Introduction and synopsis

Phases and phase transformations are more familiar in everyday life than you may realise. 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 thus causing a phase change. Bubbles rising in a glass of beer signify gases dissolved in the beer that are forming a separate phase, whereas in a pan of boiling water the bubbles of steam are formed by the water itself as it changes phase from liquid to vapour.

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 and generate 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 *Guided Learning 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 that 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 for 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! Further exercises (without solutions) are provided for practice at the end of the Unit.

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 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 diagram.

The Unit fits best with Chapter 19 in two instalments: Parts 1–4 dealing with phase diagrams, and 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*.

Examples are:

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 (Al_2O_3).

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

Components are given capital letters: A, B, C, or the element/compound symbols Cu, Zn, C, MgO. So in *brass* the main components are Cu and Zn; in *carbon steel* they are Fe and C; and in *spinel* they are MgO and Al_2O_3.

DEF. A *binary alloy* contains two components, a *ternary alloy* contains three, a *quaternary alloy* four, and so on.

Composition Alloys are defined by stating the components and their compositions in weight or atom %.

DEF. The composition in *weight* % of component A:

$$C_A = \frac{\text{Weight of component } A}{\sum \text{Weights of components}} \times 100$$

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

$$X_A = \frac{\text{Number of atoms (or mols) of component } A}{\sum \text{Number of atoms (or mols) of all components}} \times 100$$

To convert between weight and mols:

$$(\text{Weight in grams})/(\text{Atomic or molecular wt in grams/mol}) = \text{Number of mols}$$

$$(\text{Number of mols})/(\text{Atomic or molecular wt in grams/mol}) = \text{Weight in grams (g)}$$

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 single solid solution
- Two separate solid solutions
- A chemical compound with a separate 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.

A region of a material that 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 many 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 make up a single *phase*.

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

(a) phases present;
(b) weight fraction of each phase;
(c) 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 19.3. The key parameter for a given composition of temperature T and pressure p is *Gibbs free energy*, G, defined as (equation (19.1)):

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

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 the state having 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 earlier, 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. Maps with these state variables as axes are called *phase diagrams* – for binary alloys they are two-dimensional.

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

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

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 Figure GL2.1(a). Similarly, liquid changes to gas or vapour at a unique (higher) temperature, the boiling point. In practical phase diagrams, boiling is of little interest, so the diagram usually is limited to liquid and solid states.

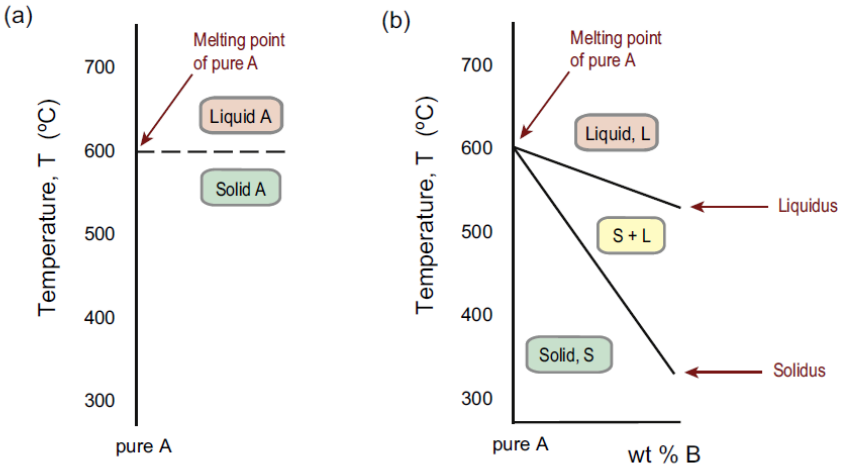


Figure GL2.1 (a) One-dimensional phase diagram for a pure substance, a temperature scale showing the phase boundary between solid and liquid – the melting point; (b) the A-rich end of a binary A–B phase diagram, illustrating partition of the melting point between solidus and liquidus boundaries.

Now if we consider the binary A–B system and add a second axis for composition, the behaviour illustrated in Figure GL2.1(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 next.

DEF. The phase boundary that 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*.

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 GL2.2, 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. Because 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.

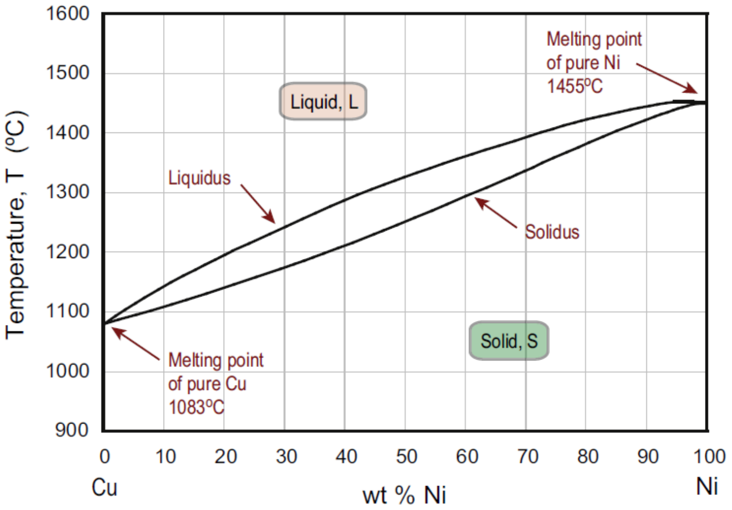


Figure GL2.2 Isomorphous phase diagram for the Cu–Ni system.

It turns out that in the solid state this behaviour 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 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, solid sugar. This too is a saturated solution, because the sugar has absorbed as much tea as it can. This is characteristic of mixtures of two equilibrium phases, both of which are solutions – both 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 GL2.3. The boundaries between the single- and two-phase regions are known as *solvus boundaries*.

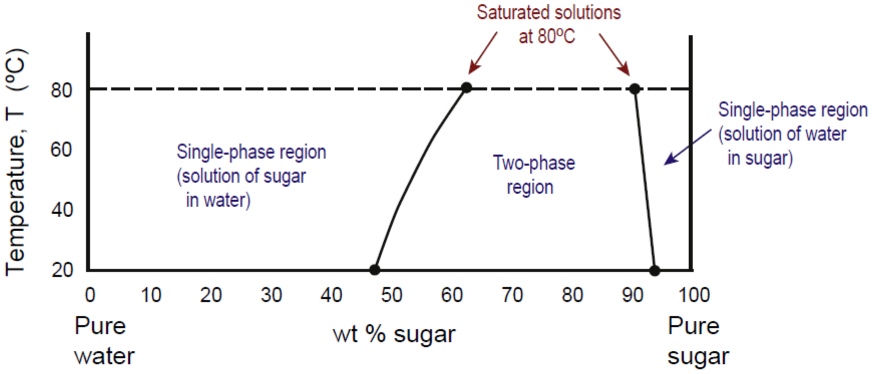


Figure GL2.3 Schematic phase diagram for sugar and tea (water) – the saturation level of both solutions increases with temperature.

What happens at a given temperature and composition is determined by the thermodynamics of mixing sugar and water. Minimising 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 GL2.3 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 favour due to environmental health concerns). Figure GL2.4 shows a partially complete Pb–Sn phase diagram. The lower part replicates the sugar-tea behaviour; the solubility of Pb in Sn (and of Sn in Pb) increases with temperature. Note that the solubilities of these elements in one another are low, especially Pb in Sn on the right of the diagram. The upper part of the diagram shows the partition behaviour from the melting points of the pure elements, as in Figure GL2.1(b).

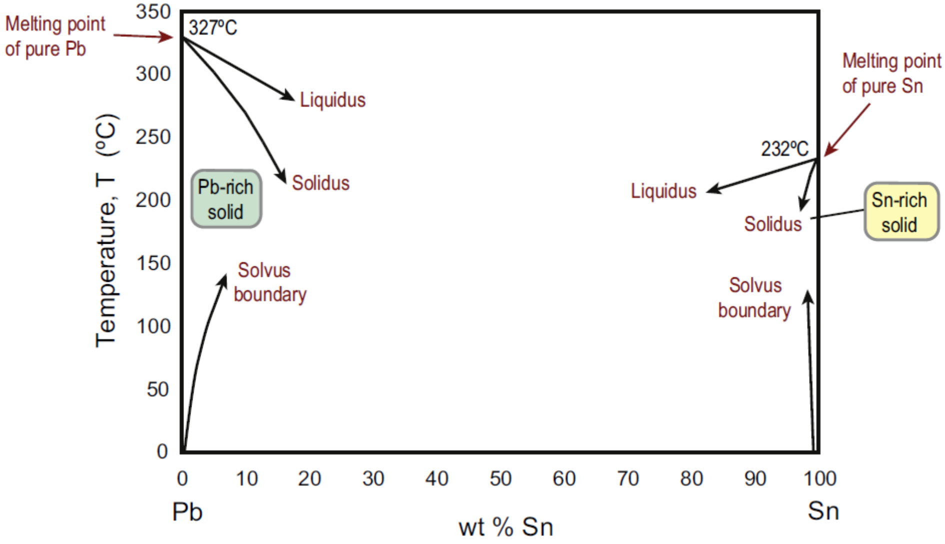


Figure GL2.4 Partial phase diagram for the Pb–Sn system, showing the limiting behaviour at high and low temperatures.

To complete the diagram, first consider where the falling solidus boundaries meet the rising solvus boundaries. Figure GL2.4 suggests that the points where they intersect will be the points of maximum solubility (highest saturation) in the single-phase solids. This closes the regions or *fields* representing single-phase solid solutions. For good thermodynamic reasons, which will not be elaborated here, peak saturation of Sn in Pb occurs at the same temperature as that for Pb in 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, with a horizontal boundary linking the two points of maximum solubility as shown in Figure GL2.5(a), closing the two-phase field (Pb) + (Sn). Note the nomenclature adopted: (Pb) for a Pb-rich single solid phase and (Sn) for an Sn-rich single solid phase.

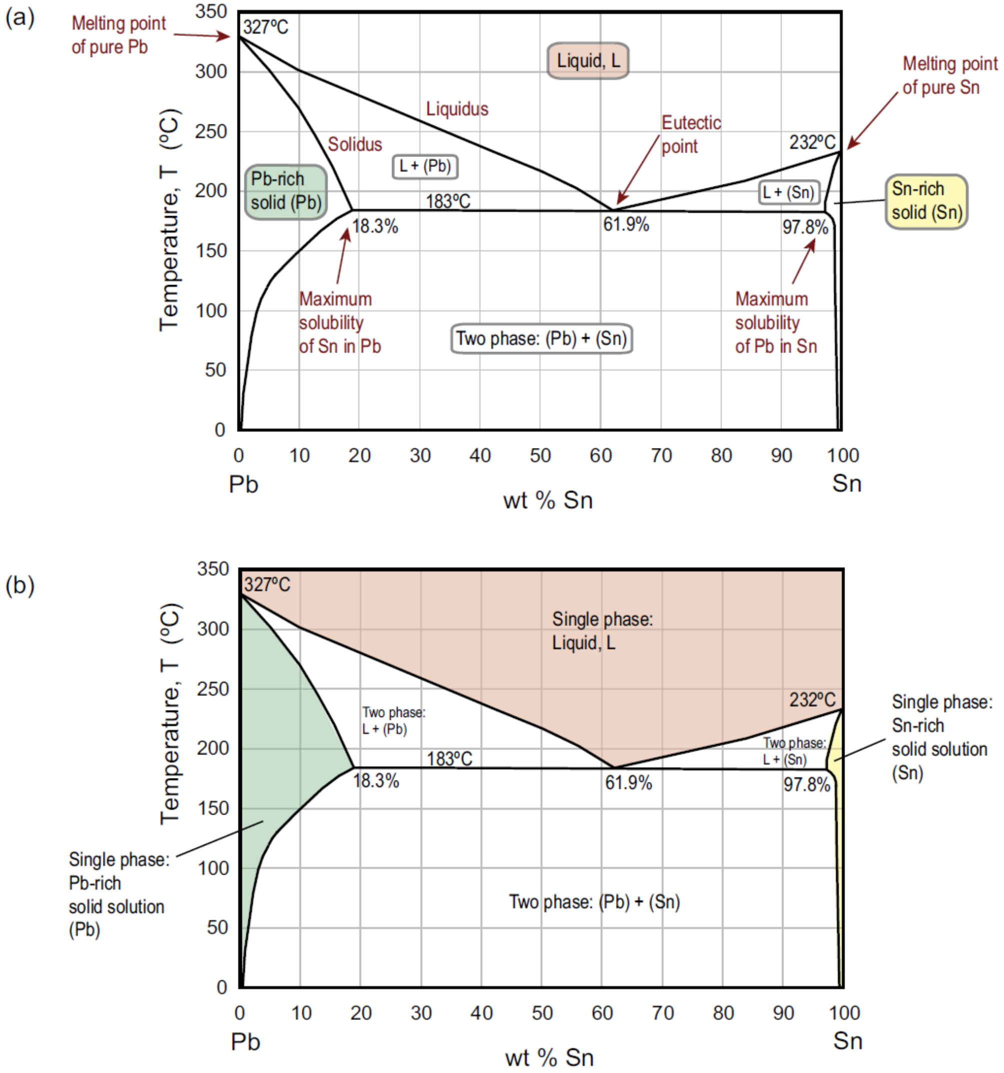


Figure GL2.5 The completed phase diagram for the Pb–Sn system, showing (a) the eutectic point closing the liquid field; (b) the single-phase fields (shaded) separated by two-phase fields.

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' – see Figure GL2.5(a). This point on the diagram is important and is known as a *eutectic point*. At this special temperature and composition, the alloy can change from 100% liquid to 100% two-phase solid at a fixed temperature. This also closes the two (liquid + solid) regions above the horizontal line through the eutectic. The single-phase fields are highlighted on the phase diagram in Figure GL2.5(b).

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

For the Pb–Sn system the eutectic point is at the composition $C_{Sn} = 61.9$ wt% and temperature $T = 183°C$. Eutectics will be discussed again later in relation to the microstructures that 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, casting, brazing, and soldering alloys are often eutectic or near-eutectic in composition.

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 labelled, either with the notation in Figure GL2.5, 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 the phase boundaries takes us from a single-phase field to a two-phase field (and vice versa) – see Figure GL2.5(b). In 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 GL2.6).

At a constitution point in a single-phase region, the *phase composition* is simply the composition of the alloy itself (e.g. point A in Figure GL2.6). 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 (e.g. point B in Figure GL2.6). 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 GL2.6. Constitution point A (temperature 300°C, alloy composition Pb-30 wt% Sn) lies in the single-phase liquid field; the

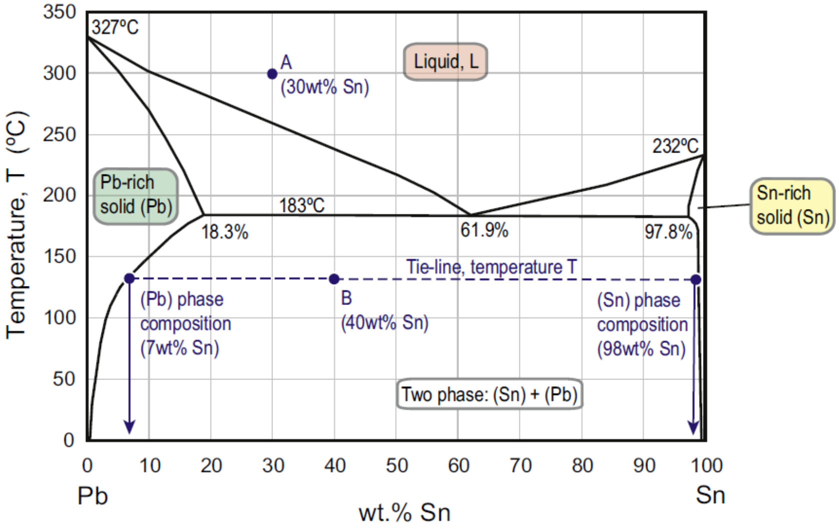


Figure GL2.6 Phase diagram for the Pb–Sn system, illustrating constitution points in single and two-phase fields and the tie-line defining the phases and compositions in the two-phase field.

phase composition is also Pb-30 wt% Sn. Constitution point B (temperature 130°C, alloy composition Pb-40 wt% 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-7 wt% Sn and Pb-98 wt% Sn, respectively.

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 W are fixed by the requirement that matter is conserved – the derivation is given as an exercise later. Consider Pb-20 wt% Sn at 250°C in Figure GL2.8, 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:

$$\textit{Pb-rich solid} \text{ with } C_{Sn}^{SOL} = 12 \text{ wt\%; } \textit{liquid} \text{ with } C_{Sn}^{LIQ} = 34 \text{ wt\%}$$

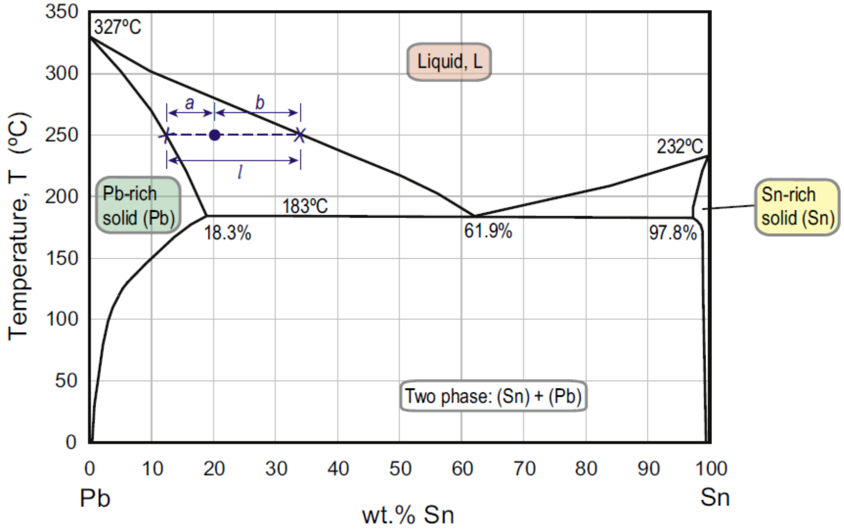


Figure GL2.8 Phase diagram for the Pb–Sn system, illustrating the lever rule for finding the weight fractions of the phases in a two-phase field.

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

$$\ell = C_{Sn}^{LIQ} - C_{Sn}^{SOL} = 34 - 12 = 22\%$$

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

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

The weight fractions of liquid and solid in the alloy are $W^{LIQ} = a/\ell$ and $W^{SOL} = b/\ell$. 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 that to the greater weight (for moment equilibrium).

Note the following:

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

To summarise: 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 previous example. 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.

Intermediate phases Many systems show *intermediate phases*, compounds that 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 a specific lattice of lower free energy than, say, a mixture of two phases. Example lattices are given in *Guided Learning Unit 1: Simple ideas of crystallography*.

The atomic % of components in a compound is called its *stoichiometry*. Compounds are written in the form noted earlier, 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 $y/(x + y)$, for example 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 (an example follows).

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 liquid field for compositions on either side often shows 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 GL2.9(a) shows the unusual (and very untypical) silver–strontium phase diagram (notice the *at% scale*). This is not exactly a well-known engineering alloy, but illustrates the 'ideal' behaviour of compounds on phase diagrams. It has four intermetallic compounds (the vertical lines), and looks like five separate phase diagrams back-to-back: the Ag–Ag_5Sr diagram, the Ag_5Sr–Ag_5Sr_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 solid 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 fundamental thermodynamics. Traversing a diagram at constant temperature must show one-phase, 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 between the two-phase fields; it is one of the compounds – but the field has essentially collapsed to a single line.

A more typical example with engineering significance is illustrated in Figure GL2.9(b), 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 33 *at%* 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 33 wt% 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 overlooked 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 a solid solution. But there is no rigorous definition as to how much spread in composition is allowed before it is no longer considered a compound.

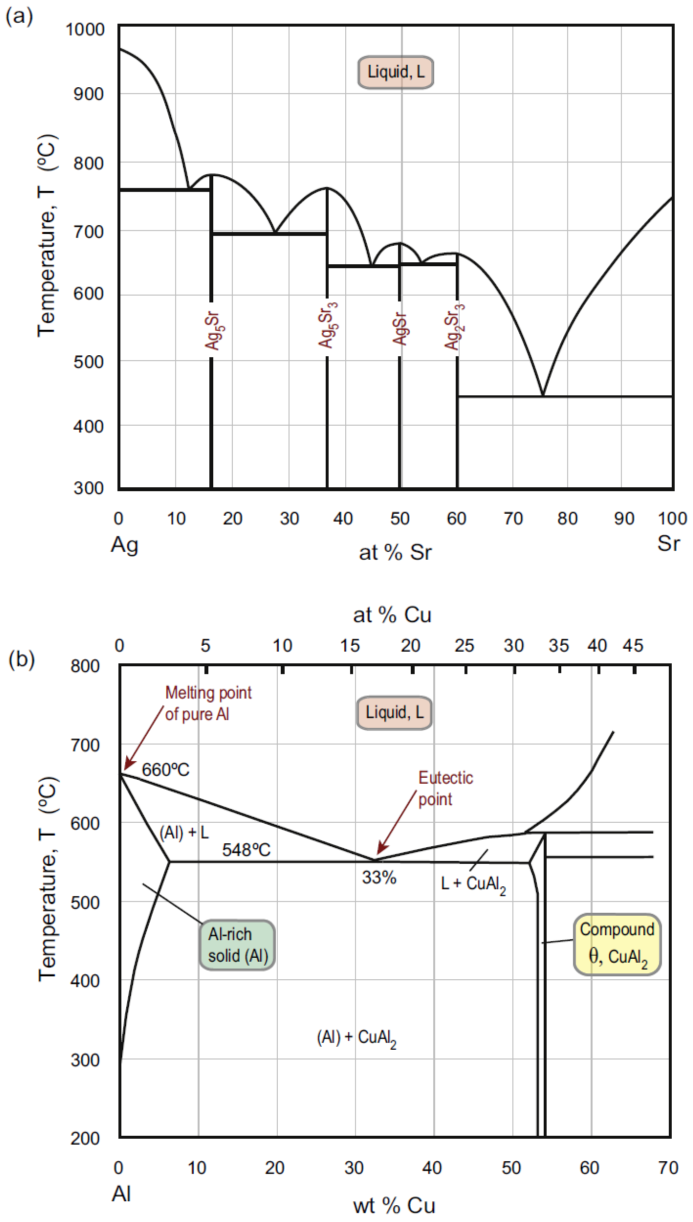


Figure GL2.9 Phase diagrams showing intermediate compounds: (a) the silver–strontium Ag–Sr system; (b) part of the aluminium–copper Al–Cu system.

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 body-centred cubic (BCC, as defined in *Guided Learning Unit 1*) lattice. On heating, pure iron changes to *austenite* (or γ-iron) at 910°C and switches to a face-centred 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 *Guided Learning 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 GL2.13 shows the iron–carbon diagram, up to 7 wt% carbon. Just below this upper limit lies the compound *iron carbide* Fe_3C (also given the name *cementite*) with 25 at% carbon. This part of the Fe–C system covers the main carbon steels and cast irons, as indicated. This diagram is more complicated than those shown previously and needs a bit of breaking down. Figure GL2.14 shows expanded extracts to clarify the diagram.

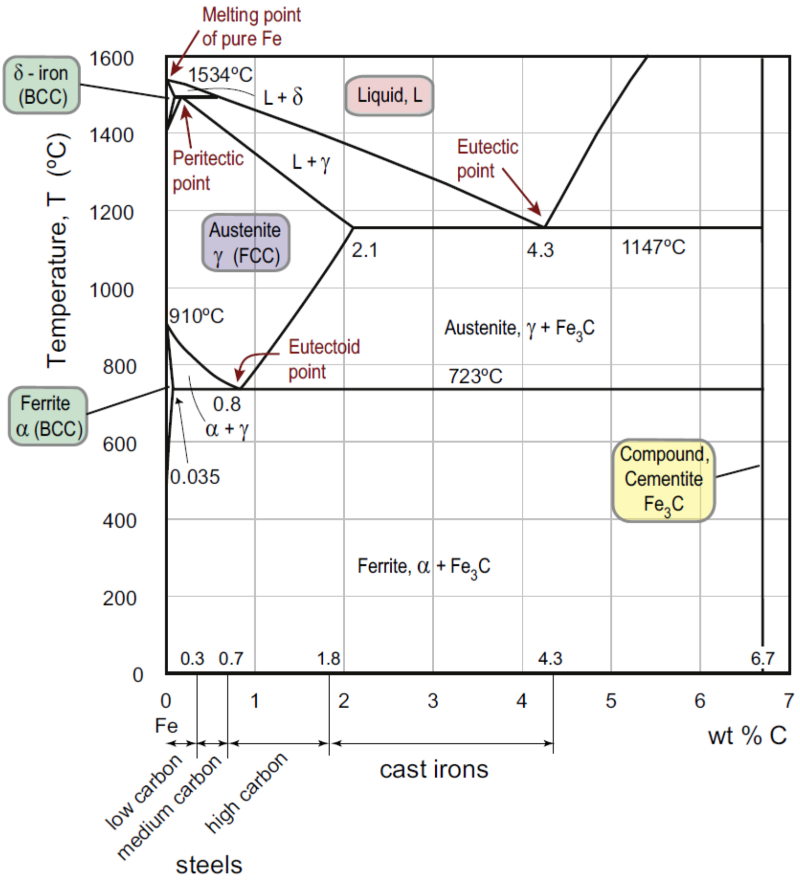


Figure GL2.13 The iron–carbon phase diagram up to 7 wt% carbon, the region covering carbon steels and cast irons.

First consider the picture below 1000°C, up to 2.0 wt% carbon (Figure GL2.14(c)). 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 behaviour seen below the melting point of a pure element, with two phase boundaries falling from this temperature and a two-phase region 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 0.8 wt% C.

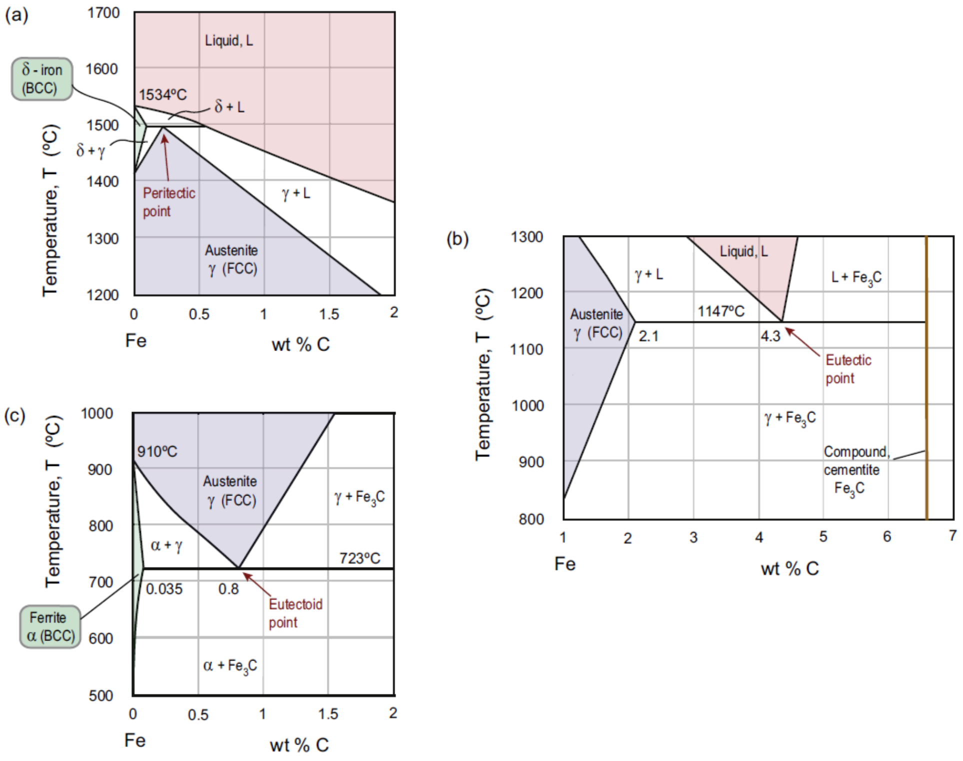


Figure GL2.14 Expanded views of parts of the iron–carbon phase diagram: (a) high temperature and low wt% C: the peritectic point; (b) high temperature and high wt% C: the eutectic point; (c) low temperature and low wt% C: the eutectoid point.

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 GL2.14(b) 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 GL2.14(a) 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; that is, 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 summarise 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 with 6.7 wt% C, at the right-hand edge of the diagram.

The system has a eutectic point at 4.3 wt% C, a eutectoid point at 0.8 wt% C, and a peritectic point at 0.2 wt% 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 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 1–4 wt% C (i.e. approaching the eutectic composition). In this case carbon can form as an equilibrium phase in the microstructure.

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:

- *eu-* means a normal 'V' meeting a horizontal line, whereas *peri–* means an inverted 'V' meeting a horizontal line.
- *-tectic* means a liquid phase is involved, whereas *-tectoid* means all phases are solid.

Figure GL2.16 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.

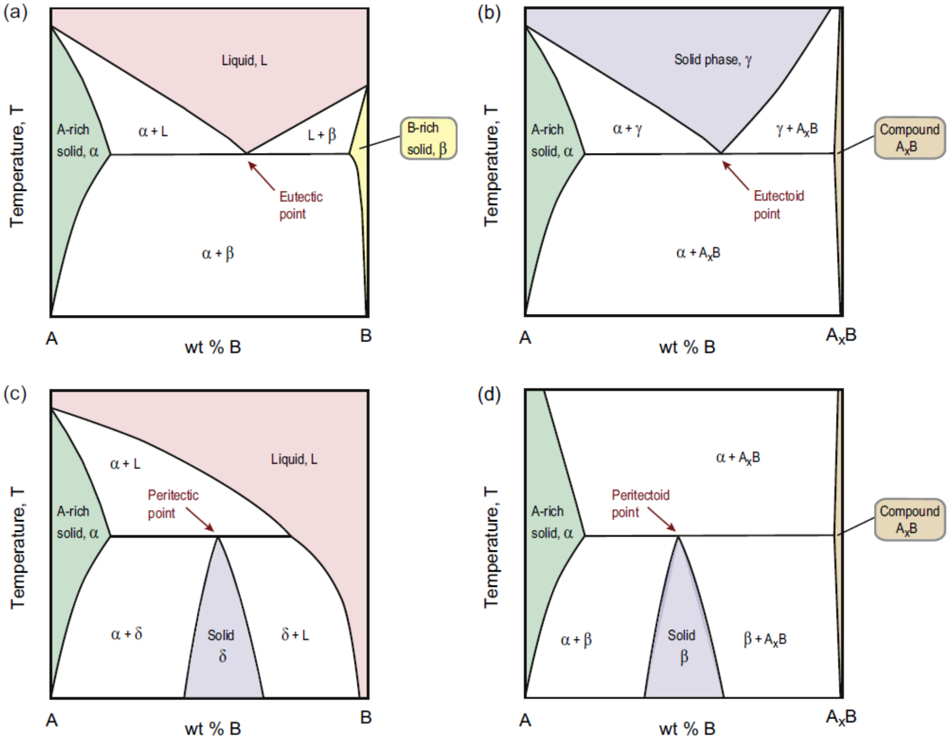


Figure GL2.16 Schematic views of: (a) eutectic point; (b) eutectoid point; (c) peritectic point; (d) peritectoid point.

Compared with 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.

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; for example, 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 GL2.17 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.

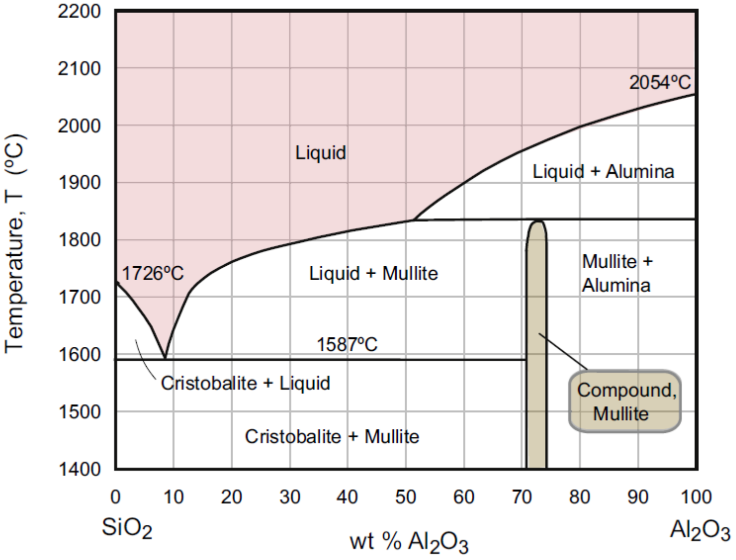


Figure GL2.17 Phase diagram for the binary ceramic silica-alumina (SiO_2–Al_2O_3) system.

Latent heat release on solidification Figure GL2.23(a) 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 significant 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*: vapour-to-liquid at the boiling point, and liquid-to-solid at the melting point. The arrest points on cooling are due to the release of the *latent heat* (of vapourization and melting, respectively). On heating the reverse occurs – an arrest in the temperature rise while heat is absorbed to melt or boil the material.

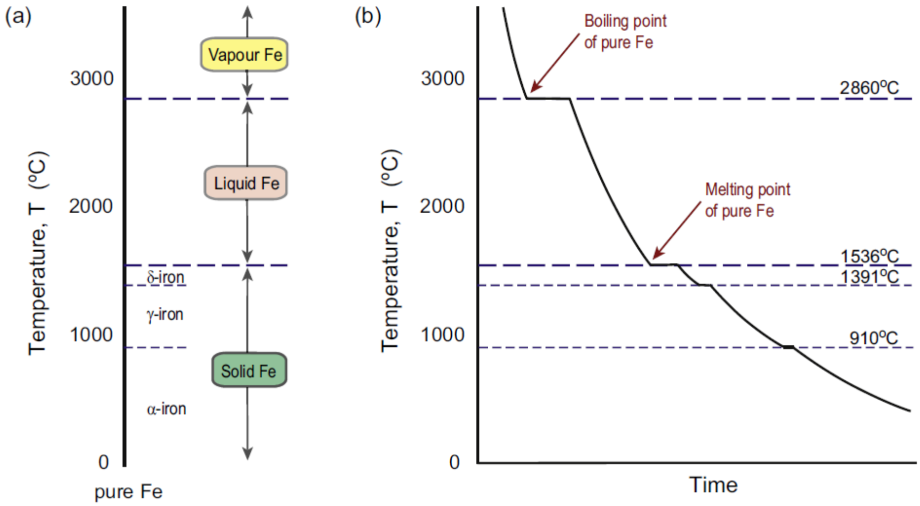


Figure GL2.23 (a) one-dimensional phase diagram for pure iron; (b) corresponding cooling curve for condensing then solidifying iron from vapour to liquid to solid.

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 GL2.23(b). The mechanisms of these solid-state changes are considered later.

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 therefore does not show a shelf at constant temperature, but the cooling rate is reduced by the progressive release of latent heat. This is illustrated in Figure GL2.24, for pure Cu and an alloy composition in the Cu–Ni system.

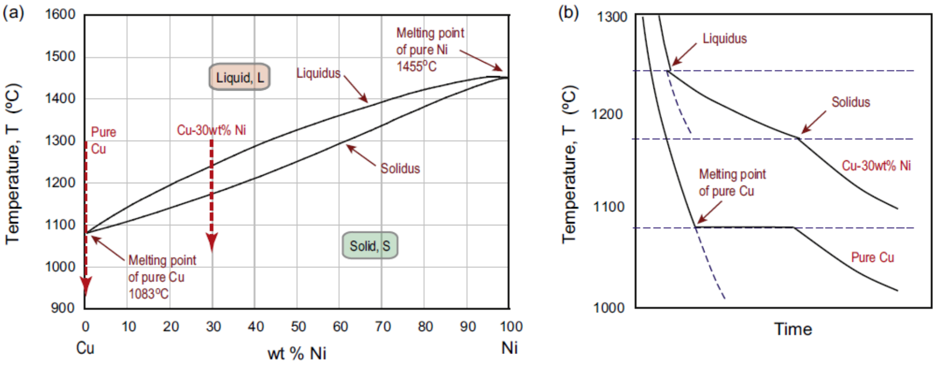


Figure GL2.24 (a) Cu–Ni phase diagram, and (b) corresponding cooling curves, for solidifying pure Cu and a Cu-30wt% Ni alloy.

Solidification of pure metals The mechanism of solidification is illustrated in Figure GL2.25. For *homogeneous nucleation*, embryonic solid colonies form spontaneously within the melt (Figure GL2.25(a)). 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 mould, or high melting point particles of another solid mixed into the liquid).

Each region grows by atoms transferring at the solid-liquid interface (Figure GL2.25(b)) – the interface advancing in the opposite direction to the atomic transfer. Growth continues until *impingement* of the solid regions occurs (Figure GL2.25(c)). 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 GL2.25(d)). We call these *grains*, and the surfaces where they meet are *grain boundaries*. Grains are typically on the length-scale of 1 µm–1 mm, and are easily revealed by optical microscopy.

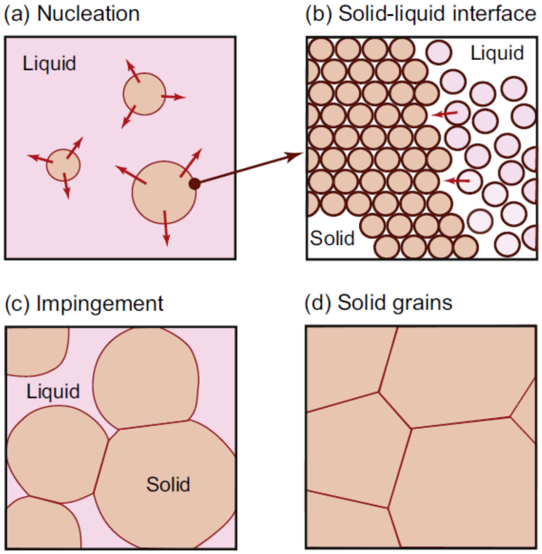


Figure GL2.25 Solidification mechanism: (a) homogeneous nucleation; (b) magnified view of atomic transfer at the solid-liquid interface; (c) growth of nuclei and the onset of impingement; (d) final solid grain structure.

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 GL2.26 shows optical micrographs of pure metals after solidification, showing equiaxed grain structures. Note that some techniques also generate colour contrast between grains, by applying surface etches that change the polarisation of the reflected light (see Figure GL2.26(b)). 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 colours do not necessarily indicate different phases!

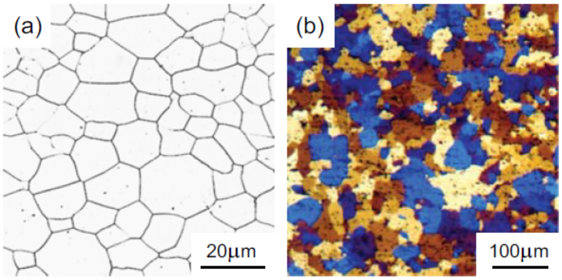


Figure GL2.26 Optical micrographs of (a) pure Fe and (b) pure Al. In (b) the etching technique produces colour contrast between different crystal orientations – but it is still all one phase. Images courtesy: ASM Micrograph Center, ASM International, 2005.

So grain structure is our first example of a microstructure formed by a phase transformation. Let's emphasise a key idea that will recur from here onward. 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.

Solidification of simple binary alloys, and phase reactions Alloys show a freezing range, between the liquidus and solidus lines. Consider solidification of Cu-30 wt% Ni on the phase diagram of Figure GL2.24. Solidification starts at 1240°C – nuclei form as in Figure GL2.25(a). In contrast to a pure metal, further cooling is needed for more solid to form, for example, at 1200°C a tie-line indicates 50% solid and 50% liquid are stable, and the microstructure would appear as in Figure GL2.25(b). To reach 100% solid (Figure GL2.25(c)) we need to keep cooling to 1170°C, 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. The phases present change when we cross boundaries on the diagram. But the Cu–Ni example above showed that, if more than one phase is present, the phases may also evolve in composition on heating or cooling, *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; and no phase reaction can take 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 GL2.9(a)).

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-10 wt% Sn (see Figure GL2.27, alloy A).

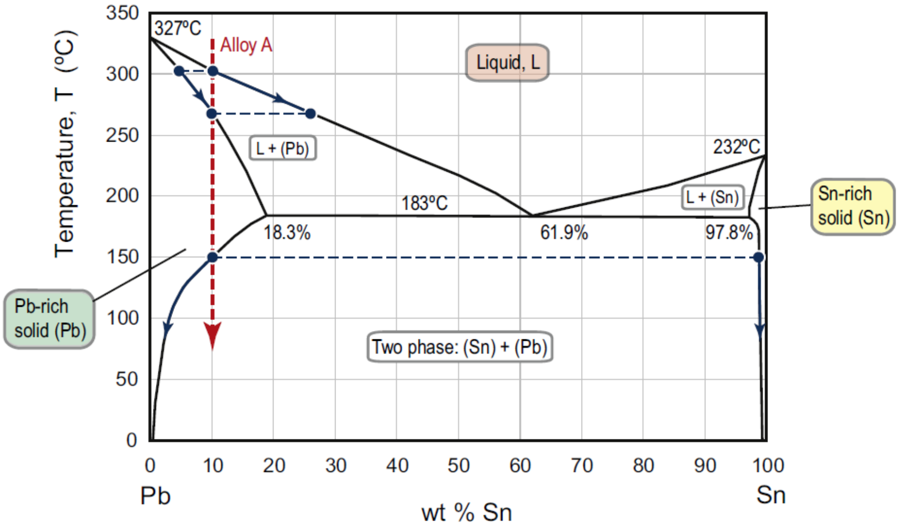


Figure GL2.27 The Pb–Sn phase diagram: solidification of a dilute alloy *A*.

The transformations and reactions are as follows, leading to the microstructure evolution shown in Figure GL2.28.

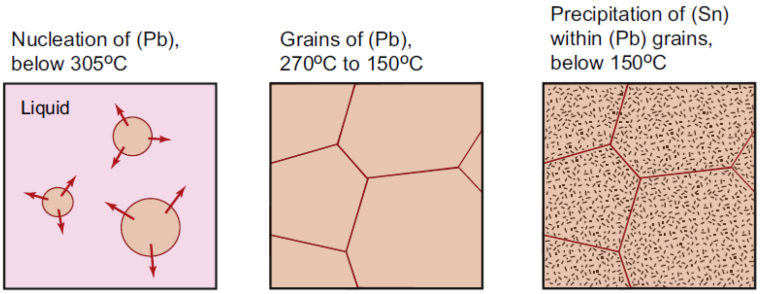


Figure GL2.28 Schematic microstructure evolution in solidification of a dilute Pb-10wt% Sn alloy.

1. *Above 305°C*: Single-phase liquid of composition identical to that of the alloy; no phase reaction.
2. *From 305 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 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 element, and a phase reaction takes place.

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 GL2.28(a)).

Exercise

E.12 Find the proportions and compositions of the phases formed on solidification of the Pb-10 wt% Sn alloy, at 250°C, and at room temperature (20°C).

Eutectic solidification Next consider the solidification of the eutectic composition itself in the Pb–Sn system (Figure GL2.29, alloy B). The eutectic composition is Pb-61.9 wt% 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 in the two-phase field immediately below 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.

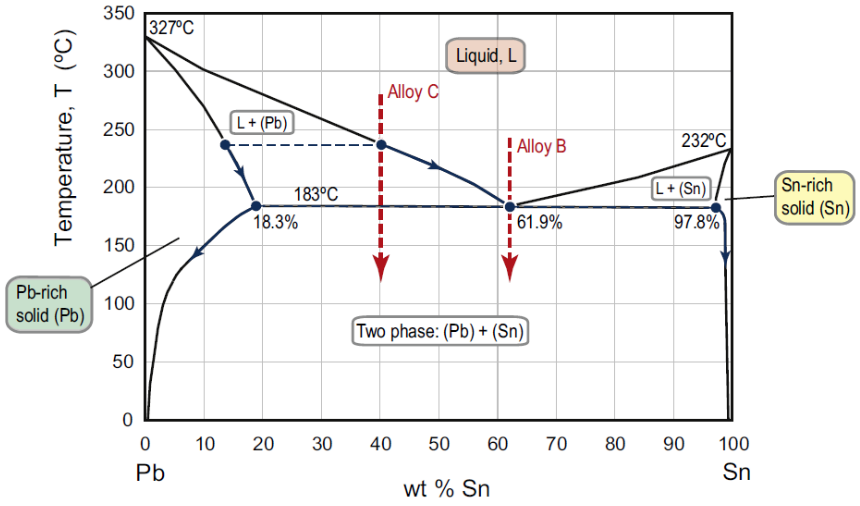


Figure GL2.29 The Pb–Sn phase diagram: solidification of eutectic alloy (B) and an off-eutectic alloy (C).

Exercise

E.13 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; that is, 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 GL2.30(a) shows a micrograph of eutectic Al–Si (the phase diagram for this system was shown in Exercise E.9).

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 toward 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.13). However, if the V is located toward 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 GL2.18(a) and GL2.30(a)).

Note in Figure GL2.30(a) 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 minimise 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 that 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 with 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).

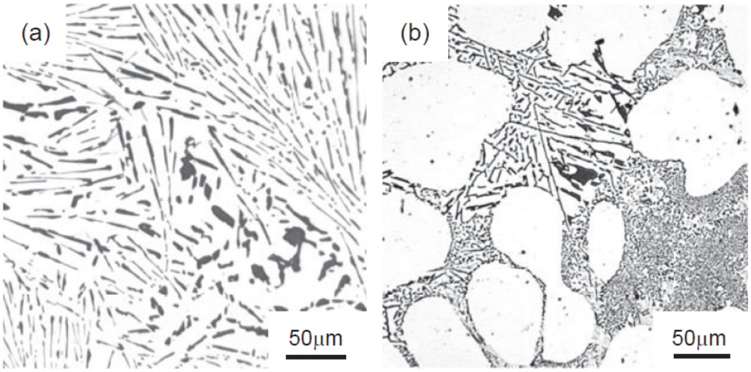


Figure GL2.30 Optical micrographs of (a) eutectic Al–Si alloy; (b) off-eutectic Al–Si alloy, showing grains of primary (Al) (white). Images courtesy: ASM Micrograph Center, ASM International, 2005.

A further phase reaction occurs on cooling of the two-phase eutectic solid, for example, 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 earlier), then at the eutectic temperature the remaining liquid undergoes the eutectic reaction (as seen in Pb–Sn earlier).

Consider solidification of Pb-40 wt% Sn (see Figure GL2.29, alloy C). The transformations and reactions are as follows, leading to the microstructure evolution illustrated in Figure GL2.31.

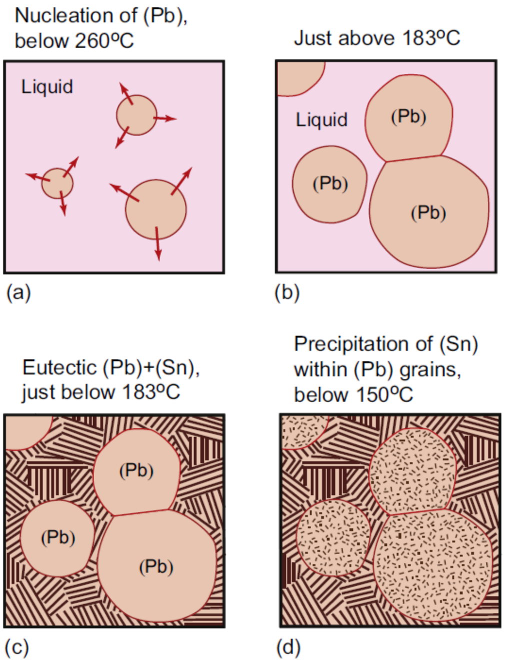


Figure GL2.31 Schematic microstructure evolution in solidification of a Pb-40wt% Sn alloy.

1. *Above 235°C*: Single-phase liquid; no phase reactions.
2. *From 235 to 183°C*: The liquidus is reached at 235°C, and nuclei of Pb-rich solid solution appear first (Figure GL2.31(a)). 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 (40 wt% Sn) is roughly halfway between that of the new solid (18.3 wt% Sn) and the residual liquid (61.9 wt% Sn); so the alloy is about half liquid, half solid, by weight (and very roughly by volume, neglecting the difference in phase densities; Figure GL31(b)).
3. *At 183°C*: The remaining liquid has reached the *eutectic point*, and this liquid undergoes solidification exactly as described before (Figure GL2.31(c)). 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 (Sn) alongside more (Pb) will be straightforward, since there are already solid grains of (Pb) 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 the features discussed so far (Figure GL2.31(d)). 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 GL2.30(b) 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 colour, 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).

Precipitation reactions Solid-state phase transformations were introduced in Part 6, following solidification of dilute binary alloys (Figures GL2.27 and GL2.28). 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 GL2.9(b), the Al-rich end of the Al–Cu system. Exercise E.7(d) considered an Al-4 wt% Cu alloy at 550 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 the grains and increasing in proportion as the temperature falls. Figure GL2.34 shows the final microstructure.

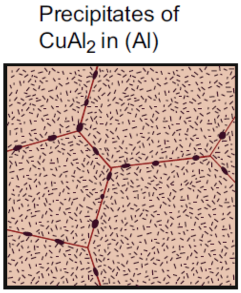


Figure GL2.34 Schematic microstructure of a slow-cooled Al-4wt% Cu alloy.

At modest magnification, the two-phase region may appear a uniform colour, 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 GL2.34 illustrates another feature that 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: first, faster nucleation can occur, as atoms can rearrange more readily into the precipitate lattice (this is a form of heterogeneous nucleation); second, 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 (intergranular 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*; that is, Fe–C alloys with compositions between pure iron and the eutectoid composition. Figure GL2.35 shows the relevant section of the Fe–C phase diagram.

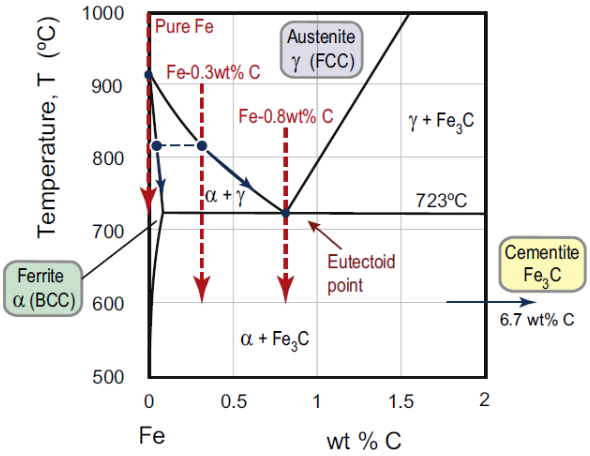
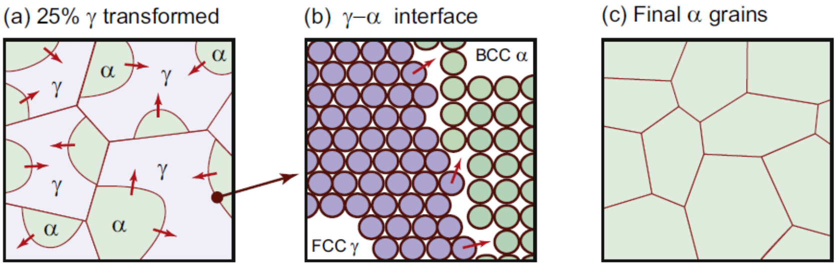


Figure GL2.35 The Fe–C phase diagram for compositions of carbon steels below 1000°C, including the eutectoid point.

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 (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 GL2.36(b)). The interface migrates in the opposite direction to the atomic jumps. Figure GL2.36(a) and (c) show the solid-solid transformation under way 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.


(a) 25% γ transformed

(b) γ–α interface

(c) Final α grains

Figure GL2.36 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 (0.8 wt% C) leads to complete transformation to ferrite and cementite, at the eutectoid temperature, 723°C (see Figure GL2.35). 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 $\alpha +$ Solid β.

The mechanism of the eutectoid reaction must transform a single solid phase into two others, both with compositions that differ from the original (given by the ends of the tie-line through the eutectoid point). In the Fe–C eutectoid reaction, austenite containing 0.8 wt% C changes into ferrite (containing almost no carbon) and cementite (Fe_3C, containing 6.7 wt% C, or 25 *atomic* % carbon). Hence carbon atoms must diffuse to form regions of high and low composition, 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 GL2.37(a)).

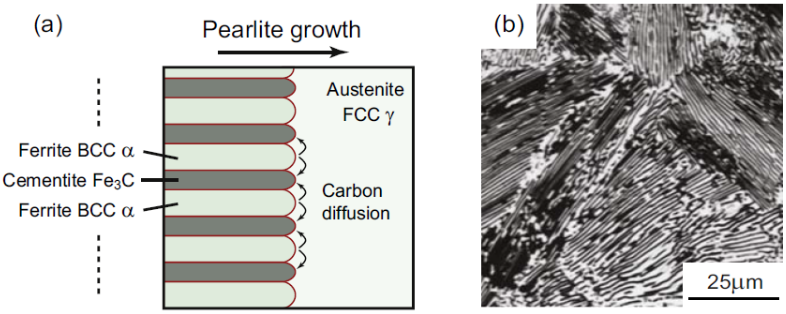


Figure GL2.37 (a) Schematic illustration of the eutectoid transformation from austenite to pearlite; (b) micrograph of pearlite. Image courtesy: ASM Micrograph Center, ASM International, 2005.

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, which enables the interface between the new phases and the austenite to traverse 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 GL2.37(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 and piano strings are examples of '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 0.3 wt% C (as indicated on Figure GL2.35). 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 2:1. The remaining austenite contains 0.8 wt% 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 GL2.38 show the reaction under way 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.

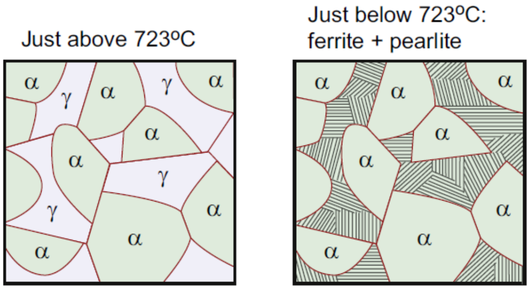


Figure GL2.38 Schematic illustration of microstructure evolution in a hypo-eutectoid steel, from ferrite + austenite to ferrite + pearlite.

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 *normalised*) 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.