from the phase diagram. Note that the proportions of the phases only vary linearly with composition along the tie-line if the diagram has a *linear weight % scale*.

Some phase diagrams have linear *atom %* scales, though they may also show a non-linear weight % scale along the top of the diagram (examples later). In this case, the lever rule for weight fraction cannot be applied by direct measurement – but the equations for weight fractions can still be applied by finding the three compositions (in wt%) and evaluating a , b and l as in the example above. Note that the concept of the atom fraction of a phase is not particularly useful, so the lever rule is not generally applied to linear atom % scales.

Exercises

E.8 Derive the lever rule for a general mixture of two phases, α and β . Let the composition of the alloy be C (wt% of alloying element), the compositions of the phases be C_α and C_β , and the weight fractions of the phases be W_α and W_β . [Hints: find an expression conserving the mass of the alloying element between the alloy and the two phases, then define a , b and l in this notation, and use the overall conservation of mass expressed in $W_\alpha + W_\beta = 1$]

E.9 Using the Pb-Sn phase diagram in Exercise E.7, consider the Pb-Sn alloy with composition $W_{\text{Sn}} = 25\%$. What are the approximate proportions by weight of the phases identified in Exercise E.7, at 250°C, 200°C and 150°C?

Intermediate Phases

Many systems show *intermediate phases*: compounds which form between components. Examples are CuAl_2 , Al_3Ni and Fe_3C . If the components are both metallic, they are called intermetallic compounds. Thermodynamically, compounds form because the particular combination of components is able to form as a single phase with specific lattice having lower free energy than, say, a mixture of two phases. Example lattices are given in the Crystallography Teach Yourself Unit. As a single phase of fixed composition, intermediate phases have unique melting points (like pure components). The higher degree of thermodynamic stability means that compounds often have higher melting points.

The atomic % of components in a compound is called its stoichiometry. Compounds are written in the form noted above, A_xB_y where x and y are integers. The at% of the components in an intermediate compound can easily be stated by inspection, $x/(x + y)$ and $y/(x + y)$, e.g. Fe_3C contains 25 at% C. In general the integer values x and y are small, since the number of atoms that define the repeating unit of the crystal lattice is also small. Compounds therefore usually appear on phase diagrams with at% scales at simple integer ratios, 25%, 33%, 50% and so on. In principle they therefore plot as a vertical line representing the single phase – with the compound then forming one of the phases in both of the two phase fields to either side (example below).

As compounds behave somewhat like pure elements, the liquid field for compositions on either side often show a falling liquidus line, with eutectics forming between the compound and a solid solution, or between two compounds if the system shows more than one. Figure P9a shows the unusual (and very untypical) silverstrontium phase diagram (notice the *at% scale*). This is not exactly a well-known engineering alloy, but illustrates the “ideal” behavior of compounds on phase diagrams. It has four intermetallic compounds (the vertical lines), and looks like 5 separate phase diagrams back-to-back: the $\text{Ag}-\text{Ag}_5\text{Sr}$ diagram, the $\text{Ag}_5\text{Sr}-\text{Ag}_5\text{Sr}_3$ diagram and so on. The liquidus boundary falls from each single phase melting point, forming five eutectics. Note that the solidus lines are vertical – they coincide with the lines representing the single phase compound. In all the adjoining two-phase fields the compositions of the phases are fixed, and do not vary with temperature.

Compounds of this type give the impression that there are two two-phase fields meeting at a vertical boundary, which violates the fundamental thermodynamics. Traversing a diagram at constant temperature must show onephase, two-phase, one-phase and so on as boundaries are crossed, with tie-lines in the two-phase fields ending at single phase boundaries. This remains the case here – there is a single phase field in between the two-phase fields, it is one of the compounds – but the field has just collapsed to a single line.

A more typical example with engineering significance is illustrated in Figure P9b, showing part of the Al-Cu diagram, on a wt% scale (with the corresponding at% scale across the top). This diagram is the basis of the important “age-hardening” Al-Cu alloys, used widely in aerospace. A compound forms at 33at% Cu: it is therefore CuAl_2 (given the name θ -phase, to signify that it is a single phase). The liquidus boundaries fall to a eutectic point at 33wt% Cu and 548°C. Now in contrast to the silver-strontium diagram, the θ field is not a single vertical line, but a tall thin region with a small spread in composition. In other words CuAl_2 can tolerate a small amount of excess Al while remaining a single phase – some of the Cu atoms are replaced by Al, and the stoichiometry may not be exactly 1:2. We can think of it as a solid solution of Al in CuAl_2 . Most practical compounds show some tendency to form a solid solution over a small range of composition close to stoichiometric, giving a thin single phase field rather than a vertical line. In consequence they are less easily over-looked or misinterpreted. In some cases the spread of composition

is so great that it ceases to be meaningful to distinguish it as a compound at all, and simply to consider it as a solid solution. But there is no rigorous definition as to how much spread in composition is allowed before it is not considered to be a compound any more – the examples below illustrate the problem.

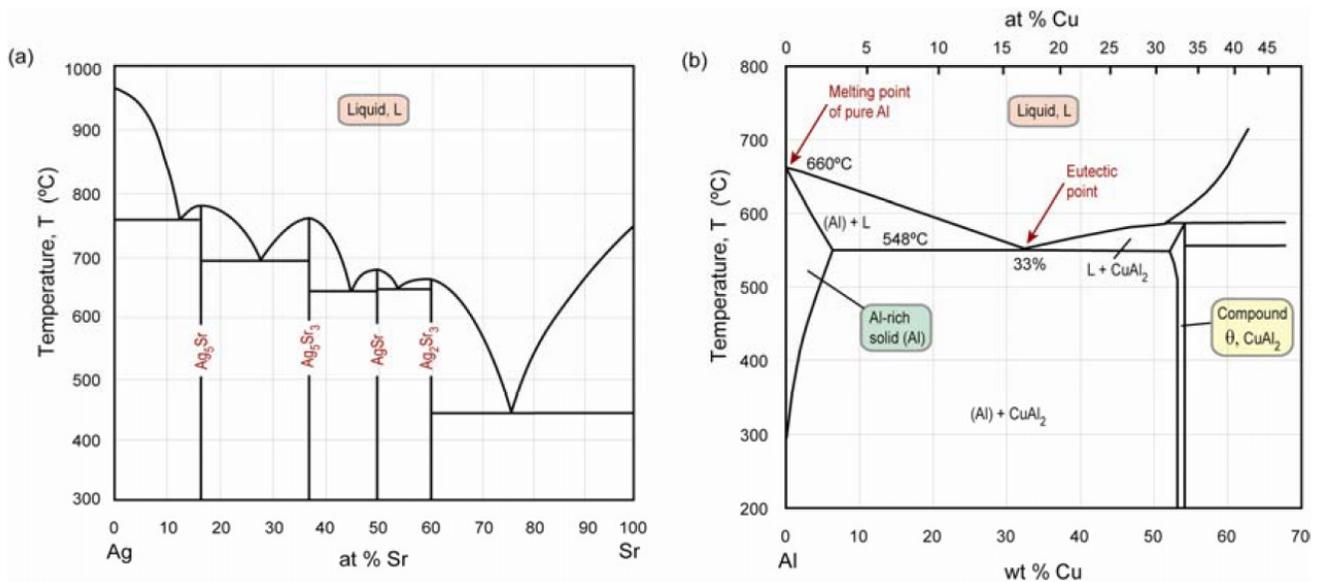


Figure P9: Phase diagrams showing intermediate compounds: (a) the silver–strontium Ag-Sr system; (b) part of the aluminum–copper Al-Cu system.

Exercises

E.10 Use Figure P9 to answer the following:

- (a) For an Ag-90at% Sr alloy at 600°C:
 - (i) Plot the constitution point on the phase diagram;
 - (ii) Identify the phases present, and find their compositions in at%;
 - (iii) The temperature is slowly reduced to 500°C. Will the phase compositions and proportions change?
- (b) For an Ag-30at% Sr alloy at 600°C:
 - (i) Plot the constitution point on the phase diagram;
 - (ii) Identify the phases present, and find their compositions in at%;
 - (iii) Will the proportions change if the temperature is reduced to 500°C? Why is this?
- (c) The atomic weight of Ag is 107.9 and that of Sr is 87.6. Calculate the compositions of the four intermetallic compounds in the Ag-Sr system in weight%.
- (d) For an Al-4wt% Cu alloy:
 - (i) Calculate the composition in at% Cu (atomic masses of Al and Cu: 26.98 and 63.54 respectively);
 - (ii) At 550°C, identify the phase(s) present, and find their compositions (in wt%) and proportions by weight;
 - (iii) Repeat for 250°C.

Answers to Exercises, Part 2:

E.6 (a) Composition: Pb-40wt% Sn; temperature: 300°C.

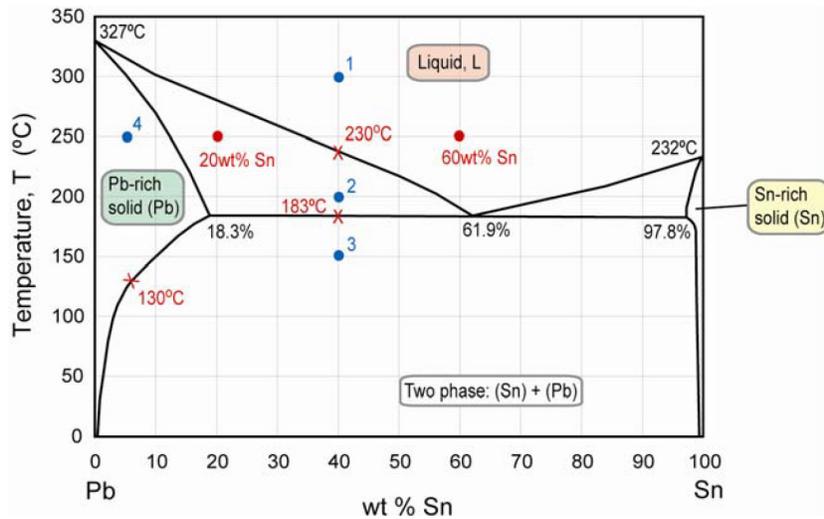


Figure E6S: Pb-Sn diagram

(b) See Figure E6S: Pb-60wt% Sn: Liquid; Pb-20wt% Sn: Liquid plus Pb-rich solid (Pb)

(c) At approx. 230°C: Liquid field changes to the phases at constitution point 2 (Liquid + Pb-rich solid). At 183°C: Liquid + Pb-rich solid changes to the phases at constitution point 3 (Pb-rich solid + Sn-rich solid).

(d) Composition: Pb-5wt% Sn; temperature: 250°C. Initial phase is Pb-rich solid (Pb). At approx. 130°C: changes to final phases: Pb-rich solid + Sn-rich solid.

E.7

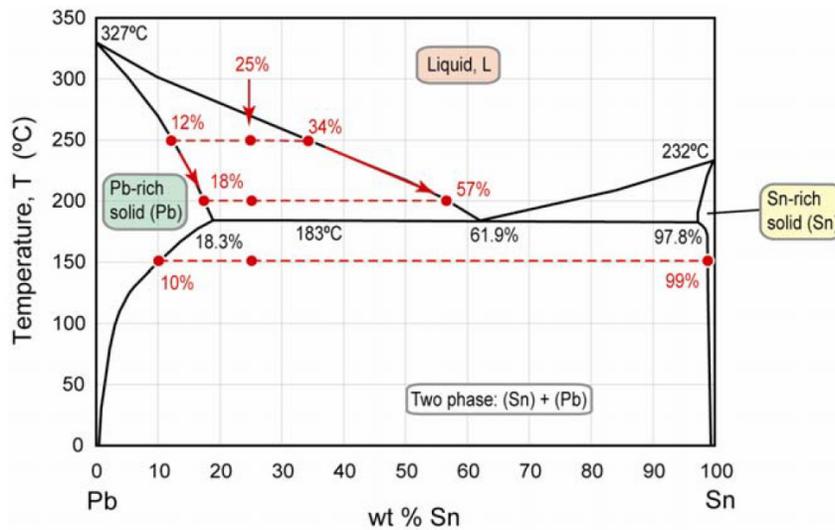


Figure E7S: Pb-Sn diagram

(a) 250°C: Pb-rich solid (12wt% Sn) and Liquid (34wt% Sn).

(b) 200°C: Pb-rich solid (18wt% Sn) and Liquid (57wt% Sn).

(c) 150°C: Pb-rich solid (10wt% Sn) and Sn-rich solid (99wt% Sn).

(d) See Figure E7S. As the phase compositions change with temperature, the overall composition is maintained by changes in the proportions of the phases.

E.8

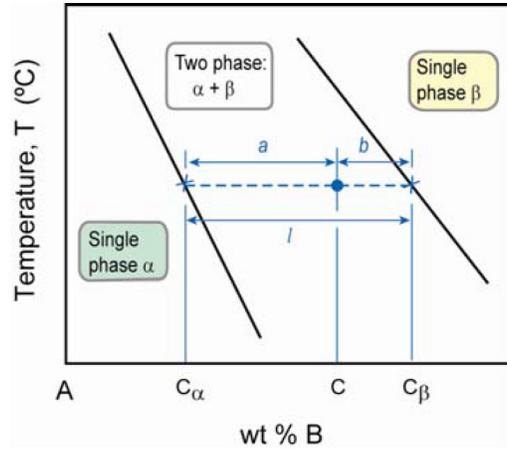


Figure E8S: Derivation of the Lever Rule

Consider unit mass of the alloy, so that the mass of the alloying element = C , the mass of phase $\alpha = W_\alpha$ and the mass of phase $\beta = W_\beta$.

The mass of the alloying element in phase $\alpha = W_\alpha C_\alpha$ and in phase $\beta = W_\beta C_\beta$

Hence to conserve mass of the alloying element: $C = W_\alpha C_\alpha + W_\beta C_\beta$ (E8.1)

From the figure: $l = C_\beta - C_\alpha$ and $a = C - C_\alpha$ and $b = C_\beta - C$ (E8.2)

Since $W_\alpha + W_\beta = 1$, $W_\alpha = 1 - W_\beta$

Substituting into eqn.(E8.1): $C = (1 - W_\beta) C_\alpha + W_\beta C_\beta = W_\beta (C_\beta - C_\alpha) + C_\alpha$

Rearranging, and comparing with eqns.(E8.2): $W_\beta = (C - C_\alpha) / (C_\beta - C_\alpha) = a / l$

Following the same procedure for W_α the result will be: $W_\alpha = (C_\beta - C) / (C_\beta - C_\alpha) = b / l$

E.9 Using the compositions identified in Exercise E.7 (or measuring from the figure):

(a) 250°C: proportion of Pb-rich solid = $(34-25)/(34-12) = 41\%$, and 59% Liquid.

(b) 200°C: proportion of Pb-rich solid = $(57-25)/(57-18) = 82\%$, and 18% Liquid.

(c) 150°C: proportion of Pb-rich solid $(99-25)/(99-10) = 83\%$ and 17% Sn-rich solid.

E.10

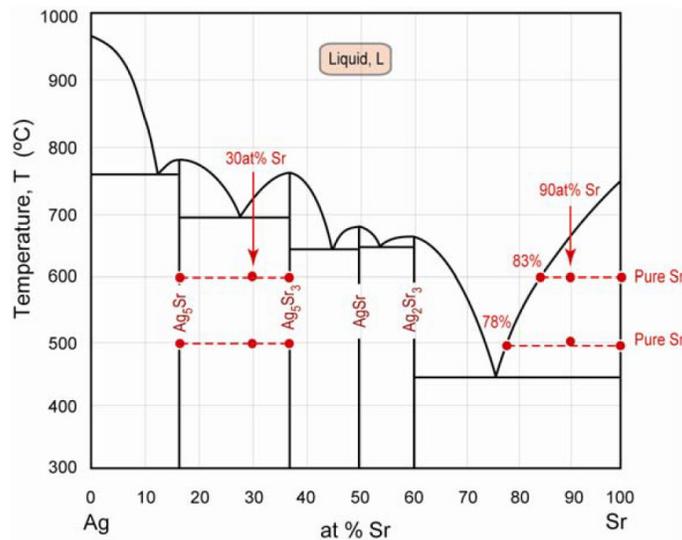


Figure E10S(a-c): Ag-Sr phase diagram

a) See Figure E10S(a-c): at 600°C: Liquid, Ag-83at% Sr and pure Sr (solid). At 500°C, the liquid concentration has changed to Ag-78at% Sr, while the second phase remains pure Sr (solid). The proportion of solid increases.

(b) See Figure E10S(a-c): at 600°C: solid compounds Ag_5Sr (16.7at% Sr) and Ag_5Sr_3 (37.5at% Sr). At 500°C, the phases remain the same in both composition (as perfect compounds) and in proportions (as the phase boundaries are vertical).

(c) Atomic weights: Ag 107.9 and Sr 87.6. By inspection, compound atomic fractions are:

Ag_5Sr : 16.7at% Sr; Ag_5Sr_3 : 37.5at% Sr; AgSr : 50at% Sr; Ag_2Sr_3 : 60at% Sr.

Using the formula for wt% from Exercise E.3 (with A = Sr, B = Ag): $W_A = (a_A X_A) / (a_A X_A + a_B X_B)$

Ag_5Sr : 14.0wt% Sr; Ag_5Sr_3 : 32.8wt% Sr; AgSr : 44.8wt% Sr; Ag_2Sr_3 : 54.9wt% Sr.

(d)

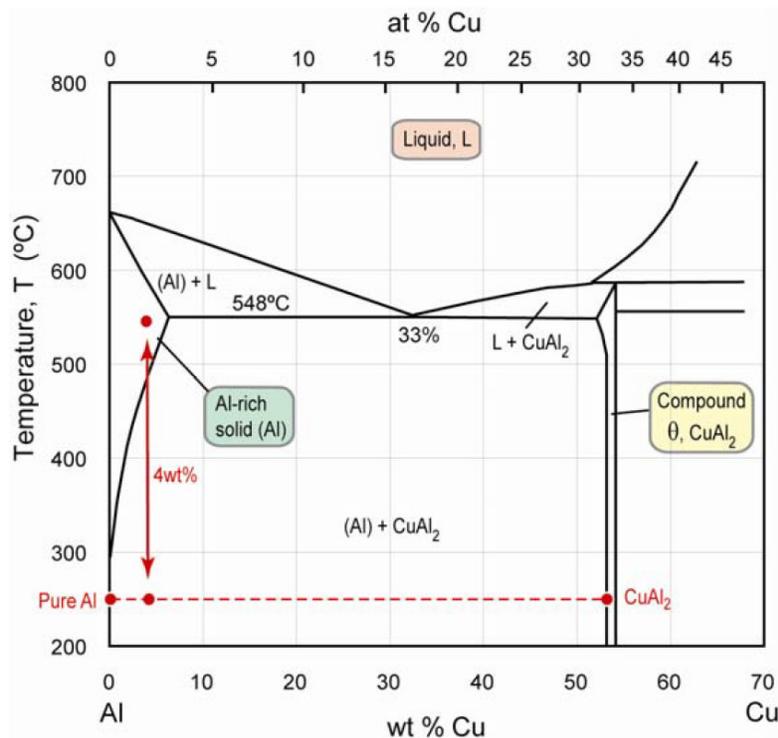


Figure E10S(d): Al-Cu phase diagram

(i) Consider 1kg of Al-4wt% Cu: so mass of Cu = 40g, mass of Al = 960g.

No. mols Cu = $40/63.54 = 0.63$; No. mols Al = $960/26.98 = 35.6$.

Atomic fraction of Cu: $X_{Cu} = 0.63/(0.63+35.6) = 1.74\text{at}\% \text{ Cu}$.

(ii) See Figure E10S(d). At 550°C, single phase Al-rich solid. Composition = alloy composition Al-4wt% Cu (proportion 100%).

(iii) See Figure E10S(d). At 250°C, two solid phases: (essentially) pure Al + compound CuAl₂ (composition 53wt% Cu). Proportions from lever rule: $(53-4)/(54-0) = 91\% \text{ (Al)}$ and $9\% \text{ CuAl}_2$.

PART 3: The iron-carbon diagram

The *iron-carbon* phase diagram is important in engineering as it provides the basis for understanding all *cast irons* and *carbon steels* and their heat treatment. First, we consider pure iron. The low temperature form of iron is called *ferrite* (or α -iron), with a BCC lattice (body-centered cubic, defined in Teach Yourself Unit 1). On heating pure iron changes to *austenite* (or γ -iron) at 910°C, and switches to a face-centered cubic (FCC) lattice. Pure austenite is stable up to 1391°C, when it changes back to BCC δ -iron, before melting at 1534°C.

A key characteristic of the iron-carbon system is the extent to which iron dissolves carbon in interstitial solid solution, forming single phases. This is where the changes between BCC and FCC are significant. In Teach Yourself Unit 1, it was shown that the *interstitial holes* are larger in FCC than in BCC. This leads to low solubility of carbon in BCC ferrite and δ -iron, and much higher solubility in FCC austenite. Note that the same names (ferrite, austenite and δ) are applied equally to the different states of pure iron and to the solid solutions they form with carbon. The nomenclature “iron-rich solid (Fe)” is not much help to us, as there are three distinct variants.

Figure P10 shows the completed iron-carbon diagram, up to 6.7wt% carbon. This upper limit corresponds to 25at% C, at which composition the compound *iron carbide* Fe_3C is formed (also given the name *cementite*). This part of the Fe-C system covers all the main cast irons and carbon steels. This diagram is more complicated than those shown previously, and needs a bit of breaking down. Figure P11 shows expanded extracts to clarify the diagram.

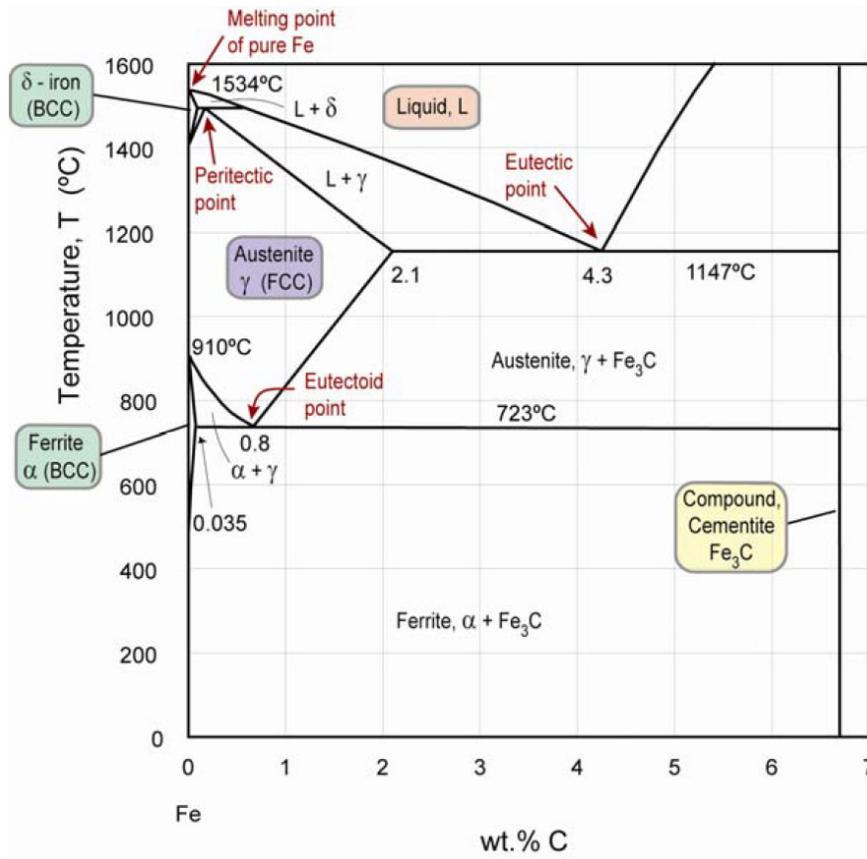


Figure P10: The iron-carbon phase diagram up to 6.7wt% carbon, the region covering cast irons and carbon steels.

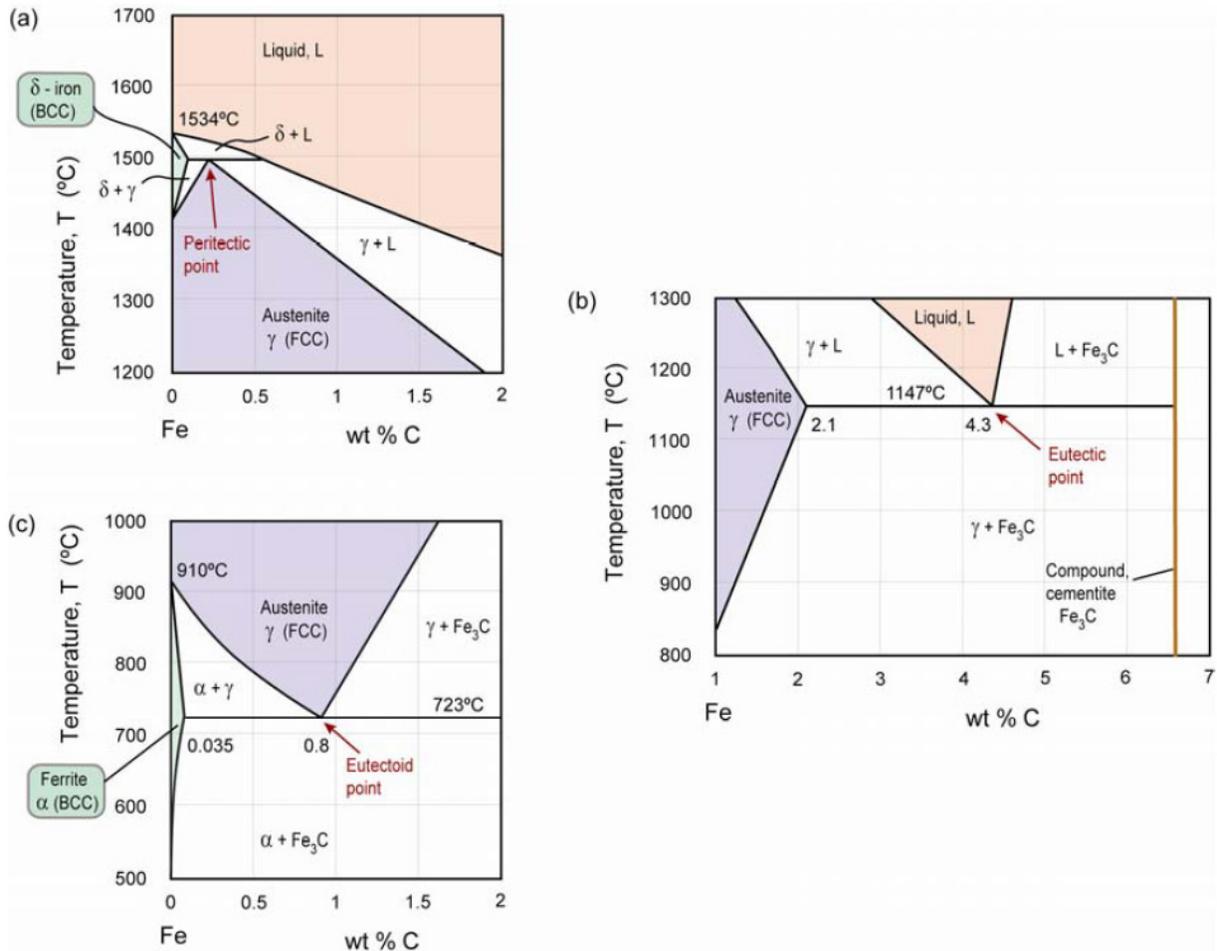


Figure P11: Expanded views of parts of the iron-carbon phase diagram: (a) high temperature and low wt% C: the peritectic point; (b) high temperature and high wt% C: the eutectic point; (c) low temperature and low wt% C: the eutectoid point.

First consider the picture below 1000°C, up to 2.0wt% carbon (Figure P11c). This shows the low solubility of carbon in ferrite, with a maximum of 0.035 wt% at 723°C. Below the transformation temperature of ferrite to austenite (910°C) the picture resembles the partition behavior seen below the melting point of a pure element, with two phase boundaries falling from this temperature and a two-phase region in between. But in this case the upper phase is a solid solution (austenite), rather than a liquid. But at the temperature of maximum C solubility in ferrite (723°C), the lower limit of the austenite field also forms a “V”, giving the minimum temperature at which austenite forms as a single phase, at a composition of 0.8wt% C.

This feature on a phase diagram is called a *eutectoid point*, and is particularly important in the context of carbon steels (as illustrated later when we consider their microstructures and heat treatments). Note the similarity in shape to a eutectic, with the key difference that the phase above the “V” is a single solid phase (as opposed to a single liquid phase in the case of a eutectic).

DEF. The lower limit of a single-phase solid field formed by two falling phase boundaries intersecting in a “V” is called a *eutectoid point*.

Following the rising boundary of the austenite field to the right and above the eutectoid point, we reach a point of maximum solubility. Figure P11b shows the top right region of the phase diagram, including this point. This shows exactly the eutectic structure seen earlier. The eutectic temperature coincides with the temperature of maximum solubility of C in austenite, with falling solidus and liquidus lines enclosing the two phase liquid + austenite region. Tie-lines in the two-phase regions to the right of and below the eutectic point end at the compound, iron carbide.

Completing the austenite field introduces another new feature, a *peritectic point* – Figure P11a shows an expanded view of the diagram at the top of the austenite field, including the δ -iron field. The austenite field closes in an inverted “V” at the peritectic point, i.e. the maximum temperature at which this single phase forms. This temperature coincides with the temperature at which δ -iron has its maximum solubility, giving a horizontal line through the peritectic point. Above the line is a two-phase field, of which one is a liquid – here liquid + δ -iron. The phases in the other two-phase fields are readily identified from tie-lines, δ + austenite (γ) to the left of the peritectic, and γ + liquid to the right.

To summarize the key nomenclature of the iron-carbon system, the single phases are:

Ferrite: α -iron (BCC) with up to 0.035 wt% C dissolved in solid solution

Austenite: γ -iron (FCC) with up to 2.1 wt% C dissolved in solid solution

δ -iron: (BCC) with up to 0.08 wt% C dissolved in solid solution

Cementite: Fe_3C , a compound (iron carbide), at the right hand edge of the diagram

The system has a eutectic point at 4.3wt% C, a eutectoid point at 0.8wt% C, and a peritectic point at 0.2wt% C.

In passing, it should perhaps be noted that this iron-carbon diagram is not strictly an equilibrium diagram. Iron carbide is in fact a metastable state – true equilibrium is reached in thermodynamic terms in two-phase mixtures of iron and carbon. However, in most circumstances iron carbide forms readily in preference to carbon as a separate phase – it is an example of the *mechanism* of phase transformations taking priority over the thermodynamics and free energy. The phase diagram including iron carbide is therefore most commonly used as a pseudo-equilibrium phase diagram. The difference does become apparent in the solidification of cast irons, alloys containing 1–4wt% C (i.e. approaching the eutectic composition). In this case carbon can form as an equilibrium phase in the microstructure.

Exercises

E.11 Use Figures P10 and P11 to answer the following:

(a) For a Fe-0.4wt% C alloy at 900°C and 600°C:

(i) Plot the constitution points on the phase diagram;

(ii) Identify the phases present, and find their compositions in wt%;

(iii) If the temperature is slowly reduced from 900°C to 600°C, at what temperatures are phase boundaries crossed? Identify the phases present after each boundary is crossed.

(b) How does slow cooling from 900°C to 600°C differ for a Fe-0.8wt% C alloy?

Answers to Exercises, Part 3:

E.11 (a) (i)

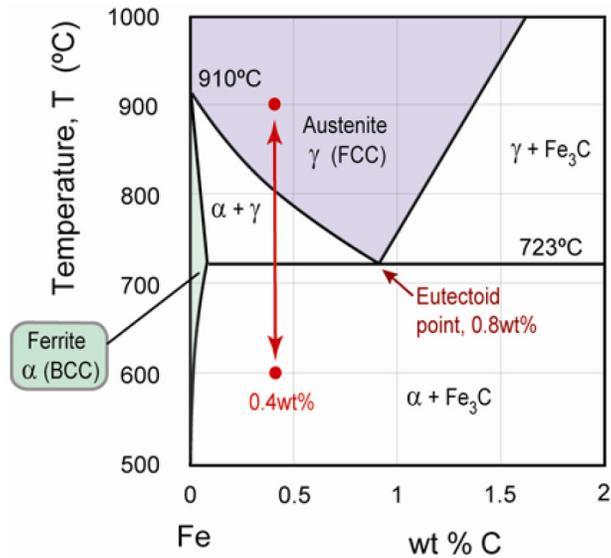


Figure E11S: Fe-C phase diagram

(ii) 900°C: single phase austenite (γ), composition 0.4wt%C;

600°C: two-phase, ferrite (α), composition close effectively 0wt%C + cementite (iron carbide, Fe_3C), composition 6.7wt%C.

(iii) at 800°C, austenite transforms to austenite + ferrite; at 723°C, the remaining austenite transforms to more ferrite, + cementite.

(b) for 0.8wt%C, austenite transforms directly to ferrite + cementite at the eutectoid point (at 723°C), rather than first forming some ferrite over a temperature interval above 723°C.

PART 4: Interpreting more complex phase diagrams

The phase diagrams covered so far illustrate almost all the features found in binary systems. This section completes the story, and shows how even very complicated diagrams can be interpreted if the rules are applied carefully.

Eutectics, Eutectoids, Peritectics and Peritectoids

Three of these features were seen on the iron-carbon diagram. Here we define the fourth – a peritectoid point – and show all four together for clarity. The nomenclature is a little confusing on first encounter.

A peritectoid point is similar in appearance to a peritectic, being an inverted “V” corresponding to an upper limit of formation of a single solid phase. But the difference is that the two phase field above is formed of two solid phases (whereas in a peritectic, one is liquid). So, to help remember which is which:

- (i) *eutec*– means a normal “V” meeting a horizontal line, while *peritec*– means an inverted “V” meeting a horizontal line;
- (ii) *-tic* means a liquid phase is involved, while *-toid* means all phases are solid.

Figure P12 shows all four for comparison. Single solid phases are denoted by Greek letters, liquid by L. Note that each point involves *three* phases – a single phase inside the “V”, and two different phases across the horizontal line.

Compared to eutectics and eutectoids, peritectics and peritectoids are of much less engineering significance. An unusual exception is the growth of single crystals of the new high temperature superconductors based on yttrium-barium-copper oxide – this is conducted by very slow cooling through a peritectic transformation.

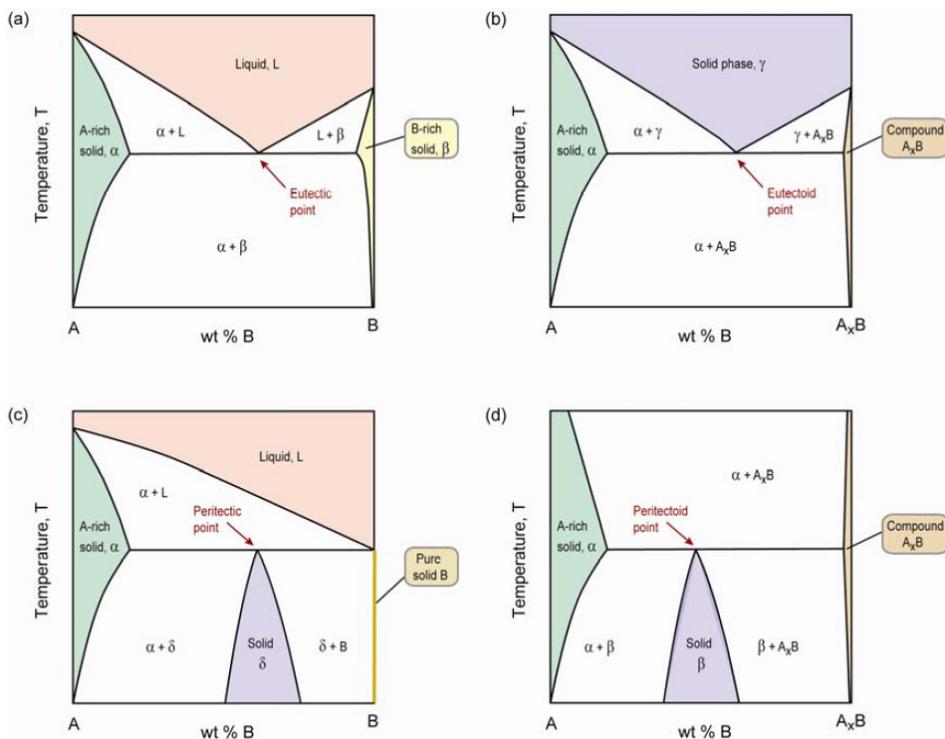


Figure P12: Schematic views of: (a) eutectic point; (b) eutectoid point; (c) peritectic point; (d) peritectoid point.

Ceramic phase diagrams

Ceramics are mostly compounds of a metal with one of the elements O, C or N. They form with specific stoichiometry to satisfy the electronic balance between the elements, e.g. alumina Al_2O_3 . In some cases, we are interested in mixtures of ceramics (or ceramic alloys). An example was mentioned earlier, *spinel* is made of Magnesia (MgO) and Alumina (Al_2O_3). Earth scientists in particular need phase diagrams for ceramics to help interpret natural minerals and microstructures.

Phase diagrams for ceramics work in exactly the same way as for metal systems, with the elements replaced by the pure compounds. Figure P13 shows the silica-alumina (SiO_2 - Al_2O_3) system. It forms an intermediate single phase, known as *mullite*. Note that the top of this single phase field closes in a peritectic point – above this point, the two phase field is liquid + Al_2O_3 .

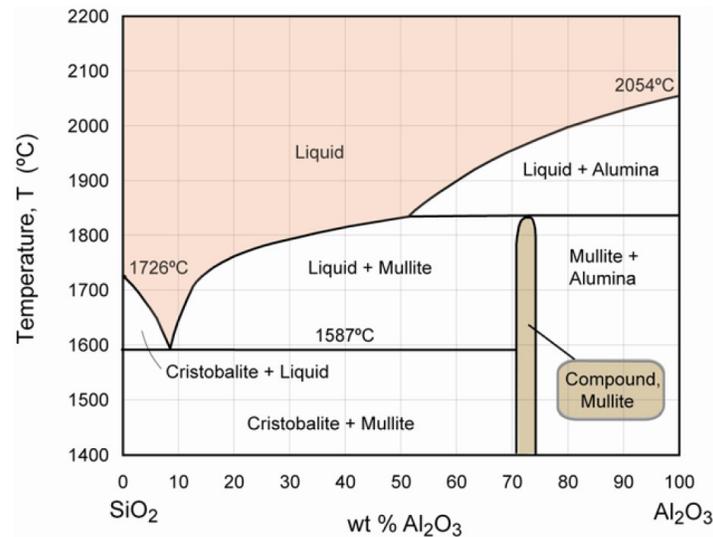


Figure P13: Phase diagram for the binary ceramic silica-alumina (SiO_2 - Al_2O_3) system.

Exercises

E.12 The two phase diagrams (or parts of diagrams) below both have a eutectic point.

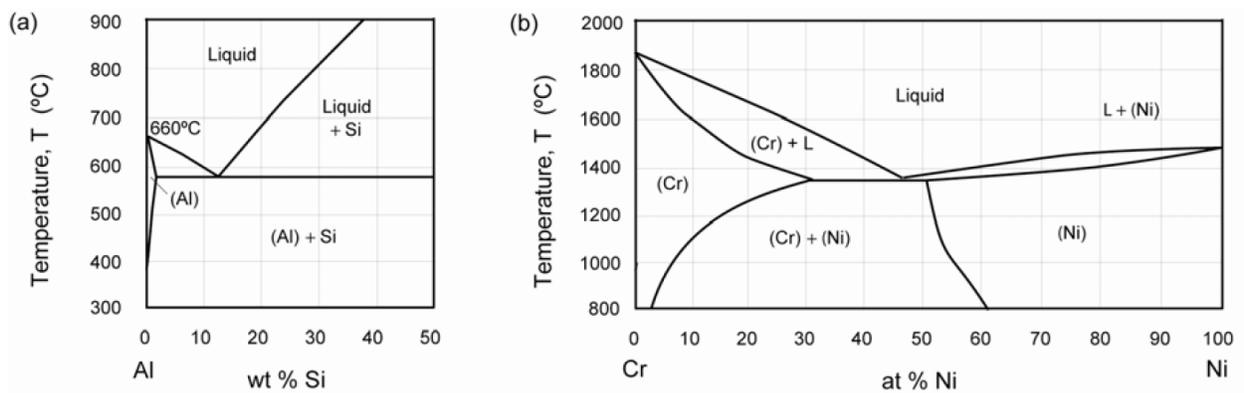


Figure E12: aluminum-silicon Al-Si and chromium-nickel Cr-Ni phase diagrams

Mark the eutectic point on each figure, and find the eutectic temperature and composition in wt% in each system. (Note: the atomic masses of Cr and Ni are 52.00 and 58.71 respectively).

E.13 The phase diagram for the copper-zinc system (which includes *brasses*) is shown in the Figure below. Use the diagram to answer the following questions.

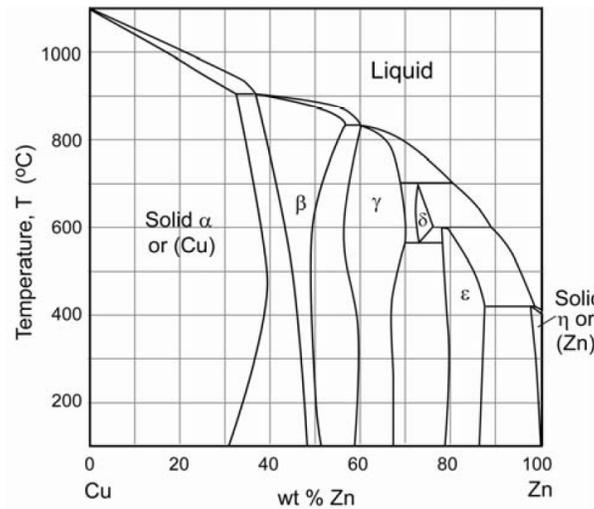


Figure E13 copper-zinc Cu-Zn phase diagram

- (a) (i) shade the single phase regions;
(ii) highlight the eutectoid point and five peritectic points in the copper-zinc system, and write down their compositions and temperatures.
- (b) The two common commercial brasses are: *70/30 brass*: $W_{Cu} = 70\%$, and *60/40 brass*: $W_{Cu} = 60\%$. Locate their constitution points on the diagram at 200°C.
- (i) What distinguishes the two alloys?
(ii) What roughly is the melting point of 70/30 brass?
(iii) What are the phases in 60/40 brass at 200°C? Find their compositions and proportions.

E.14 The copper-tin system (which includes *bronzes*) is shown in the Figure below.

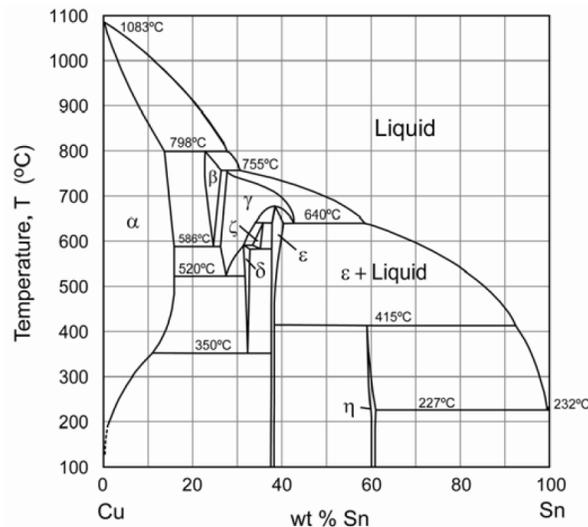


Figure E14 copper-tin Cu-Sn phase diagram

- (i) shade the single phase regions;
(ii) highlight the four eutectoids in this system, and write down their compositions and temperatures.

E.15 Use the phase diagram for the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system in Figure P13 to answer the following:
 (a) the intermediate compound mullite may be considered as having the formula $\text{SiO}_2(\text{Al}_2\text{O}_3)_x$. Find the approximate value of x . The atomic masses of Si, Al and O are 28.1, 16.0 and 26.9 respectively.
 (b) use the lever rule to find the equilibrium constitution of a 50 wt% Al_2O_3 alloy at 1700°C . Is it valid to measure directly from the diagram in this case? Why?

Answers to Exercises, Part 4:

E.12

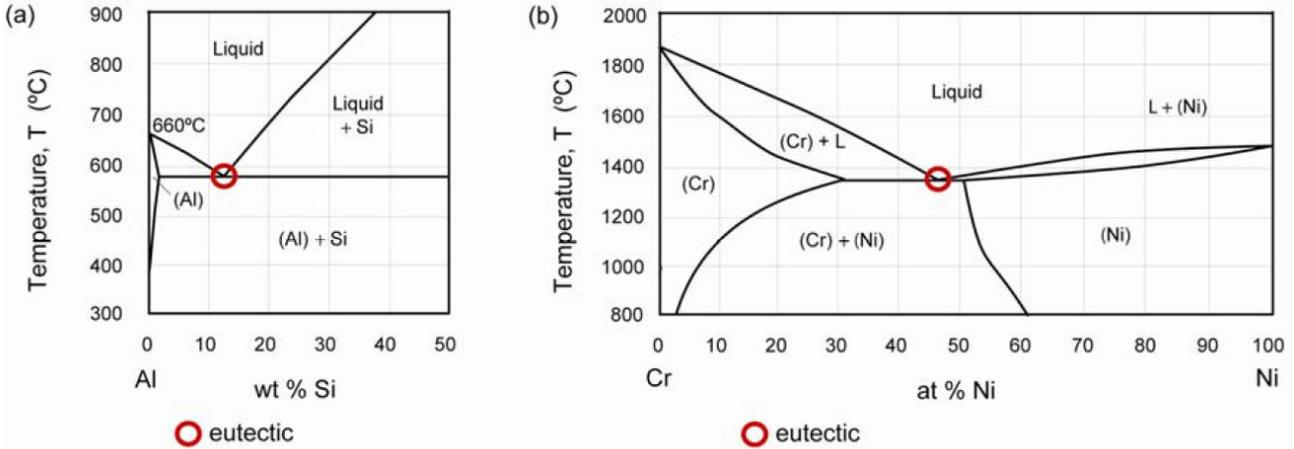


Figure E12S: Al-Si and Cr-Ni phase diagrams

Al-Si: eutectic at 580°C , composition 12wt% Si.

Cr-Ni: eutectic at 1350°C , composition 47at% Ni.

Conversion to wt%: $\text{wt\% Ni} = (0.47 \times 58.71) / (0.53 \times 52.0 + 0.47 \times 58.71) = 50.0 \text{ wt\% Ni}$

E.13 (a)

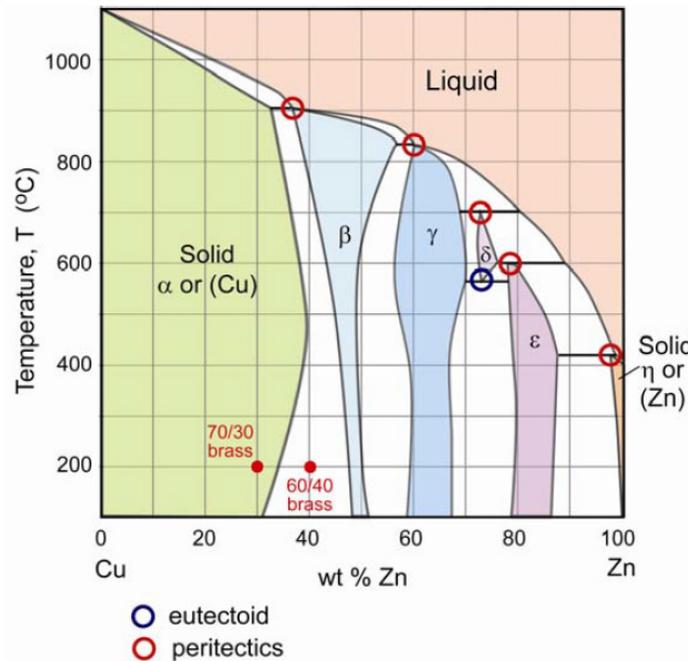


Figure E13S: Cu-Zn phase diagram

Eutectoid: $W_{Zn} = 73\text{wt}\%$, $T = 555^\circ\text{C}$

Peritectics:

- (1) $W_{Zn} = 37\text{wt}\%$, $T = 900^\circ\text{C}$
- (2) $W_{Zn} = 60\text{wt}\%$, $T = 825^\circ\text{C}$
- (3) $W_{Zn} = 73\text{wt}\%$, $T = 700^\circ\text{C}$
- (4) $W_{Zn} = 79\text{wt}\%$, $T = 600^\circ\text{C}$
- (5) $W_{Zn} = 99\text{wt}\%$, $T = 420^\circ\text{C}$

(b) 70/30 brass is single-phase, but 60/40 brass is two-phase.

70/30 brass starts to melt at 920°C and is completely liquid at 960°C .

At 200°C : α (copper-rich solid) and β (roughly CuZn). $W_{Zn} \approx 33\%$, $W_{Zn} \approx 48\%$

Proportions roughly 50-50; more precisely: proportion of $\alpha = (48-40)/(48-33) = 53\%$, and $47\% \beta$.

E.14

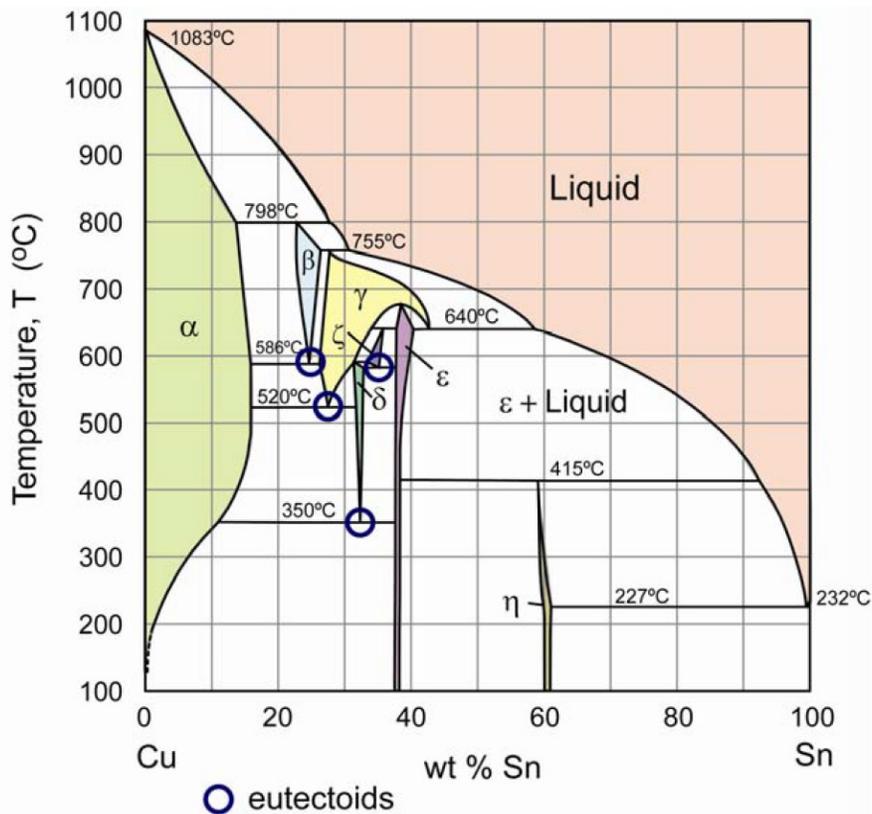


Figure E14S: Cu-Sn phase diagram

Eutectoids:

- (1) $W_{Zn} = 24\text{wt}\%$, $T = 586^\circ\text{C}$
- (2) $W_{Zn} = 35\text{wt}\%$, $T = 580^\circ\text{C}$
- (3) $W_{Zn} = 28\text{wt}\%$, $T = 520^\circ\text{C}$
- (4) $W_{Zn} = 32\text{wt}\%$, $T = 350^\circ\text{C}$

E.15

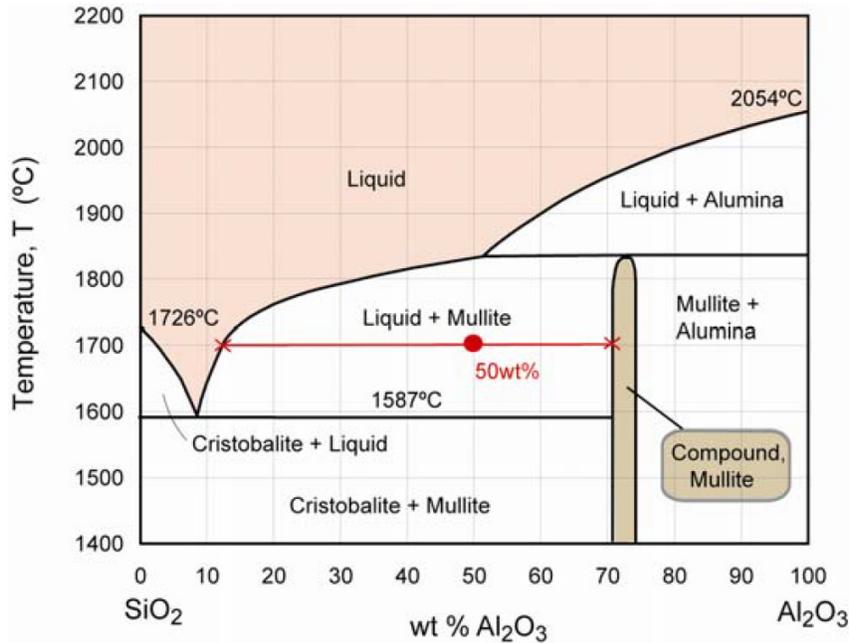


Figure E15S: SiO₂-Al₂O₃ phase diagram

(a) Mullite contains approximately 73wt% Al₂O₃ (27% SiO₂).

The molecular weight of SiO₂ is $28.1 + (16 \times 2) = 60.1$

The molecular weight of Al₂O₃ is $(26.9 \times 2) + (16 \times 3) = 101.8$

Molecular weight of mullite = 1 mol of SiO₂ + x mols of Al₂O₃ = $60.1 + 101.8x$

Alumina fraction by weight $\approx 0.73 \approx 101.8x / (60.1 + 101.8x)$

Hence $x \approx 1.6$.

(b) At 1700°C and 50wt% Al₂O₃, the phases are liquid containing 13 wt% Al₂O₃ and mullite containing 71 wt% Al₂O₃.

Weight fraction of liquid = $(71-50)/(71-13) = 36\%$

Weight fraction of mullite = $(50-13)/(71-13) = 64\%$.

It would be valid to measure the lengths of the tie-line directly in this case because the phase diagram has a *linear* weight % scale.

PART 5: Phase transformations and microstructural evolution

After completing Parts 1-4 you should be able:

- to recognize the important features of binary phase diagrams, and to identify whether fields are single phase or two-phase;
- to find the proportions and compositions of the equilibrium phases, at a given temperature and alloy composition.

Parts 5-8 link this understanding of phase diagrams to microstructure evolution in important industrial processes. Almost all manufacturing processes involve some combination of heating and cooling. For example:

- casting is filling a mold with molten metal, which solidifies and cools;
- hot forming shapes metal billets, giving complex temperature histories due to heat conduction into the tooling and surrounding air;
- welding often causes a thermal cycle of heating followed by cooling;
- a final stage of manufacture is often a separate heat treatment, of the whole component or just its surface.

When the temperature varies in a process, the equilibrium condition of the material keeps changing (e.g. as boundaries on the phase diagram are crossed) – hence *phase transformations* take place. These transformations determine which phases are present after processing, and how they are distributed amongst one another - that is, the final *microstructure*. This in turn controls the material properties. So, for a complete understanding of properties and processing, we need to know more about the microstructure than is given by a phase diagram. As we will see, controlling properties relies on managing not just which phases are present, but also their *morphology*. For instance, in a two-phase solid the shape of the phases and their *dispersion* within one another often has a strong influence on the properties.

Phase diagrams give important information needed to predict the phase transformations and final microstructure which result from a given thermal history. The real microstructure may not be at equilibrium, but phase diagrams give a starting point from which other (non-equilibrium) microstructures can often be inferred. In Parts 5-7 we consider slow cooling, when it is reasonable to assume that the microstructure can always evolve to maintain equilibrium; Part 8 looks at cases where we deliberately cool quickly to bypass equilibrium and achieve a different microstructural outcome.

Observing phases and phase transformations

Phase diagrams tell us the equilibrium phases, their compositions and proportions. But you might wonder how this information was produced in the first place. And how do we know whether a real process is actually following equilibrium? Many techniques are available to quantify the phases present in a microstructure. Here we give a brief overview. Table P1 summarizes the various methods and their physical basis.

Technique	Physical basis
Dilatometry	Measurement of dimensional changes at high resolution to detect changes of density and symmetry caused by phase change.
Electrical resistivity	Measurement of electrical resistivity changes associated with difference in electron mean free path before and after phase change.
Calorimetry: differential thermal analysis	Sensitive differential measurement of release or take-up of latent heat associated with phase change.
Optical microscopy	Differential reflection of light, either in color or intensity, by phases or by a surface film created by chemical or electro-etching.
X-ray diffraction	Diffraction of X-radiation by the crystal lattice of each phase, giving diffraction patterns from which crystal structure and volume fraction of phases can be inferred.
Scanning electron microscopy (SEM)	Differential back-scattering of electrons by differing phases giving both an image and compositional information.
Transmission electron microscopy (TEM)	Diffraction of an electron beam by the crystal lattice of each phase, giving both an image of the structure and, from the diffraction pattern, its crystal structure.

Table P1: Techniques for observing phases and microstructures

Optical and electron microscopy have been revolutionized by digital image capture, enabling automatic quantification by counting pixels, measuring areas and so on. Optical microscopy is well-suited to imaging grain structures in crystalline materials, and phase dispersions at length scales from a few microns upwards. Higher resolution imaging of phases requires SEM and TEM. Diffraction images reveal how electron or X-ray paths through the sample is modified by the atomic planes, and scattered by fine-scale second phase particles.

Microscopic observation techniques can be time-consuming and expensive, and are limited in their capabilities away from room temperature. A number of indirect methods use some form of *remote sensing* to monitor phase changes, utilizing other physical phenomena that depend directly on the phases present. Precision dilatometry uses accurate measurement of the dimensions of a sample to track the underlying changes in proportions of phases of different density, during thermal cycles. Another indirect measurement used at room temperature is electrical resistivity, which is particularly sensitive to solid solution levels.

Phases and phase transformations are fundamentally thermodynamic in their origins, that is, they are governed by the free energy. Changes in phases therefore liberate or absorb heat – the *latent heat* of melting being a familiar concept: heat must be added to turn ice into water, without any change in temperature. Measuring the heat input or output to a sample, or *calorimetry*, can therefore reveal the phases present. All phase changes have an associated latent heat, but it may be small relative to the thermal energy associated with the material simply being hot. This leads to the concept of *differential thermal analysis*: a sample with the same thermal mass as the test sample, but showing no phase transformations, is cooled (or heated) with the test sample. Latent heat exchanges lead to small temperatures *differences* between the samples. These are amplified to reveal the phase change temperatures, and the extent of transformation.

Phase diagrams have been built up experimentally using many of these techniques. Increasingly they are also determined by thermodynamic computation, from first principles. Many software packages are available to compute sub-domains in alloy phase diagrams containing many different elements. They are nonetheless dependent on good experimental data for calibration of the computations.

Key concepts in phase transformations

The fundamental thermodynamics and kinetics of phase transformations are described in Chapter 19 of the Text. The key concepts in phase transformations are as follows:

- phase transformations are driven by the resulting change in free energy (defined in Part 1), also known as the *driving force*;
- at the phase boundaries, the free energies of the states on either side of the boundary are equal – the driving force $\Delta G = 0$;
- phase changes almost always involve diffusion as the kinetic mechanism by which atomic rearrangement occurs;
- phase transformations occur via a two-stage process of *nucleation* and *growth*, in which nucleation may be spontaneous (homogeneous), or take place on some kind of interface (heterogeneous);
- *TTT diagrams* capture the extent of an isothermal transformation as a function of hold temperature and time, giving characteristic C-curves for diffusion-controlled phase transformations;
- in continuous cooling, there is a *critical cooling rate* which will just avoid the onset of the diffusional transformations.

To relate these concepts to phase diagrams and cooling in real industrial processes, we begin with examples of slow cooling, in which the material state can track equilibrium: Part 6 considers solidification, and Part 7 covers solid state phase changes. Finally in Part 8, heat treatment examples that bypass equilibrium are considered, exploiting quenching (rapid cooling) to manipulate the phases formed and their morphology.

PART 6: Equilibrium solidification

Latent heat release on solidification

Figure P14 shows the phases found in pure iron (i.e. the phase diagram becomes a single temperature axis). If we cool iron slowly from above its boiling point, the temperature as a function of time shows two shelves in the cooling curve, called *arrest points*, at the boiling and melting points (at atmospheric pressure, iron boils at 2860°C and melts at 1536°C). At each temperature there is a *phase change*: vapor-to liquid at the boiling point, and liquid-to-solid at the melting point. The arrest point on cooling is due to the release of the *latent heat*. On heating the reverse occurs – an arrest in the temperature rise while heat is absorbed to melt or boil the material.

Pure iron solidifies initially to BCC δ -iron, but undergoes further solid-state phase transformations on cooling, first to FCC γ -iron at 1391°C, and then back to BCC α -iron at 914°C. These transformations *also* release latent heat, but the amount is much smaller, as indicated by the modest arrests in the cooling history in Figure P14. The mechanisms of these solid state changes are considered later.

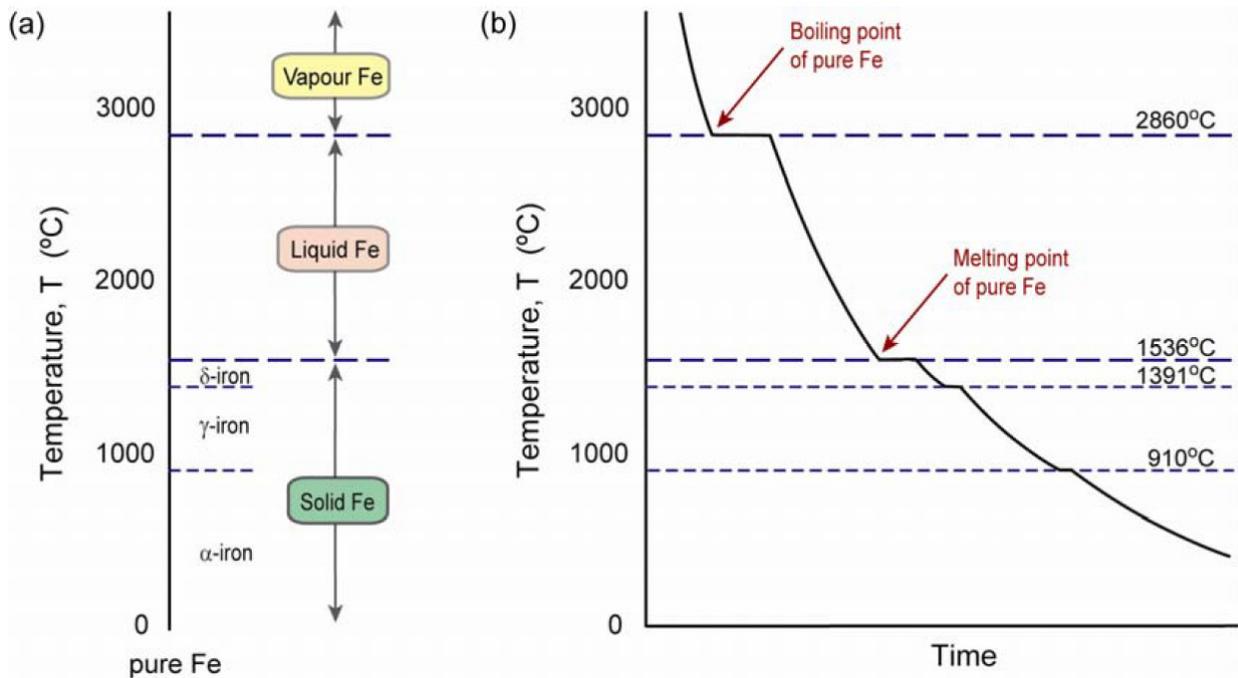


Figure P14: (a) one-dimensional phase diagram for pure iron; (b) corresponding cooling curve for condensing then solidifying iron from vapor to liquid to solid

Alloys frequently solidify over a *range* of temperature (between the liquidus and solidus lines). In this case the latent heat is released progressively as the temperature falls between the liquidus and solidus. The cooling curve does not therefore show a shelf at constant temperature, but the cooling rate is reduced by the progressive release of latent heat. This is illustrated in Figure P15, for two compositions in the Cu-Ni system.

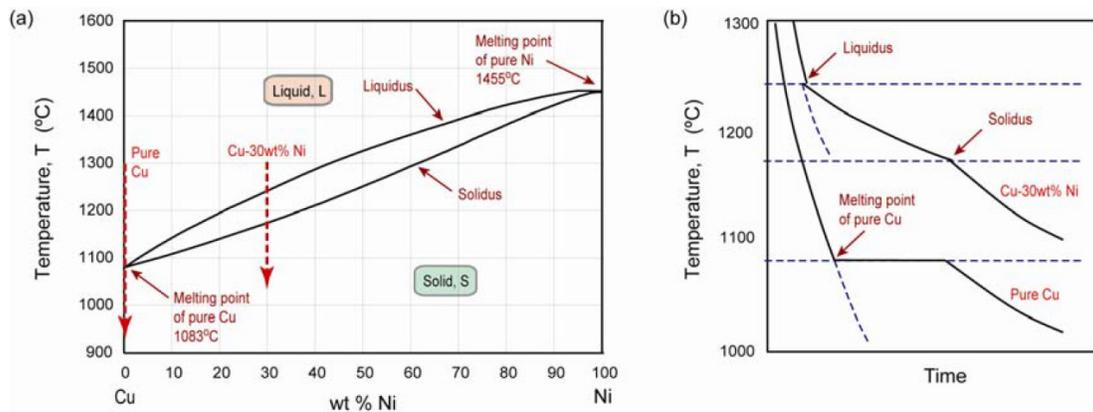


Figure P15: (a) Cu-Ni phase diagram, and (b) corresponding cooling curves, for solidifying pure Cu and a Cu-30wt% Ni alloy

Solidification of pure metals

The mechanism of solidification is illustrated in Figure P16. For *homogeneous nucleation*, solid colonies form spontaneously within the melt (Figure P16a). They grow stably provided they can reach a critical radius. This initial barrier reflects the surface energy of the solid-liquid interface, which uses up some of the free energy released by the transformation – the probability of forming stable nuclei increases rapidly as the liquid is undercooled below the transformation temperature. *Heterogeneous nucleation* facilitates the process, with solid nuclei forming more readily on a pre-existing solid in contact with the liquid (e.g. the walls of the mold, or high melting point particles of another solid mixed into the liquid).

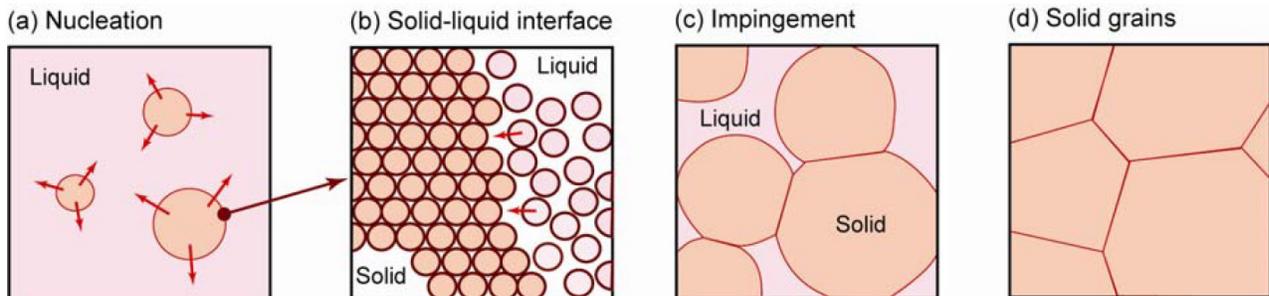


Figure P16: Solidification mechanism: (a) homogeneous nucleation; (b) magnified view of atomic transfer at the solid-liquid interface; (c) growth of nuclei and the onset of impingement; (d) final solid grain structure.

Each region grows by atoms transferring at the solid-liquid interface (Figure P16b) – the interface advancing in the opposite direction to the atomic transfer. Growth continues until *impingement* of the solid regions occurs (Figure P16c). Since each nucleus has its own independent crystal orientation, there is a misfit in atomic packing where they impinge. The individual crystallites remain identifiable once solidification is complete (Figure 16d). We call these *grains*, and the surfaces where they meet are *grain boundaries*. Grains are typically on the length-scale of $1\mu\text{m} - 1\text{mm}$, and are easily revealed by optical microscopy. Polished surfaces are chemically etched to “round off” the boundaries where they meet the surface, and light is then scattered at the boundaries, which appear dark. Figure P17 shows optical micrographs of pure metals after solidification, showing equiaxed grain structures. Note that some techniques also generate color contrast between grains, by applying surface etches which change the polarity of the reflected light (see Figure P17b). Here is an early warning of the need for caution in interpreting micrographs – the image of pure Al in the Figure shows a single phase, so multiple colors do not necessarily indicate different phases!

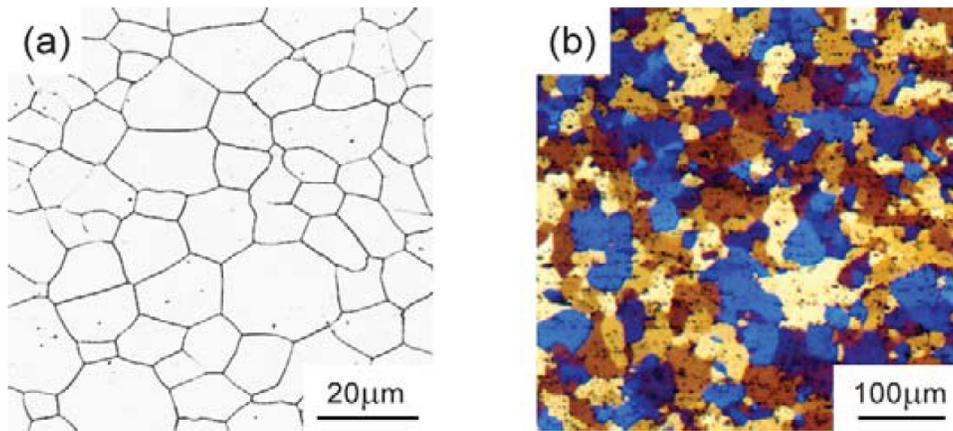


Figure P17: Optical micrographs of (a) pure Fe and (b) pure Al. In (b) the etching technique produces color contrast between different crystal orientations – but it is still all one phase.
(Images courtesy of ASM Micrograph Center, ASM International, 2005)

So grain structure is our first example of a microstructure formed by a phase transformation. Let's emphasize a key idea which will recur from here onwards. The phase diagram tells us that the liquid should transform to a single-phase solid – and that's all. It *doesn't* tell us the grain size – this depends on the density of nucleation sites, and the kinetics of the diffusive mechanism of forming solid at the interface. These in turn depend on just how slowly the liquid cools. So to describe the microstructure for *any* phase transformation, we need to bring in some additional knowledge. This example also highlights why processing details are so important in determining microstructure and properties. And it suggests the use of processing “tricks” to modify what happens (e.g. adding lots of fine particles to the melt to promote copious heterogeneous nucleation; the result? – a much finer grain size). Process-microstructure interactions such as these are discussed in Chapter 19 of the Text.

Solidification of simple binary alloys, and phase reactions

Alloys show a freezing range, between the liquidus and solidus lines. Consider solidification of Cu-30wt% Ni on the phase diagram of Figure P15. Solidification starts at 1240oC – nuclei form as in Figure P16(a). In contrast to a pure metal, further cooling is needed for more solid to form, for example, at 1200oC a tie-line indicates 50% solid and 50% liquid are stable, and the microstructure would appear as in Figure P16(b). To reach 100% solid (Figure P16c) we need to keep cooling to 1170oC, and the end result looks much the same as in the pure case (with the difference that the phase forming these grains is a Ni-rich solid solution, not something we can detect optically). Note that the compositions of the solid and liquid both evolve, following the ends of the tie-line.

So when an alloy is cooled, the constitution point for the alloy drops vertically on the phase diagram. Phases transform when we cross boundaries on the diagram, but the Cu-Ni example shows that phases may also evolve in composition, *without* a change in the phases present. We call this a *phase reaction*.

DEF. When any phase compositions change with temperature, a *phase reaction* is taking place.

In a single phase field, the composition of the phase is always that of the alloy – no phase reaction takes place on cooling. In a two-phase region the compositions of the two phases are given by the ends of the tie-line through the constitution point. In general, as the constitution point falls vertically, the ends of the tie-line do *not* – instead they run along oblique phase boundaries. The compositions of the two phases change with temperature, and phase reactions occur. The exception would be where both boundaries at

the end of the tie-line are vertical. This is not something associated with liquidus and solidus boundaries, but is seen in the solid state, particularly with compounds (recall the unusual Ag-Sr phase diagram in Figure P9a).

Solidification of dilute alloys

The Cu-Ni system is unusual in that the solid that forms initially is unchanged on further cooling – no transformations or reactions take place. But most binary systems show eutectics, with two-phase fields over a wide range of composition at room temperature. First we will consider solidification of a relatively dilute alloy in the Pb-Sn system, Pb-10wt% Sn (see Figure P18 – alloy A).

Figure P18: The Pb-Sn phase diagram: solidification of a dilute alloy A

The transformations and reactions are as follows, leading to the microstructure evolution shown in Figure P19.

1. *Above 305°C*: Single-phase liquid of composition identical to that of the alloy; no phase reaction.
2. *From 305°C to 270°C*: The liquidus line is reached at 305°C; the reaction liquid → solid (Pb-rich solid solution) starts. The solid contains less tin than the liquid (see first tie-line), so the liquid becomes richer in tin and the composition of the liquid moves down the liquidus line, as shown by the arrow. The composition of the solid in equilibrium with this liquid changes too, becoming richer in tin also, as shown by the arrow on the solidus line: a *phase reaction* is taking place. The *proportion* of liquid changes from 100% (first tie-line) to 0% (second tie-line).
3. *From 270°C to 150°C*: Single-phase solid of composition identical to that of the alloy; no phase reaction.
4. *From 150°C to room temperature*. The Pb-rich phase becomes unstable when the phase boundary at 150°C is crossed. It breaks down into *two solid phases*, with compositions given by the ends of the tie-line, and proportions given by the lever rule. On cooling the compositions of the two solid phases change as shown by the arrows: each dissolves less of the other, and a phase reaction takes place.

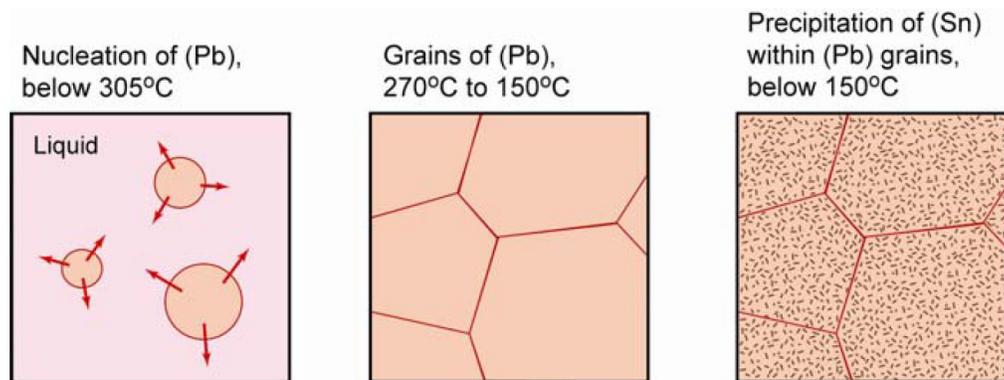


Figure P19: Schematic microstructure evolution in solidification of a dilute Pb-10wt% Sn alloy.

The formation of the Sn-rich phase takes place by *precipitation* from the solid solution. This mechanism too involves nucleation and growth, but on a much finer scale than the grain structure. Small clusters of Sn-rich solid nucleate spontaneously within the Pb-rich matrix. The fraction of this phase increases as the nuclei grow, by depleting the surrounding matrix of some of its Sn. The compositions of the phases (particles and matrix) continually adjust by inter-diffusion of Pb and Sn atoms. The practicalities of solid-state precipitation are discussed further in Part 7.

Note that the phase diagram tells us the proportions of the phases, in weight %. The density of the phases is not the same, so this does not convert directly into volume % (or area fraction in a metallographically prepared cross-section). Nonetheless, provided the phase densities are not too dissimilar, the phase proportions give some idea of the proportions we expect to see in the microstructure (good enough for sketching, as in Figure P19).

Exercise

E.16 Find the proportions and compositions of the phases formed on solidification of the Pb-10wt% Sn alloy at 250°C and room temperature (20°C).

Eutectic solidification

Next consider the solidification of the eutectic composition itself in the Pb-Sn system (Figure P20 – alloy B). The eutectic composition is Pb-61.9wt% Sn. When liquid of this composition reaches the eutectic temperature (183°C), the liquid can transform to 100% solid without further cooling – this is a unique characteristic of eutectic alloys, and in this respect they resemble pure components. But the final microstructure will be very different, since two solid phases form simultaneously (with proportions and compositions governed by the tie-line through the eutectic point). This transformation is called the *eutectic reaction*.

DEF. A eutectic reaction is a three-phase reaction by which, on cooling, a liquid transforms into two solid phases at constant temperature: Liquid, L → Solid α + Solid β.

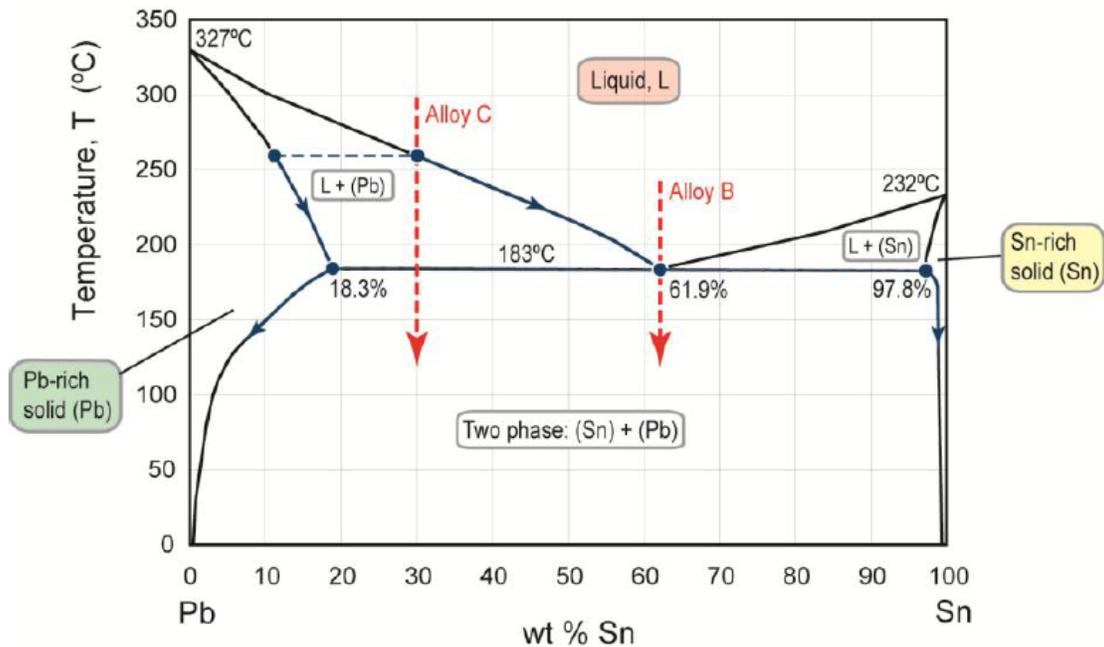


Figure P20: The Pb-Sn phase diagram: solidification of eutectic alloy (B) and an off-eutectic alloy (C)

Exercise

E.17 Find the proportions and compositions of the solid phases formed on solidification at the eutectic point in the Pb-Sn system.

So how does this transformation take place? The phase diagram provides clues – the Pb and Sn in the liquid are uniformly mixed, but after transformation we have Pb-rich solid and Sn-rich solid. Pb and Sn must therefore inter-diffuse to generate regions in which each dominates. This must happen at an interface between liquid and two-phase solid. It will therefore be easier if the diffusion distance is kept small, i.e. the two phases separate out on a small scale, such that no single atom has to diffuse too far to be able to join a growing colony of (Pb) or (Sn). Eutectics usually therefore form as intimate mixtures of the two phases, on a length scale much smaller than a typical grain size – Figure P21a shows a micrograph of eutectic Al-Si (the phase diagram for this system was shown in Exercise E.12).

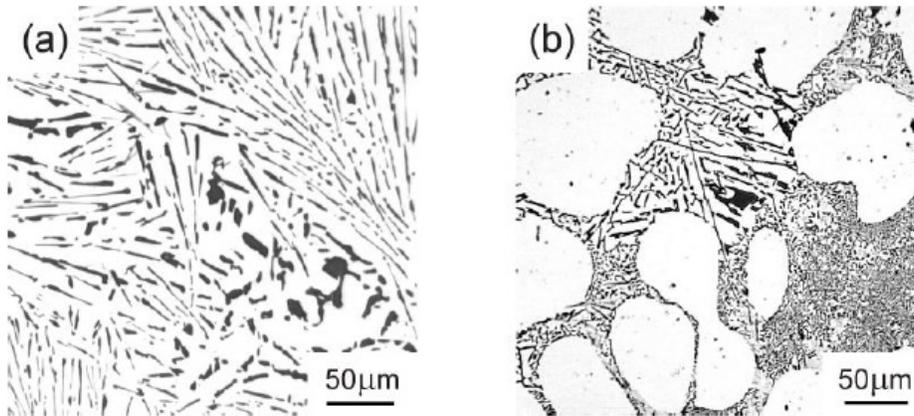


Figure P21: Optical micrographs of
(a) eutectic Al-Si alloy;
(b) off-eutectic Al-Si alloy, showing grains of primary (Al) (white).
(Images courtesy of ASM Micrograph Center, ASM International, 2005)

The proportions of the phases in a eutectic can vary widely, depending on the position of the “V” along the eutectic tie-line. But in broad terms we can think of two characteristic dispersions of the phases. If the eutectic point is towards the middle of the tie-line, the proportions of the two phases are roughly equal, and neither can be thought of as a matrix containing the other phase. This is the case in Pb-Sn (the proportions were found in Exercise E.17). However, if the V is located towards one end of the tie-line, then one phase forms a matrix containing the second phase as isolated particles. This is the case in Al-Si (Figures E.12 and P21a).

Note in Figure P21a that the *shape* of the phases is elongated into plates or needles. There are two reasons why this often occurs. One is that growth of the interface is planar at the atomic scale, with plates extending in the growth direction to minimize diffusion distances. The other is that the boundary between the phases is also a crystallographic boundary, and some pairs of orientations have a lower surface energy which will grow more rapidly. Forming a fine mixture of phases does mean that there is a price to be paid in surface energy between phases – the area of interface per unit volume is large. But this is a small energy penalty compared to the free energy release in the transformation as a whole. So again we find that the detail of the transformation mechanism has an important influence on the microstructure (and hence properties).

A further phase reaction occurs on cooling of the two-phase eutectic solid, e.g. for Pb-Sn, from 183°C to room temperature. As the phase boundaries on the phase diagram are not vertical, the compositions and proportions of the two solid phases evolve on cooling. Diffusion distances are automatically small within

the eutectic, so both phases can become purer and adjust their proportions, by inter-diffusion.

Solidification of off-eutectic compositions

Casting alloys are often off-eutectic, with a composition to one or other side of the “V” on the phase diagram. The solidified microstructure in these cases can now be inferred – above the eutectic, partial solidification of a single phase solid solution occurs (as seen in Cu-Ni above), then at the eutectic temperature the remaining liquid undergoes the eutectic reaction (as seen in Pb-Sn above).

Consider solidification of Pb-30wt% Sn (see Figure P20, alloy C). The transformations and reactions are as follows, leading to the microstructure evolution illustrated in Figure P22.

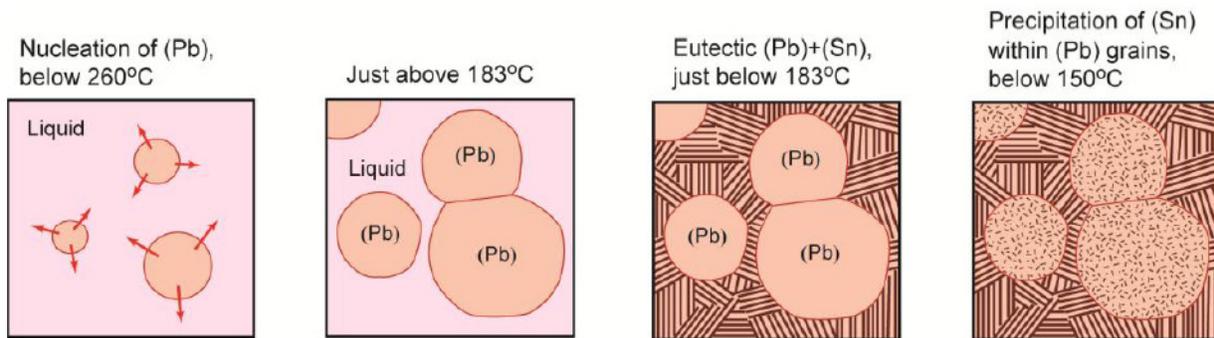


Figure P22: Schematic microstructure evolution in solidification of a dilute Pb-30wt% Sn alloy.

1. *Above 260°C:* Single-phase liquid; no phase reactions.
2. *From 260°C to 183°C:* The liquidus is reached at 260°C, and nuclei of Pb-rich solid solution appears first (Figure P22a). The composition of the liquid moves along the liquidus line, that of the solid along the solidus line. This regime ends when the temperature reaches 183°C. Note that the alloy composition in weight % (64) is roughly half way between that of the new solid (81wt%) and the residual liquid (38wt%); so the alloy is about half liquid, half solid, by weight (and very roughly by volume, neglecting the difference in phase densities – Figure P22b).
3. *At 183°C:* The remaining liquid has reached the eutectic point, and this liquid undergoes solidification exactly as described before (Figure P22c). Note that the proportions of primary (Pb) and eutectic microstructure are exactly the same as the solid-liquid proportions just above the eutectic temperature. Nucleation of the eutectic will be straightforward, since there are already solid grains present on which the eutectic can form.
4. *From 183°C to room temperature:* The two types of microstructure each evolve: (a) the Pb-rich solid becomes unstable, and Sn-rich solid precipitates (exactly as before, in 10 wt% alloy). (b) the eutectic region evolves exactly as 100% eutectic did before: both phases change composition by inter-diffusion, becoming purer.

The final microstructure therefore combines all of the features discussed so far (Figure P22d). Note that in this final microstructure there are just two phases, with the Pb-rich and Sn-rich regions in the eutectic being exactly the same phases in the (Pb) grains containing (Sn) precipitates. The phase diagram only tells us the overall phase proportions (from the tie-line at room temperature). But their spatial dispersion (and hence properties) involves understanding of how the cooling history interacts with the phase diagram, and the mechanisms of phase transformations.

Figure P21b shows a micrograph of an off-eutectic Al-Si alloy. The primary Al grains are surrounded by eutectic microstructure. The primary grains have a uniform color, appearing therefore to be a single

phase. This may be because the scale of the precipitates is too fine to resolve in this image – another word of warning about potential over-interpretation of micrographs. On the other hand, it is possible that the microstructure has not followed equilibrium in practice – the grains have remained as a solid solution due to some difficulty in nucleating the second solid phase. In this case the phase will be *supersaturated* in solute, and the phase is *metastable* (i.e. thermodynamically stable at room temperature at a higher free energy level than the equilibrium state).

Exercises

E.18 Not all alloys in the lead-tin system show a eutectic reaction on slow cooling: pure lead, for example, does not. Examine the Pb–Sn phase diagram and identify the composition range for which you would expect a eutectic reaction to be possible.

E.19 (a) A eutectic reaction was defined in the text. Define what happens on heating a solid of eutectic composition. Over what temperature range does melting occur?

(b) For a Pb-35wt% Sn alloy, identify the temperatures at which melting starts and finishes on heating, and describe how the proportion of liquid evolves during melting.

E.20 Figure E12 (a) showed the phase diagram for the Al-Si system (the basis of aluminum casting alloys). Use this figure to answer the following:

(a) Describe the solidification of an Al-20wt% Si alloy, sketching the microstructure at key temperatures (e.g. onset of solidification, just above and just below the eutectic). Estimate the phase proportions in two-phase regions, and sketch the microstructures accordingly.

(b) How would the final microstructure differ for Al-Si alloys of: (i) Al-1wt% Si; (ii) eutectic composition?

Segregation

It has been noted that when solidification starts, either on the walls of a mold or spontaneously as nuclei throughout the melt, the first solid to form is purer in composition than the alloy itself (due to *partition* of the liquidus and solidus lines). For example, in Pb-10wt% Sn (considered earlier), the first solid appearing at 305°C has a composition of 5wt% Sn. This means that tin is *rejected* at the surface of the growing crystals, and the liquid grows richer in tin: that is why the liquid composition moves along the liquidus line. From 305 to 270°C the amount of primary (Pb) increases, and its equilibrium composition increases, following the solidus line. This means that lead must diffuse *out* of the solid (Pb), and tin must diffuse *in*. This diffusion takes time. If cooling is very slow, time is available and equilibrium may be maintained. But practical cooling rates are not usually slow enough to allow sufficient time for diffusion, so there is a *composition gradient* in each (Pb) grain, from the middle to the outside. This gradient is called *segregation*, and is found in almost all alloys (see Figure P23).

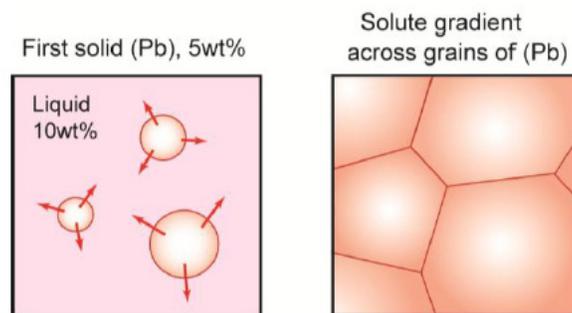


Figure P23: Segregation in solidification of binary alloys.

Segregation can to some extent be "smoothed out" after casting by *homogenization*: holding a casting at temperature to allow some redistribution of solute by diffusion. It can never be eliminated completely.

One consequence of segregation is that the last liquid to solidify will be richer in solute than expected from the phase diagram (as the solid is purer than it should be). This may lead to the formation of eutectics at the grain boundaries (the last part to solidify), even in alloys which are not expected to show a eutectic (i.e. compositions beyond the range of the tie-line through the eutectic point). The temperature at which melting would start on heating is thus lower than expected from the phase diagram, i.e. the eutectic temperature, not the solidus temperature.

Segregation is even more important with respect to *impurities*. No alloy is truly binary, ternary, or whatever, but will contain traces of other elements (e.g. from the ore used as the source of the metal). Impurities also dissolve more readily in the liquid than in the solid. Hence when alloys solidify, the impurities concentrate in the last bit to solidify. Even if the alloy contains only a fraction of 1% of a given impurity overall, if the solid will not dissolve it in solution the concentration can be locally much higher on the grain boundaries. This is damaging if the impurity forms brittle phases, which can be disastrous from the point of view of toughness. An example is sulfur in steel, which forms brittle iron sulphide. Rather than trying to remove the traces of impurity from the melt, the way to solve the problem is further alloying. Plain carbon steels all contain manganese, which forms MnS at higher temperatures during solidification and therefore ties up the sulfur before segregation takes place, rendering it harmless.

Another example of detrimental impurity segregation is in *fusion welding*. This is like casting on a small scale, with a melt pool under a moving heat source solidifying as it goes. Solidification finishes on the weld center-line, and segregation concentrates impurities there. Contraction of the joint can generate high enough thermal stresses to crack the weld along the weakened grain boundaries down the weld center: this is known as solidification cracking.

Answers to Exercises, Part 6:

E.16 At 250°C, 100% Pb-rich solid (composition same as alloy, 10wt% Sn). At 200°C, two phases: Pb-rich solid (1wt% Sn) and Sn-rich solid (99wt% Sn). Proportion of Pb-rich solid = $(99-10)/(99-1) = 0.91$, or 91wt% (hence 9wt% Sn-rich solid).

E.17 The phases are Pb-rich solid (18.3wt% Sn) and Sn-rich solid (97.8wt% Sn). The proportion of Pb-rich solid is $(97.8-61.9)/(97.8-18.3) = 0.45$, or 45wt% (hence 55wt% Sn-rich solid).

E.18 From $W_{\text{Sn}} = 18.3\%$ to $W_{\text{Sn}} = 97.8\%$ (i.e. the ends of the tie-line through the eutectic point – alloys outside this range reach 100% solid above the eutectic temperature).

E.19 (a) As this is an equilibrium diagram, on heating the reaction simply goes in reverse. The two solids "react" to give a single liquid. In general, on heating: $\alpha + \beta \rightarrow \text{Liquid}$. Eutectics melt at constant temperature.

(b) For Pb-35wt% Sn, melting starts at the eutectic microstructure and finishes at 250°C. At the eutectic temperature, all of the solid eutectic microstructure melts, giving roughly 40% liquid. On heating to 250°C, the remaining solid (the original Pb-rich grains) melts progressively.

E.20 (a) Cooling of Al-20wt% Si casting alloy – see phase diagram and schematics in Fig. E20S.

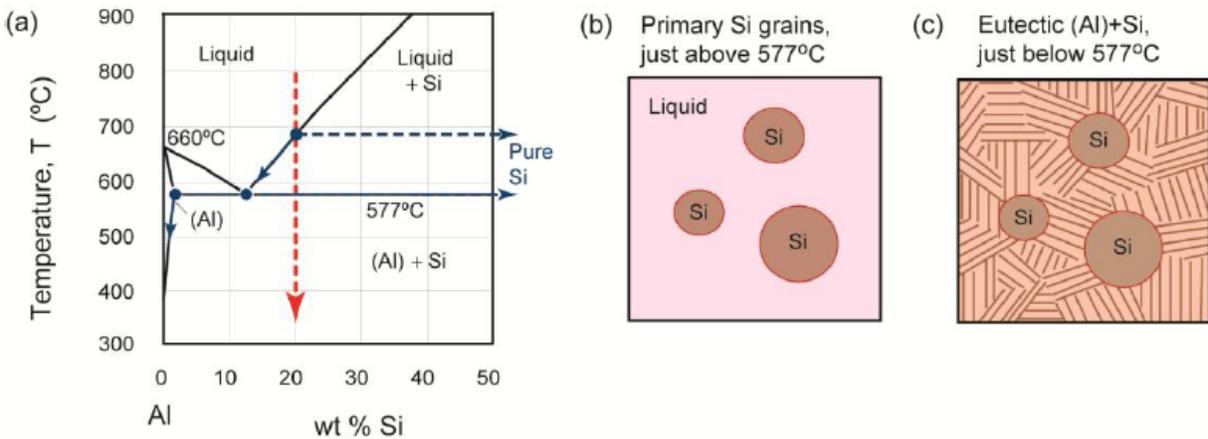


Figure E20S: (a) Al-Si phase diagram and (b) microstructure evolution on solidification of Al-20wt% Si.

1. Above 680°C: Single-phase liquid, with composition of the alloy; no phase reaction.
2. From 680 to 577°C: The liquidus is reached at about 680°C, when primary solid Si (pure, not a solution) starts to separate out. As the temperature falls the liquid composition moves along the liquidus line, and the amount of solid Si increases. At the eutectic temperature (577°C), the proportion of solid is $(20-12)/(100-12) = 9\%$, see Figure E20S(b).
3. At 577°C: The eutectic reaction takes place: the remaining liquid decomposes into solid (Al) mixed with solid Si, on a fine scale, Figure E20S(c). The proportion of Si in the eutectic is $(12-2)/(100-2) = 10\%$. So the Si forms as a dispersion within a matrix of (Al), usually in the characteristic needle-shape of a eutectic.
4. From 577°C to room temperature: On further cooling the (Al) in the eutectic needs to grow purer and reject Si. So in the eutectic structure, Si diffuses out of the (Al). The final appearance of the microstructure still looks like Figure E20S(c).

(b) (i) An Al-1wt% Si would solidify to 100% (Al) grains with no eutectic, and would be expected to precipitate Si within the grains on cooling to room temperature (assuming Si is able to nucleate and grow in the solid state – if not, the (Al) grains remain as metastable supersaturated solid solution).

(ii) A solidified alloy of eutectic composition would be 100% eutectic, with no primary Si.

PART 7: Equilibrium solid-state phase changes

Precipitation reactions

Solid-state phase transformations were introduced in Part 6, following solidification of dilute binary alloys (Figures P18 and P19). The solid formed first from the liquid as grains of single phase solid solution, but on further cooling the solvus boundary is crossed into a two-phase region. One of the new phases is present already, but the falling solubility means that the excess solute needs to be absorbed by the second phase. This type of transformation is a *precipitation* reaction: $\alpha \rightarrow \alpha + \beta$

In many systems, the second phase in this two-phase region is a *compound*, with precipitates forming on slow cooling having a specific stoichiometry, rather than being another solid solution. This is important for making alloys with high strength – compounds are generally hard and resistant to dislocations. This offers the potential for *precipitation hardening* (Chapter 6) – the mechanism of formation of the second phase explaining the name.

Refer to Figure P9(b), the Al-rich end of the Al-Cu system. Exercise E10(d) considered an Al-4wt% Cu alloy

at 550°C and 250°C. On cooling between these temperatures, at 490°C the solvus boundary is crossed and the θ -phase (CuAl_2) starts to precipitate, nucleating homogeneously within all of the grains and increasing in proportion as the temperature falls. Figure P24 shows the final microstructure.

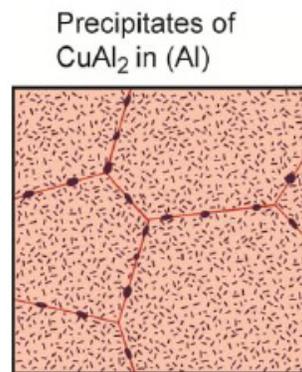


Figure P24: Schematic microstructure of a slow-cooled Al-4wt% Cu alloy.

At modest magnification, the two-phase region may appear a uniform color, and higher resolution is needed to distinguish the precipitates from the matrix. The scale of the microstructure is dictated by the kinetic mechanism. By forming very large numbers of small precipitates, the average diffusion distance for solute is short, enabling the transformation to occur in the solid state. The precipitate spacing is therefore much finer than in a eutectic. But in common with a eutectic microstructure, there is an energy penalty in forming a large area per unit volume of interface between the phases, but again the free energy release dominates over the surface energy.

From the point of view of precipitation hardening, it is the spacing of precipitates that matters. In practice the precipitates formed by slow cooling are still too far apart to be effective in obstructing dislocations. Useful strengthening comes from forming a much finer dispersion of precipitates – the means to achieve this in Al-Cu and other alloys is discussed in Part 8.

The precipitation illustrated here is expected on cooling due to the thermodynamics of the system. But nucleation of precipitates depends strongly on the kinetic mechanism. As noted earlier it can be difficult to form a new lattice within an existing solid crystal – the existence of a driving force may not be sufficient to cause the phase change, leaving a metastable supersaturated solid solution on cooling. Whether or not a given system will precipitate is an alloy-specific detail, not indicated by the phase diagram.

Figure P24 illustrates another feature which may be observed in precipitation reactions, on the grain boundaries. Here the precipitates are larger than within the bulk of the grains. Two factors contribute to this effect, both due to the extra “space” associated with the boundary: firstly, faster nucleation can occur, as atoms can rearrange more readily into the precipitate lattice (this is a form of heterogeneous nucleation); secondly, the boundaries provide faster diffusion paths for solute to be drawn in to build up the precipitates. This doesn’t always occur – again it depends on the alloy system – but it can have important practical consequences. Coarser precipitation on the grain boundaries may weaken the boundaries, with possible loss of toughness (inter-granular fracture) or susceptibility to corrosive attack, forming grain boundary cracks.

Phase transformations in carbon steels

The iron-carbon system was introduced in Part 3, including the various single phase forms of iron-carbon solid solutions, the compound iron carbide, and the eutectoid point. Here we investigate the important phase transformations that occur in *carbon steels*, i.e. Fe-C alloys with compositions between pure iron and the eutectoid composition. Figure P25 shows the relevant section of the Fe-C phase diagram.

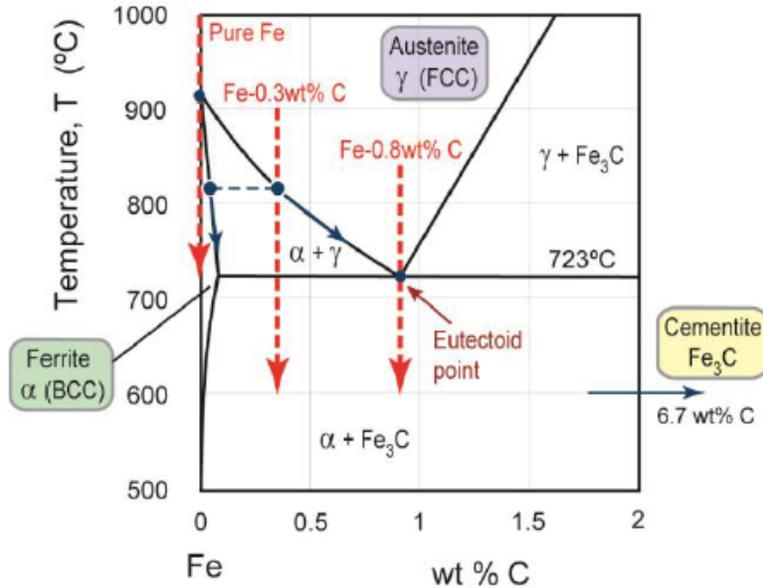


Figure P25: The Fe-C phase diagram for compositions of carbon steels below 1000°C, including the eutectoid point

First consider cooling of pure iron, starting with FCC γ -iron at 1000°C. At 910°C, a solid-state change to BCC α -iron occurs phase changes also (at constant temperature). *Nucleation* starts at the grain boundaries, where there is more space for BCC nuclei to form. The α grains grow by atoms jumping across the boundary between the two phases, adopting the crystal structure of the growing phase as they do so (shown schematically in Figure P26b). The interface migrates in the opposite direction to the atomic jumps. Figures P26(a,c) show the solid-solid transformation underway and complete at 910°C. When the growing α colonies impinge, new α - α grain boundaries are formed. Since there is typically more than one α nucleus per γ grain, the average grain size is reduced by this transformation.

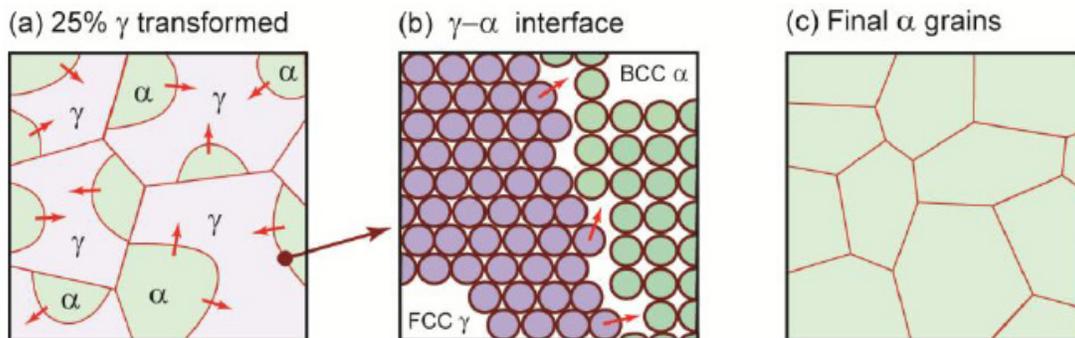


Figure P26: Schematic illustration of the transformation from FCC γ -iron to BCC α -iron in pure iron:
 (a) γ - α grain structure after 20% transformation;
 (b) atomic transfer mechanism at the phase interface;
 (c) final α -iron grain structure.

The eutectoid reaction

The eutectoid point in the Fe-C system was introduced in Part 3. Cooling austenite of eutectoid composition (0.8wt% C) leads to complete transformation to ferrite and cementite, at the eutectoid temperature, 723°C (see Figure P25). More generally we therefore define a eutectoid reaction as follows:

DEF. A eutectoid reaction is a three-phase reaction by which, on cooling, a single phase solid transforms into two different solid phases at constant temperature: Solid $\gamma \rightarrow$ Solid α + Solid β .

The mechanism of the eutectoid reaction must transform a single solid phase into two others, both with compositions which differ from the original (given by the ends of the tie-line through the eutectoid point). In the Fe-C eutectoid reaction, austenite containing 0.8wt% C changes into ferrite (containing almost no carbon) and cementite (Fe_3C , containing 6.7wt% C, or 25 *atomic* % carbon). Hence carbon atoms must diffuse into high and low concentrations, at the same time as the FCC austenite lattice transforms into BCC ferrite and cementite lattices. Nuclei of small plates of ferrite and cementite form at the grain boundaries of the austenite, and carbon diffusion takes place on a very local scale just ahead of the interface. The plates of ferrite and cementite grow in tandem, consuming the austenite as they go – see Figure P27(a).

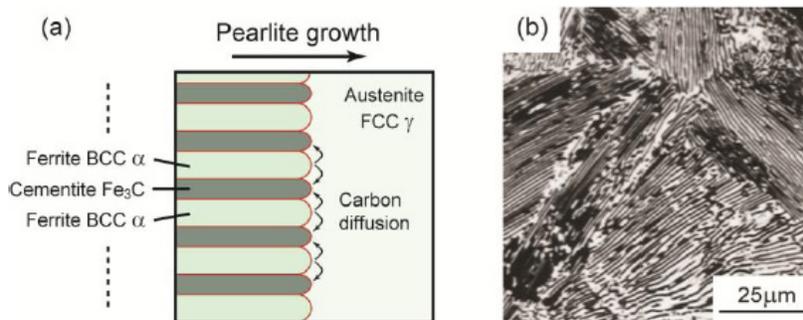


Figure P27: (a) Schematic illustration of the eutectoid transformation from austenite to pearlite; (b) micrograph of pearlite. (Image courtesy of ASM Micrograph Center, ASM International, 2005)

The resulting grains therefore consist of alternate plates of ferrite and cementite. This structure again has a very large area of phase boundary between ferrite and cementite, with associated surface energy penalty. However, kinetics dictate the mechanism of transformation, such that C atoms on average diffuse only one plate spacing, while the interface between the new phases and the austenite traverses whole grains.

The eutectoid ferrite-cementite microstructure has a special name: *pearlite* (because it has a pearly appearance). Note that pearlite is a two-phase microstructure *not* a phase, in spite of the similarity in nomenclature. The micrograph in Figure P27(b) shows pearlite, at high magnification. The length scale of the plates in pearlite is again much finer than in a eutectic, due to the solid-state diffusion. At lower magnification, pearlite may just appear as dark etching grains. This is easily mistaken for a single phase – it is not, but this is another example of a dispersion of two phases at a scale below the resolution of the microscopy technique.

Phase transformations in hypo-eutectoid steels

Some commercial steels have a eutectoid composition – steel for railway track is an example of a "pearlitic steel". Most carbon steels are "hypo-eutectoid", containing less than 0.8 wt%. Mild steels contain 0.1-0.2 wt% C, medium carbon steels around 0.4 wt%. Here we will look at how the equilibrium microstructures relate to the phase diagram.

Consider slow cooling of a medium carbon steel containing 0.3wt% C (as indicated on Figure P25). Starting with austenite at 900°C, we have a solid solution of C in FCC austenite. At 820°C, we enter the two phase region: ferrite plus austenite. The formation of ferrite follows the same mechanism as in pure iron, nucleating on the austenite grain boundaries. The ferrite rejects carbon into the remaining austenite, the composition of which increases accordingly. Grains of ferrite grow until, just above 723°C, the proportion of ferrite to austenite is roughly 50:50. The remaining austenite contains 0.8wt% C – it is at the eutectoid point. This austenite then decomposes as before into pearlite – the two-phase mixture of ferrite and cementite.

The schematics in Figure P28 show the reaction underway just above and just below the eutectoid temperature. Note that as before the final structure is still only two-phase, but different grains have very different microstructures. The ferrite within the pearlite structure is the same stuff as the ferrite forming whole grains - it is all one phase.

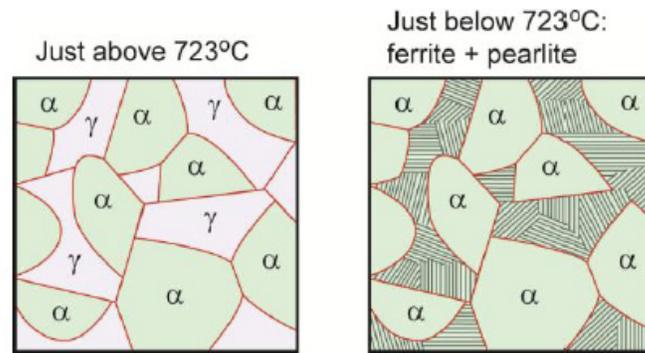


Figure P28: Schematic illustration of microstructure evolution in a 0.3wt% C hypo-eutectoid steel, from austenite to ferrite + pearlite

Iron carbide is a hard phase, and the pearlite structure is effective in obstructing dislocation motion (due to the plate-like structure). But ferrite itself has a relatively high intrinsic strength, with very high toughness. Carbon steels that have been slow-cooled (or *normalized*) to a ferrite and pearlite microstructure provide an excellent combination of strength and toughness, widely exploited for structural and mechanical applications. As in pure iron the transformation from austenite leads to a reduction in grain size, as each old grain nucleates more than one new grain. This is used commercially for grain refinement – an important heat treatment as it simultaneously enhances both yield strength and toughness.

Ferrite and pearlite microstructures are strong and tough – but we can do even better by *quenching and tempering* carbon steels. This heat treatment leads to the same phases, but in a different morphology, enhancing the strength without loss of toughness. We return to this in Part 8.

Exercises

E.21 An Al-10wt% Cu alloy was slow cooled and the length scales measured by various techniques in the final microstructures, as follows: primary grain size = 100μm; phase spacing in the eutectic = 1μm; precipitates within the primary grains 0.05μm. Identify the phases involved in each of these microstructural features, and explain the differences in length scale.

E.22 Pure iron cooled slowly contains 100% ferrite; the eutectoid composition contains 100% pearlite. Estimate the carbon content of the hypo-eutectoid steel shown below, and sketch the structure of a 0.2wt% carbon steel after slow cooling to room temperature.

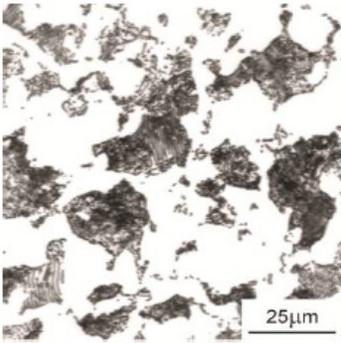


Figure E22: Optical micrograph of the ferrite-pearlite microstructure in a hypo-eutectoid carbon steel. (Image courtesy of ASM Micrograph Center, ASM International, 2005)

E.23 *Hyper-eutectoid* steels contain $> 0.8\text{wt}\% \text{C}$. A high carbon steel containing $1.0\text{wt}\% \text{C}$ is cooled slowly from 1000°C in the austenite field. Refer to the Fe-C phase diagram in Figure P25 to answer the following:

(i) At what temperature does a phase transformation begin, and what new phase then appears?

Why do you think this phase tends to nucleate and grow along the austenite grain boundaries?

(ii) What happens to the compositions of the phases on cooling to just above 723°C ?

(iii) What phase transformation takes place at 723°C ?

(iv) What are the final phases at room temperature, their compositions and proportions? Sketch the expected final microstructure.

Answers to Exercises, Part 7:

E.21 Al-10wt% Cu first forms primary grains of Al-rich solid, then a eutectic mixture of (Al) and CuAl_2 . The (Al) grains then become unstable and CuAl_2 precipitates form. The scale of the grains is largest, being determined by the spontaneous nucleation of (Al) in the liquid. The eutectic microstructure is finer-scale, since the temperature is now lower, atomic mobility is reduced, and the microstructural scale is strongly influenced by the kinetics of inter-diffusion of Al and Cu, enabling transformation into two phases of widely different Cu contents. The precipitation of CuAl_2 is a solid state process at lower temperature still, with the kinetics of nucleation dictating that large numbers of small precipitates form.

E.22 (a) Carbon content $\approx 0.4\text{wt}\%$: the structure is about 50% pearlite, so the carbon content is about 50% of $0.8\text{wt}\%$. To understand this, apply the lever rule *just above* the eutectoid temperature in the $\alpha+\gamma$ region: it is approximately 50% ferrite, 50% austenite. The pearlite all comes from the austenite at $0.8\text{ wt}\%$, so the ferrite:austenite ratio just above the eutectoid temperature is identical to the final ferrite:pearlite ratio. Similarly, $0.2\text{wt}\%$ C would give about $0.2/0.8 = 25\%$ pearlite at equilibrium, as shown schematically in Figure E22-23S(a).

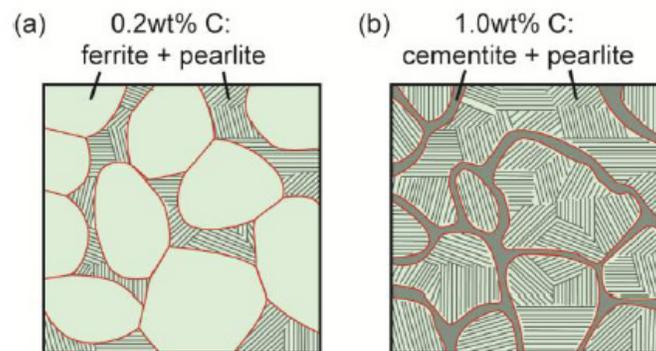


Figure E22-23S: schematic microstructures: (a) ferrite-pearlite in $0.2\text{wt}\%$ C steel;
(b) cementite-pearlite in $1.0\text{wt}\%$ C steel

E.23 (i) Transformation begins at 865°C , and the new phase to appear on the austenite grain boundaries is cementite, or iron carbide, Fe_3C . Cementite has a more complex crystal lattice, so it is easier to nucleate on the grain boundaries and to spread along them.

(ii) Carbon must diffuse out of the austenite to form the cementite, following the phase boundary down to the eutectoid composition. So just above the eutectoid temperature we have austenite containing $0.8\text{ wt}\%$ C and Fe_3C containing $6.7\text{wt}\%$ C.

(iii) At 723°C , the eutectoid reaction takes place – the austenite transforms to pearlite (two-phase mixture of ferrite and more cementite).

(iv) Final phases at room temperature: ferrite, $\approx 0\text{ wt}\%$ C; cementite, $6.7\text{wt}\%$ C.

Proportion of ferrite: $5.7/6.7 = 85\text{ wt}\%$; cementite: $1.0/6.7 = 15\%$.

The expected microstructure is shown in Figure E22-23S(b).

PART 8: Non-equilibrium solid-state phase changes

The transformations considered thus far assume that the alloy is able to remain at equilibrium during cooling – i.e. cooling is slow, and diffusion remains sufficiently rapid for phase fractions and compositions to adjust. In a couple of instances though, it has been noted that this may not be the case. The practical limitations of kinetic mechanisms operating at finite cooling rates intervene. For example, we noted in casting that solute gradients build up across grains (segregation). And precipitation reactions may not occur, due to barriers to nucleation of the second phase, leaving a metastable supersaturated solid solution.

In this section, a number of important heat treatments are explored. The common starting point in each case is to solutionize the alloy, dissolving the alloying additions in a high temperature single phase. Then by deliberately applying non-equilibrium cooling, different microstructural outcomes with enhanced properties can be achieved. Further details of the resulting properties are discussed in Chapter 19.

Non-heat-treatable aluminum alloys

The *wrought* aluminum alloys are those that are shaped by deformation processing, as opposed to the *casting* alloys, which are cast directly to shape. Both are sub-divided into non-heat-treatable, and heat-treatable, reflecting the fact that only some respond to heat treatments to modify their properties (particularly strength). Wrought Al alloys are all relatively dilute in alloying additions – all below the upper limit of solubility in aluminum.

Virtually all wrought aluminum alloys contain magnesium – this is actually the single biggest application of Mg, greater than the manufacture of products in Mg alloys. The non-heat-treatable wrought Al-Mg alloys and the closely related Al-Mg-Mn alloys are familiar from the aluminum beverage can, but also find widespread structural use, including ship-building (partly attributable to good corrosion resistance).

Figure P29(a) shows the Al-rich end of the Al-Mg phase diagram. It looks as though any alloy up to about 14wt% Mg solutionized in the single phase α -field should form precipitates of the complex Mg_5Al_8 compound on cooling. But here is an example in which kinetics dominates over thermodynamics. Figure P29(b) shows the corresponding TTT diagram for formation of this compound, for a typical alloy containing 6wt% Mg solutionized at 400°C. Long times are needed to start the phase transformation – the critical cooling rate is sufficiently low that a metastable Al-rich solid solution is easily retained at room temperature with a moderate quench. It is in this state that the alloys are used commercially, with cold deformation often used to strengthen the alloy further by work hardening.

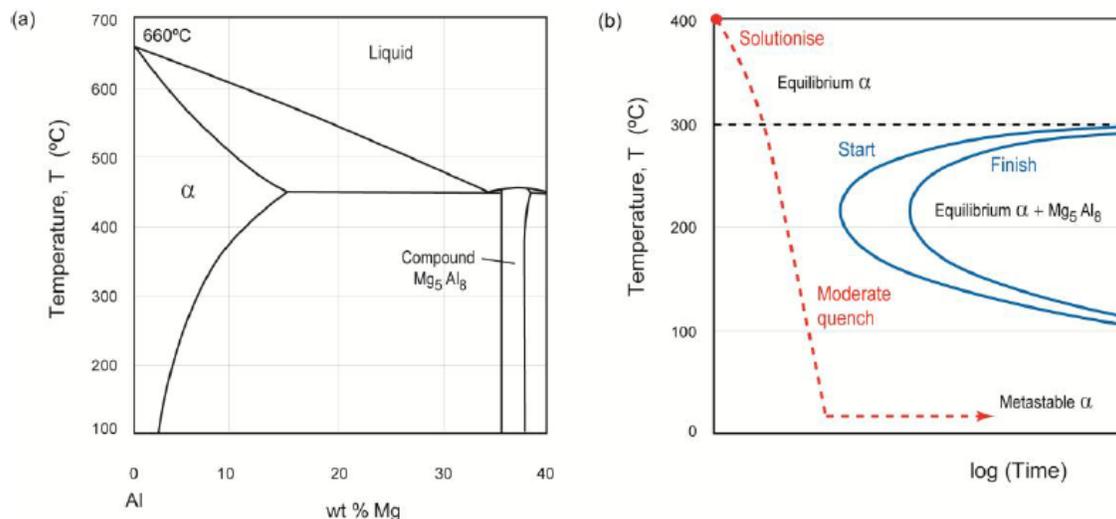


Figure P29: (a) Al-rich end of the Al-Mg phase diagram; (b) schematic TTT diagram for precipitation of equilibrium Mg_5Al_8 in an Al-6wt% Mg alloy.

Heat-treatable aluminum alloys

Commercial heat-treatable wrought aluminum alloys combine additions of magnesium with one or more of Si, Zn, Cu and other metallic elements. But the key behavior exploited in heat treatment is found in some binary systems, such as Al-Cu. Comparing Figure P29(a) for Al-Mg alloys with Figure P9 for Al-Cu alloys, the diagrams appear superficially the same for dilute alloys. But in Al-Cu alloys, cooling at moderate rates follows equilibrium – the compound $CuAl_2$ precipitates out in a matrix of (Al) (recall Figure P24). The difference is simply down to the greater ease of nucleation in this system – again, a technical detail beyond the scope of the phase diagram.

It was noted earlier that the $CuAl_2$ precipitates formed on slow cooling are actually rather far apart, from the perspective of interacting with dislocations, giving little strengthening. What we want is a much finer dispersion, i.e. many more nuclei forming, with diffusion distances to the nuclei being much shorter. This can be achieved by a two-step heat treatment: first by *quenching* to room temperature, at a cooling rate above the critical cooling rate for precipitation to occur, then by *aging* at an intermediate temperature. The quench “traps” the high temperature state as a metastable supersaturated solid solution at room temperature, from which we can then precipitate on a fine scale during aging.

As so often in metallurgy, this precipitation during aging is more complicated than expected. The quench achieves the desired result – a supersaturated solid solution of Cu in Al. But aging at temperatures between room temperature and about 200°C does *not* cause equilibrium $CuAl_2$ precipitates to form. Instead, metastable second phases form – the TTT diagram for Al-Cu shows further C-curves for these phases at low temperature, as shown in Figure P30(a).

This subtle difference in behavior could not be anticipated from the phase diagram at all, but gives us the high strength precipitation hardened alloys on which aerospace depends, as increasingly do other transportation systems (rail and road). During the aging treatment of Al-Cu after quenching, the yield strength evolves as shown in Figure P30(b). For *artificial aging* at temperatures above room temperature, the strength rises to a peak before falling to a value below the as-quenched value. The solid solution strength in the as-quenched state is replaced with precipitation hardening, and it is this which produces the peak strength. *Natural aging* takes place at room temperature, with the strength rising to a plateau value below the peak of the curve for artificial aging.

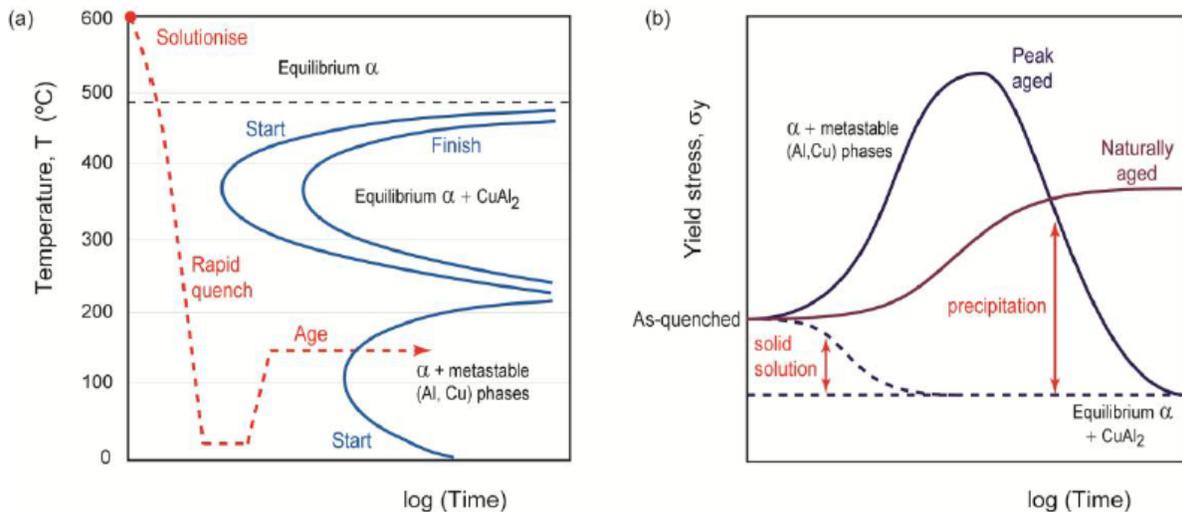


Figure P30: (a) TTT diagram for precipitation of equilibrium and metastable phases in dilute Al-Cu alloys; (b) the “aging curve”, showing how yield strength evolves with time.

The full detail of the precipitate evolution during aging need not concern us here (see *Further Reading* for more information). In fact a whole sequence of metastable second phases form, starting with clusters of pure Cu, and progressively re-nucleating and growing through various Al-Cu phases towards the equilibrium θ phase (CuAl_2). At the same time, the precipitates *coarsen* (i.e. their average size increases, while their number decreases), and the way they interact with dislocations changes. In combination this leads to the aging curve shown in Figure P30(b). Note that equilibrium is eventually achieved in the final “over-aged” condition, with coarse precipitates of CuAl_2 . The structure is then much as it would have been after slow cooling from the solutionizing temperature. It is clear from Figure P30(b) how important it is to develop the right metastable two-phase microstructure to achieve useful strength in these alloys.

Heat-treatment of carbon steels

The Al-Cu example highlighted the key characteristics required for effective precipitation hardening: (i) high solubility of alloying elements at high temperature (to enable an initially uniform distribution of solute); and (ii) low solubility at room temperature, with a two-phase region including a hard compound absorbing most of the alloying additions (to enable fine-scale hard precipitates to be formed). The Fe-C system shows exactly the same key characteristics. Figure P25 shows the high solubility for carbon in iron in the austenite condition, with very low solubility in ferrite, and the prospect of forming precipitates of iron carbide.

A typical medium carbon steel can therefore be “austenitized” (i.e. solutionized in the austenite field) at 850-900°C. We have seen that slow cooling in this case leads to the mixed ferrite-pearlite microstructure, in itself used extensively for its excellent strength and toughness. But we can do better still. Following the same reasoning as before, quenching at a rate above the critical cooling rate will trap the carbon in supersaturated solution. Reheating to temperatures around 500-600°C for an hour or two enables fine-scale precipitates of iron carbide to be formed: in steels this stage is known as *tempering*.

In general terms therefore, quenching and tempering carbon steels parallels age hardening of aluminum alloys. But there are important differences. Firstly, the phase that precipitates is in this case the equilibrium one – iron carbide, in a matrix of ferrite. But secondly, there is also the transformation from FCC iron to BCC iron when it is cooled from the solutionizing temperature (which was not an issue in aluminum, which remains FCC throughout).

Phase transformations usually require diffusion to enable the atoms to re-arrange into the new phases. But here we have an unusual phase transformation, in which the FCC iron lattice is able to transform during the quench, *without* diffusion. The resulting single phase is called *martensite*. It is metastable, and is a super-saturated solid solution of carbon in iron. The iron lattice wishes to form BCC ferrite, but this has very low solubility for carbon, whereas martensite contains the whole carbon content of the alloy. As a result, martensite forms with a somewhat distorted body-centered lattice (called “body-centered tetragonal”).

The transformation has a conventional driving force, as there is a difference in free energy, ΔG , between austenite and martensite. But the mechanism is quite distinct, as illustrated in Figure P31(a). Small regions at austenite grain boundaries shear to form nuclei of the new lattice, and these propagate very rapidly across the grains forming thin lens-shaped plates of martensite (Figure P31b). Figure P31(c) shows how this is achieved at the atomic scale purely by straining the FCC lattice – there is a simple geometric relationship between the atom sites in FCC and a body-centered structure. This non-diffusive phase change is known as a *displacive transformation*.

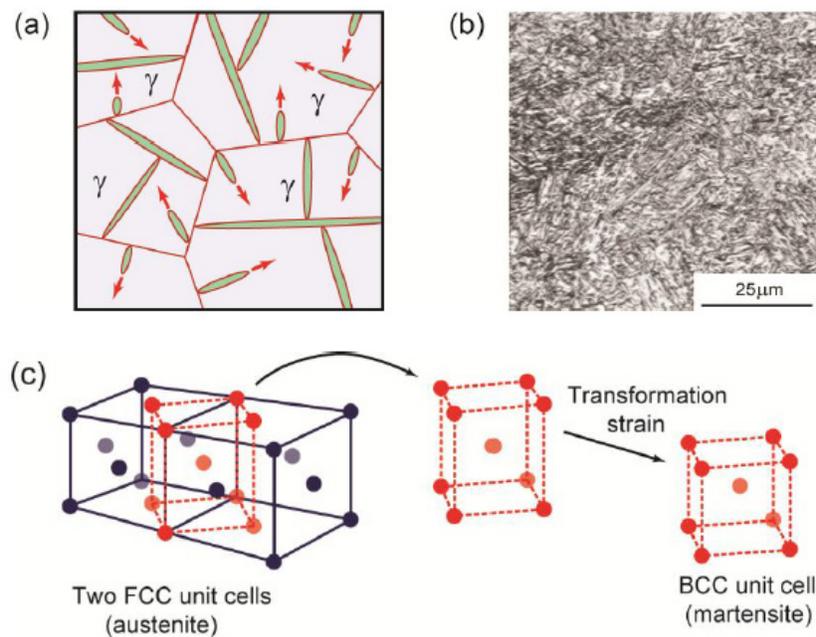


Figure P31: the martensite transformation: (a) nucleation from austenite grain boundaries; (b) micrograph of martensite (Image courtesy of ASM Micrograph Center, ASM International, 2005); (c) lattice relationship between FCC unit cells (blue) and the body-centered unit cell (red) which strains to form the distorted structure of martensite.

The martensite transformation in a given steel has a characteristic temperature at which the transformation starts, and a second (lower) temperature at which it goes to completion. Since diffusion is not involved, the extent of transformation is independent of time – the start and finish of the transformation are shown on TTT diagrams by horizontal lines at the martensite start and finish temperatures – see Figure P32(a).

Finally, what is the effect of quenching and tempering on properties? Since martensite contains far more carbon in solution than can normally be accommodated by BCC ferrite, the distorted lattice is resistant to dislocation motion and the hardness (and yield stress) is high. But as a result the microstructure is brittle, with a low fracture toughness similar to that of a ceramic. On tempering, fine precipitates of

Fe₃C nucleate and grow, removing the carbon from solution and giving precipitation strength instead. The resulting yield strength is below that of martensite – the yield stress evolves with tempering time as shown in Figure P32(b). But tempering restores the fracture toughness to acceptable levels, comparable to that of the normalized ferrite-pearlite microstructure. The net effect is a yield stress of order 2-3 times greater in the tempered martensite.

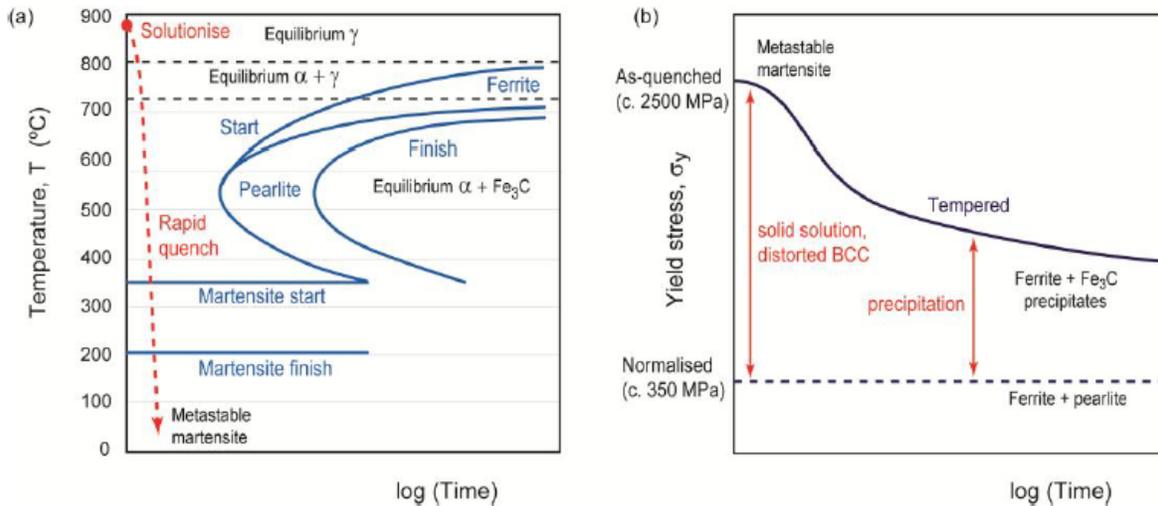


Figure P32: (a) appearance of martensite start and finish on a TTT diagram; (b) evolution of yield stress during tempering of carbon steels after quenching.

This outcome in terms of properties explains the widespread use of the quench-and-temper treatment for tools and machinery. But this heat treatment has some practical consequences in manufacturing steel components. Quenching red-hot steel into cold water or oil induces thermal stresses, which may result in quench cracking, due to the inherent brittleness of the martensite. Furthermore, there is a limit to how fast the center of a component can be made to cool, due to the timescale of heat conduction across the section – the center cooling rate falls as the size of component increases. There will therefore be a limiting component size which can be quenched at a rate above the critical cooling rate for the steel. For plain carbon steels (Fe-C alloys), the critical cooling rate is high – only small components can form martensite throughout the whole section (and thereby be tempered afterwards). The solution to this problem turns out to be more alloying. Additions of a few wt% of elements such as Ni, Cr and Mo significantly retard the diffusional transformations from austenite to ferrite and pearlite, shifting the C-curves on the TTT diagram to the right. Martensite can then form at a greatly reduced cooling rate, so it can be formed throughout a larger cross-section prior to tempering (and with lower thermal stress). The ability of a steel to form martensite on quenching is known as its *hardenability*. This is one of the many reasons for producing *alloy steels*.

So the lesson of heat treatment of steels is again that the phase diagram points the way to a promising microstructure (due to high and low carbon solubility in iron at different temperatures) but the detailed behavior is complicated. It also illustrates that phase transformations can be further manipulated by alloying – steels are prime examples of our mantra: composition + processing → microstructure + properties.

Further reading

Ashby, M.F. and Jones, D.R.H. (2005) Engineering Materials II, 3rd edition. ISBN0-7506-6381-2 (Popular treatment of material classes, and how processing affects microstructure and properties.)

ASM Handbook Series (1971–2004) Volume 4, Heat Treatment; Volume 5, Surface Engineering; Volume 6, Welding, Brazing and Soldering; Volume 7, Powder Metal Technologies; Volume 14, Forming and Forging; Volume 15, Casting; and Volume 16, Machining; ASM International, Metals Park, OH, USA. (A comprehensive set of handbooks on processing, occasionally updated, and now available online at www.asminternational.org/hbk/index.jsp.)

MATTER - www.matter.org.uk. (Introduction to phase diagrams, and many other topics). Specific coverage of steels [www.matter.org.uk/steelmatter] and aluminum alloys [www.aluminium.org.uk].

Final Exercises

E.24 The figure below shows the Ti-Al phase diagram (important for the standard commercial alloy Ti-6% Al-4% V).

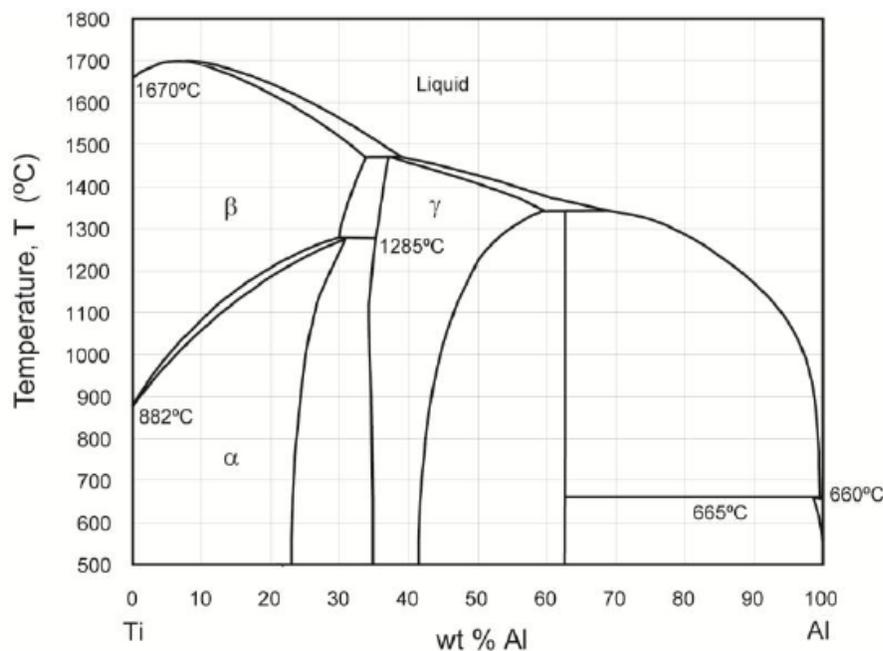


Figure E24: titanium-aluminum Ti-Al phase diagram

- Shade all single-phase fields.
- Ring the three peritectic points, and one peritectoid point.
- One intermetallic compound can clearly be identified – what is its formula (atomic weights of Ti and Al are 47.90 and 26.98 respectively)?
- One single phase field spans a wide temperature range with a moderate spread of composition, and with one edge of the field being approximately a vertical line. Identify this limiting composition in wt%, and assess whether the single phase may be considered to be a solid solution based on an intermetallic compound at this composition.
- At what temperature does a Ti-6wt% Al alloy start to melt?
- Over what temperature range does it change from α (HCP) to β (BCC)?

E.25 By analogy with the definitions for eutectic and eutectoid reactions, and consideration of the phase diagrams in Part 2, define:

- (i) a peritectic reaction.
- (ii) a peritectoid reaction.

E.26 The figure below shows the copper-antimony Cu-Sb phase diagram

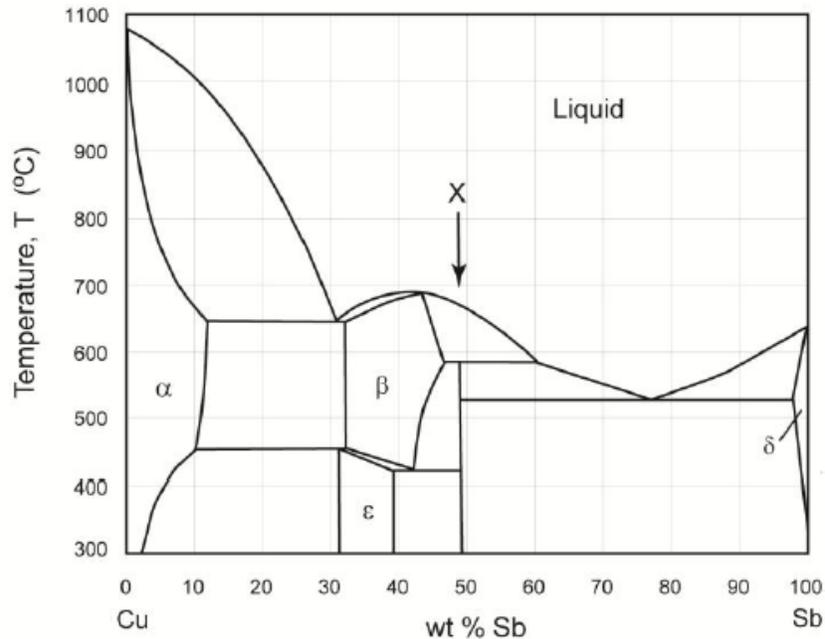


Figure E26: copper-antimony Cu-Sb phase diagram

(a) Find the chemical formula for the compound marked X (atomic weights of Cu and Sb are 63.54 and 121.75 respectively).

(b) The Cu-Sb system contains 2 eutectics, 1 eutectoid, 1 peritectic and 1 peritectoid. Mark them all on the figure, write down the temperature and composition of each point, and identify the phases involved in each reaction, on cooling.

(c) An alloy containing 95 wt% Sb is cooled slowly to room temperature from the melt. Describe the phase changes that occur during cooling, using schematic sketches of the microstructure at key temperatures to illustrate your answer.

(d) Sketch a temperature-time curve for the 95 wt% Sb alloy over the range 650 to 450°C and account for the shape of the curve.

E.27 Figure E27 shows the aluminum-silver (Al-Ag) phase diagram.

(a) An entrepreneur sees an opportunity for casting decorative artifacts in “budget silver”, using an Al-Ag alloy. Suggest suitable compositions, explaining your reasoning.

(b) Al-Ag is known to exhibit age hardening, as illustrated earlier for Al-Cu. Identify suitable compositions for wrought heat-treatable Al-Ag alloys, and propose a possible heat treatment sequence to achieve high strength.

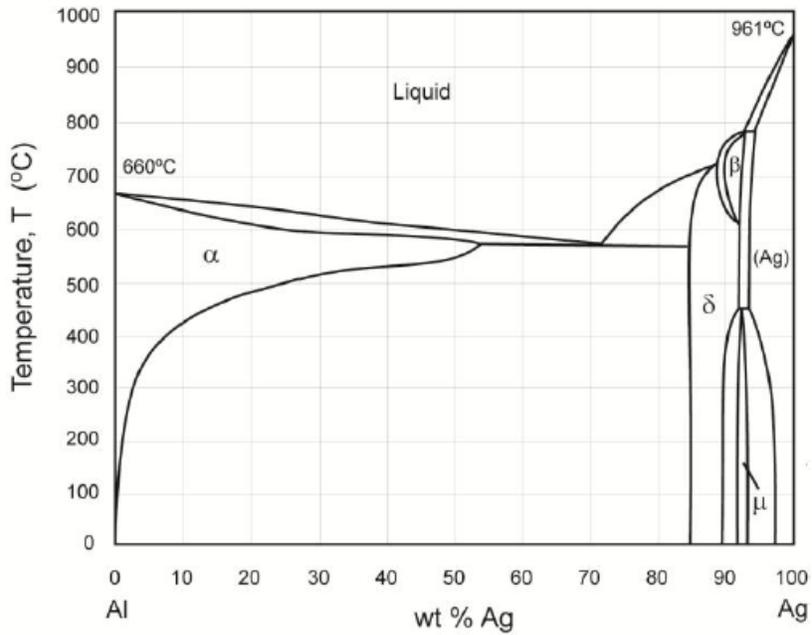


Figure E27: aluminum-silver Al-Ag phase diagram

Answers to Final Exercises:
E.24

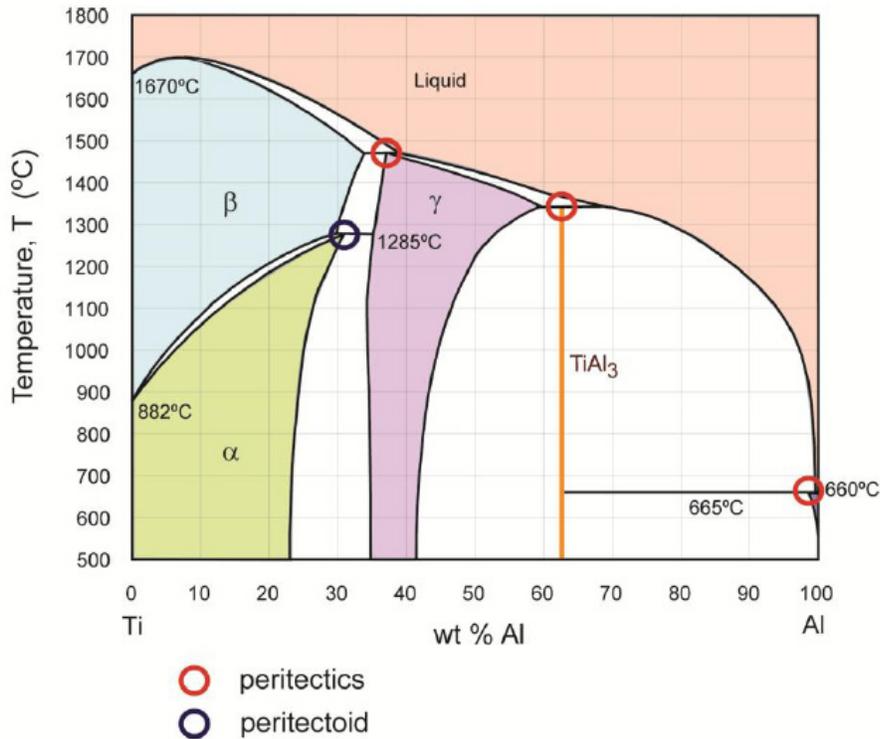


Figure E24S: Ti-Al phase diagram

(a,b) See Figure E24S.

(c) Compound at approx. 62wt% Al: call it $TiAl_x$.

$$wt\% \text{ Al} = 0.62 = \frac{26.98x}{47.9 + 26.98x}$$

Solving for x: $x(1 - 0.62) \cdot 26.98 = 0.62 \cdot 47.9$, hence $x = 2.9$. Compound therefore $TiAl_3$.

(d) The γ phase has the characteristics described. One side of this field is approximately vertical, at composition around 35wt% Al. Assume underlying compound is $TiAl_\gamma$.

$$\text{wt\% Al} = 0.35 = \frac{26.98\gamma}{(47.9+26.98\gamma)}$$

Solving for γ : $\gamma(1-0.35)*26.98 = 0.35*47.9$, hence $\gamma = 0.96$. Single phase therefore compound $TiAl$, with excess Al forming a solid solution.

(e) 1680°C

(f) 980°C – 1010°C

E.25 (i) A peritectic reaction is a three-phase reaction by which, on cooling, two phases (one of them liquid) react to give a single new solid phase:



(ii) A peritectoid reaction is a three-phase reaction by which, on cooling, two solid phases react to give a single new solid phase:



E.26 (a) Compound at approx. 48wt% Sb: call it $CuSb_x$.

$$\text{wt\% Sb} = 0.48 = \frac{121.75x}{(63.54+121.75x)}$$

Solving for x : $x(1-0.48)*121.75 = 0.48*63.54$, hence $x = 0.48$. Compound therefore Cu_2Sb .

(b) See Figure E26S(b).

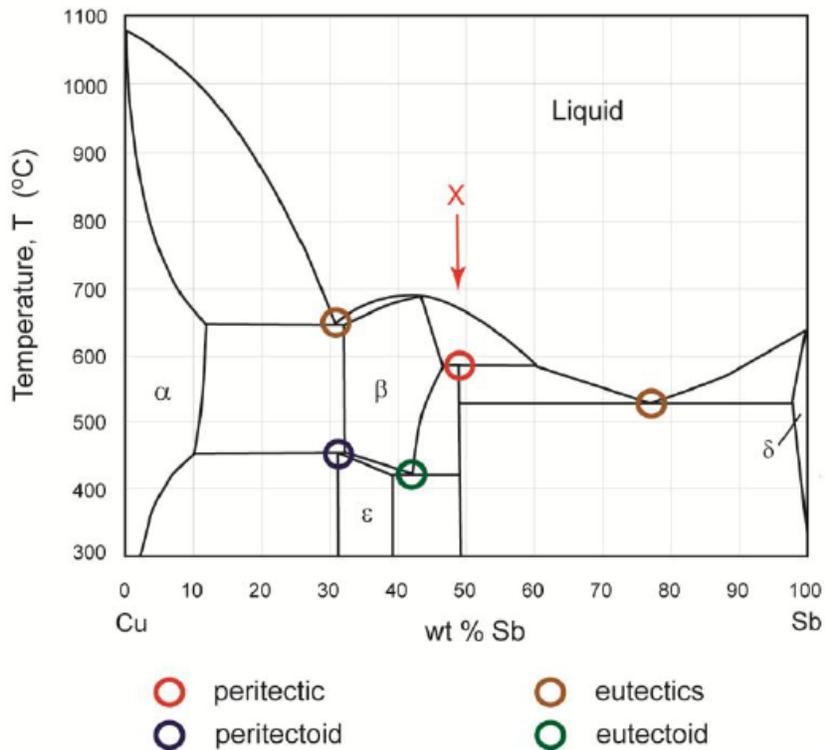


Figure E26S(b): Cu-Sb phase diagram

Eutectic 1: 650°C, 31wt% Sb: $\text{Liquid} \rightarrow \alpha + \beta$

Eutectic 2: 525°C, 77wt% Sb: $\text{Liquid} \rightarrow Cu_2Sb + \beta$

Eutectoid: 420°C, 42wt% Sb: $\beta \rightarrow \epsilon + Cu_2Sb$

Peritectic: 590°C, 48wt% Sb: $\text{Liquid} \rightarrow \alpha + \beta$

Peritectoid: 450°C, 32wt% Sb: $\text{Liquid} \rightarrow \alpha + \beta$

(c) 95wt% Sb on cooling – see Figure E26S(c):

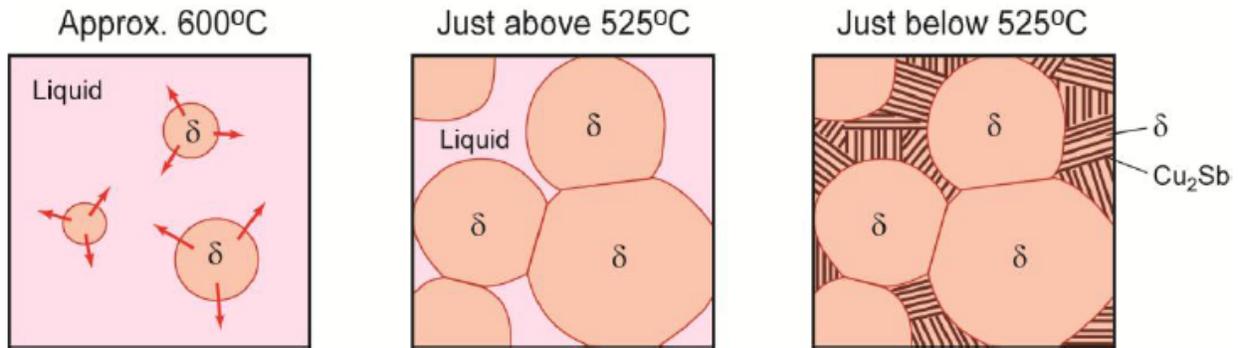


Figure E26S(c): microstructure evolution on solidification of Cu-95wt% Sb alloy

- At 610°C, solidification starts with nucleation of primary δ (Sb-rich solid solution).
- Just before eutectic temperature (525°C), proportion of δ approx. $(95-77)/(98-77) = 86\%$ (by weight), and 14% remaining liquid at the eutectic composition. At this proportion, the solid grains will have impinged, leaving isolated pockets of liquid.
- On cooling through the eutectic temperature, the liquid zones form two-phase $\text{Cu}_2\text{Sb} + \delta$ with the proportion of Cu_2Sb being approximately $(98-77)/(98-48) = 42\%$ (by weight) – the phases are fairly balanced, as the eutectic V is towards the center of its tie-line.

On further cooling, the δ phase purifies towards pure Sb, releasing Cu. In the eutectic, the phase proportions can adjust to accommodate this. In the primary δ grains, Cu_2Sb would need to precipitate throughout the grains to absorb the excess Cu – even though thermodynamics dictates that this should happen, it will depend strongly on the kinetics of nucleation as to whether it does occur in practice.

(d) Cooling curve for solidification of 95wt% Sb:

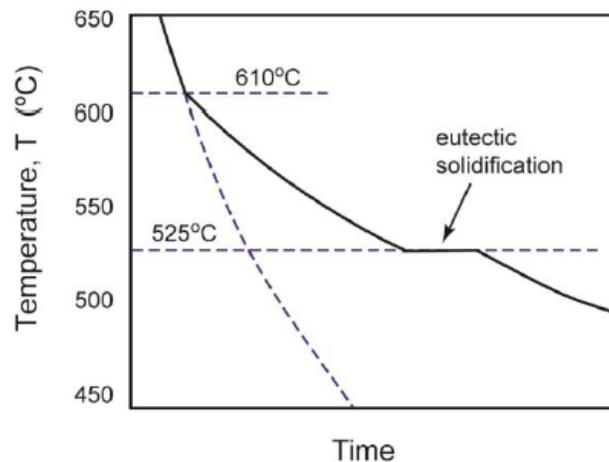


Figure E26S(d): cooling curve for solidification of Cu-95wt% Sb alloy

From 610°C to 525°C, the slope of the cooling curve is reduced, as latent heat is released progressively. Then arrest of cooling occurs at 525°C, the eutectic temperature, as the remaining liquid solidifies at that temperature. The duration of the arrest is shorter, as the proportion of eutectic is only 14%.

E.27 (a) Casting alloys are usually around the eutectic composition – Al-72wt% Ag in this system. This is in order to exploit the minimum temperature for full melting at a eutectic, and the reasonable properties of a two-phase eutectic microstructure. As the slope of the liquidus (towards Al) is low, it would be possible to reduce the Ag content considerably (and thus the cost!) without a significant increase in casting temperature. For example Al-60wt% Ag would have a mixed structure of primary Al and eutectic. Since Al-Ag is easily heat treated, it may be preferable to use less silver still and cast a dilute alloy (e.g. Al-10wt% Ag), with a subsequent solutionizing and aging treatment – see (b) below.

(b) Aluminum dissolves up to 55.6wt% of Ag. Any alloy up to this concentration could be solutionized at 560°C. Lower concentrations would be a lot cheaper, and by analogy with Al-Cu it may be sufficient to use a dilute composition such as 5wt% Ag to achieve effective hardening. This alloy can also be solutionized at a lower temperature (400°C), before quenching to room temperature, and aging in the 2-phase field (at 100-200°C). Metastable precipitates are expected, as in Al-Cu, giving an aging curve.

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