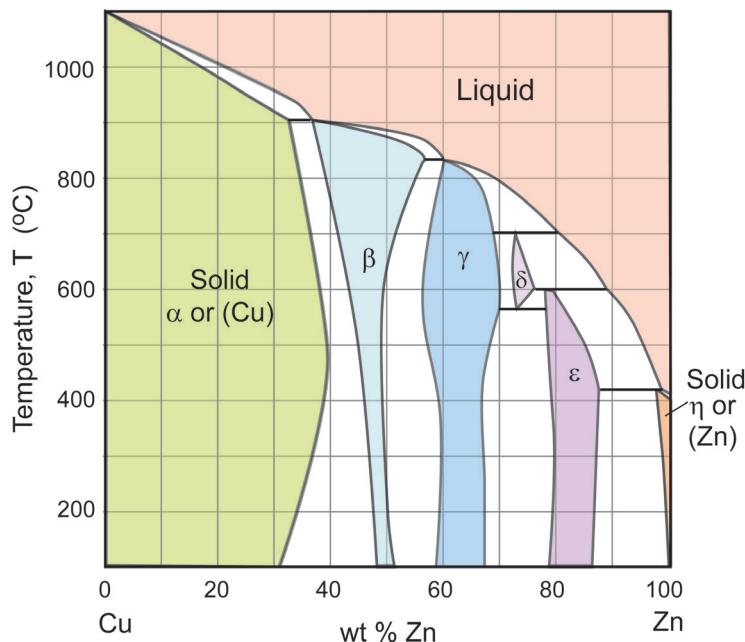


## Teach Yourself Phase Diagrams



H.R. Shercliff, G.J. McShane, D. Delamore

(Adapted from Ashby M.F., Shercliff H.R. & Cebon D., *Materials: Engineering, Science, Processing and Design*)

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## PART 1: Introduction and Background Information

### 1.1. Introduction

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 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 changing 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, generating the microstructure. Our mantra for this topic is thus:

$$\text{Composition} + \text{Processing} \rightarrow \text{Microstructure} + \text{Properties}$$

*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 document 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 document you should be able to do the following:

- Interpret the equilibrium phases at any point on binary phase diagrams.
- Predict the microstructures which may result from simple processing histories of important engineering alloys.

Key definitions are marked “DEF” as they appear. Exercises are provided in Examples Paper 3/1, covering each topic – do these as you go along to build up your knowledge systematically. Further reading is provided at the end.

- **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;
- **Part 5** introduces phase transformations and shows 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).

### 1.2. Phases

*Pure Substances*: For pure substances, the idea of a phase is familiar: ice, water and steam are the solid, liquid and gaseous states of pure H<sub>2</sub>O – each is a distinct phase. 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.

**DEF.** All parts of a material with the same atomic structure are a single *phase*.

*Mixtures*: Consider first a familiar example: a mixture of sugar and tea. If the tea is hot enough, the sugar will dissolve completely. The result is a solution of sugar in tea – a single phase. If the tea goes cold, a sugary sediment develops. This has a distinct atomic structure from the surrounding liquid, and so the cup now contains two separate phases. Processing of metallic alloys (which are mixtures of elements) 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, therefore forming a single phase. But in the solid state, things are more complex – for

example, in a binary alloy (i.e. a mixture of two components) the solid microstructure usually takes one of three forms (examples later):

- A single solid solution (one phase);
- Two separated solid solutions (two phases);
- A chemical compound (phase 1), with a separated solid solution (phase 2).

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. In the three types of solid microstructures listed above, each solid solution or chemical compound would be an identifiable phase.

### 1.3. Alloys, Components and Concentration

#### Alloys

**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 ( $Al_2O_3$ ).

#### Components

**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.

#### Composition

Alloys are defined by their composition – i.e. the concentrations of the components in weight % (wt%) or atom % (at%). The compositions of phases, too, may be defined in weight % or atom %.

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

$$W_A = \frac{\text{weight of component A}}{\sum \text{weights of all components}} \times 100$$

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

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

Composition (of component A) is sometimes written as  $C_A$  (in which case it is important to specify wt% or at%). To convert between weight and mols:

- (Weight in grams) / (atomic or molecular wt. in grams/mol) = number of mols.
- (Number of mols) × (atomic or molecular wt. in grams/mol) = weight in grams (g).

### 1.4. Thermodynamics of Phase Equilibrium

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

- The phases present;
- The weight fraction of each phase;
- 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 further in lectures. In summary, for a given composition held at fixed temperature  $T$  and pressure  $p$ , the Gibbs free energy,  $G$ , is defined as:

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

Here,  $U$  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.

### 1.5. 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  $W_B$  (or  $X_B$ ), 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, 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.

**Now do Examples Paper 1, questions 1-5.**

## PART 2: Simple Phase Diagrams

### 2.1. Pure Materials

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 in equilibrium – see Fig. 1(a). Similarly, liquid changes to vapour 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.

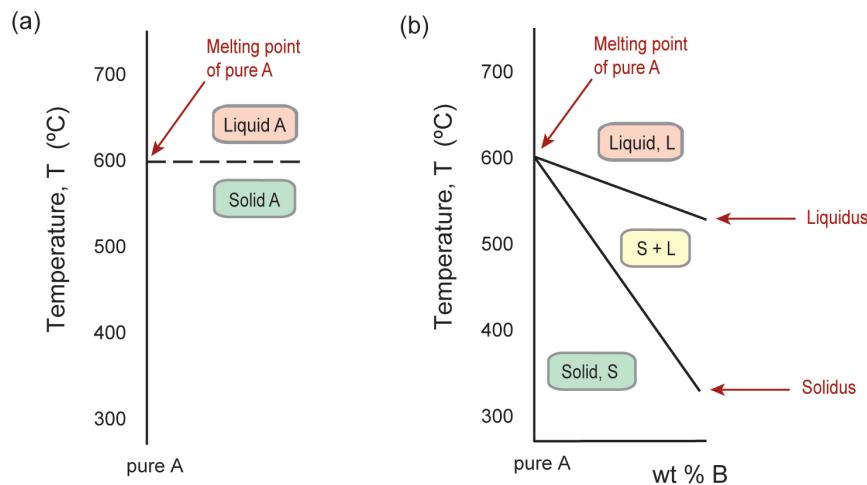


Figure 1: (a) One-dimensional phase diagram for a pure substance: a temperature scale showing the phase boundary between solid and liquid – the melting point; (b) the A-rich end of a binary A-B phase diagram, illustrating partition of the melting point between solidus and liquidus boundaries.

### 2.2. A Simple Binary System

Now if we consider the binary A-B system and add a second axis for composition, the behaviour illustrated in Fig. 1(b) is commonly observed. This figure shows a separation between the upper limit of 100% solid and the lower limit of 100% liquid separate, so that 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*.

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 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. 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.

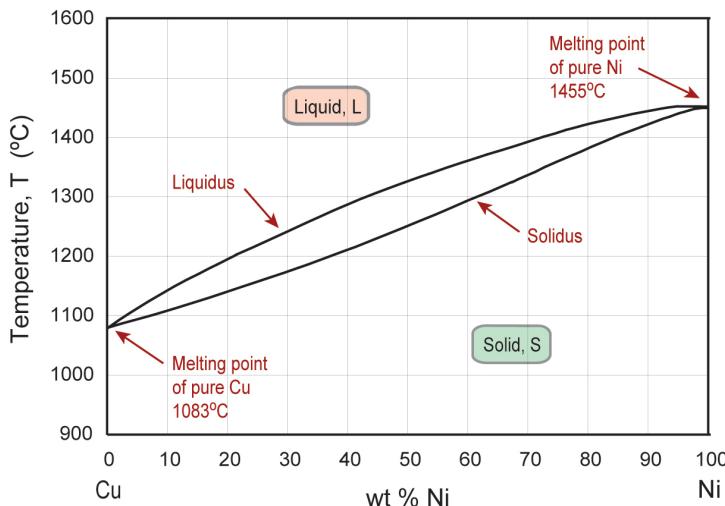


Figure 2: Isomorphous phase diagram for the Cu-Ni system

### 2.3. Cooling Curves and Latent Heat

Consider cooling pure Cu slowly from above its melting temperature, as indicated by the left-hand arrow in Figure 3(a). The temperature as a function of time – Figure 3(b) – shows a shelf in the cooling curve, called an *arrest point*, at the melting point (at atmospheric pressure Cu melts at 1083°C). At this temperature there is a *phase change*: liquid to solid. 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. Thermodynamically, the latent heat is the change in enthalpy, at constant temperature, as the material state changes.

Alloys frequently solidify over a *range* of temperature (between the liquidus and solidus lines) – see the example of Cu-30wt% Ni in Figure 3(a) (right-hand arrow). 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 3(b), for the alloy Cu-30wt% Ni.

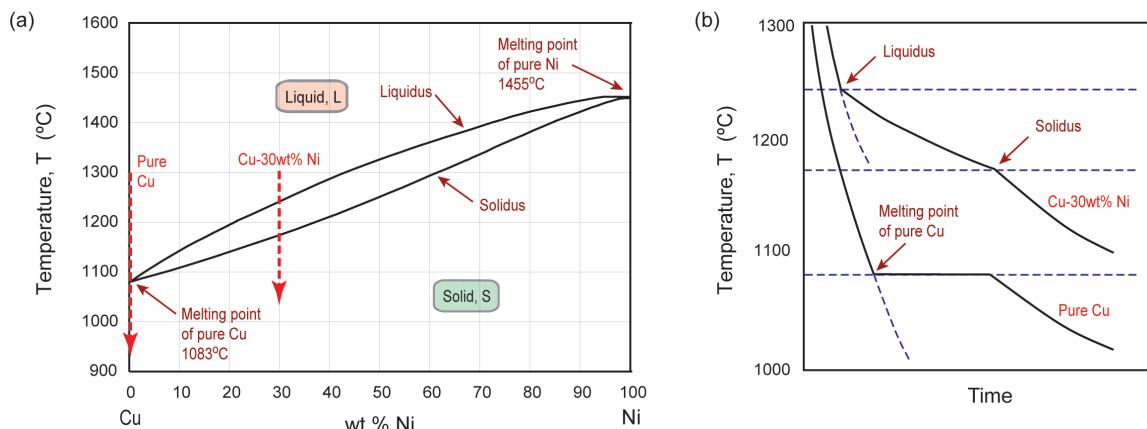


Figure 3: (a) Cu-Ni phase diagram, and (b) corresponding cooling curves, for solidifying pure Cu and a Cu-30wt% Ni alloy.

### 2.4. The Solubility Limit

In the previous section we discussed a simple binary system, Cu-Ni, which has the feature that at low temperatures the two components (Cu and Ni) can form a single phase solid solution for any composition between pure Cu and pure Ni. 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* by revisiting an everyday example: a cup of tea.

### Solvus Boundaries

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 a 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 4. The boundaries between the single and two-phase regions are known as *solvus boundaries*.

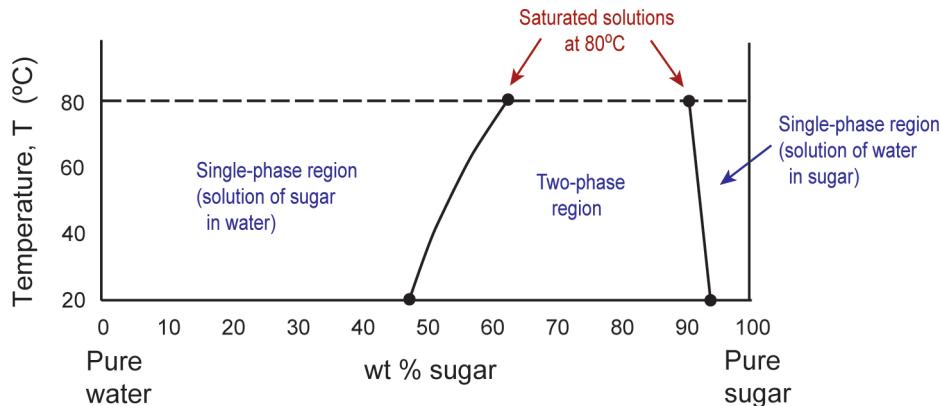


Figure 4: Schematic phase diagram for sugar and tea (water) – the saturation level of both solutions increase with temperature.

What happens at a given temperature and composition is determined by the thermodynamics of mixing sugar and water. 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. These concepts will be covered in more detail in lectures.

### Constructing a Phase Diagram with Solubility Limits

The picture in Figure 4 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 5 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 is 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 both pure elements, as in Figure 1(b).

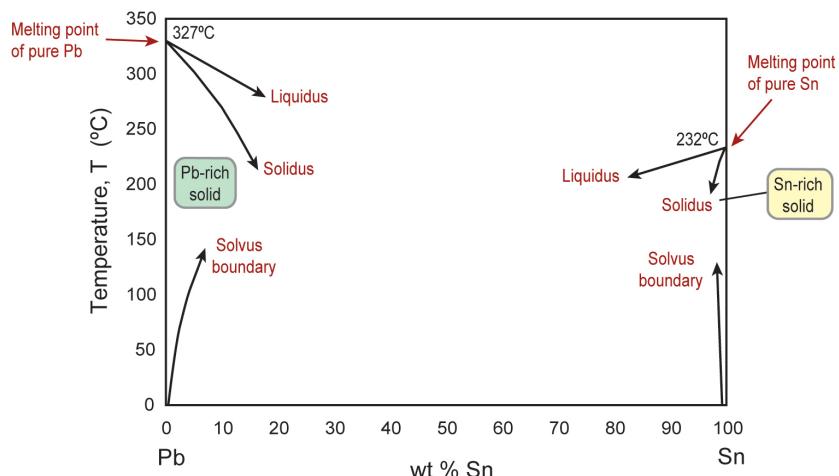


Figure 5: partial phase diagram for the Pb-Sn system, showing the limiting behaviour at high and low temperatures.

To complete the diagram, first consider where the falling solidus boundaries meet the rising solvus boundaries. Figure 6 shows that the points where they intersect represent the points of maximum solubility (highest saturation) in the single phase solids. This closes the regions representing single phase solid solutions – any region in which the phases present are fixed 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 6, closing the two-phase field, (Pb) + (Sn).

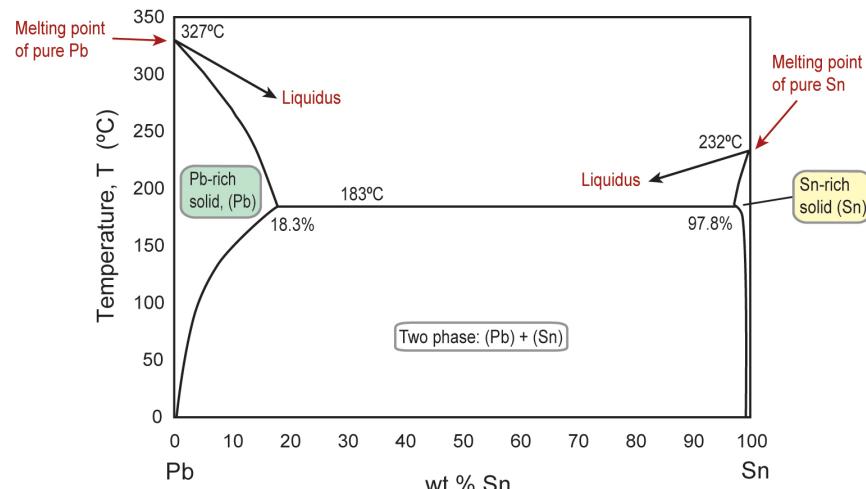


Figure 6: partial phase diagram for the Pb-Sn system, showing the completed single phase solid and two phase solid fields.

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 7 shows the completed Pb-Sn phase diagram. For the Pb-Sn system the eutectic point is at the composition  $W_{Sn} = 61.9$  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.

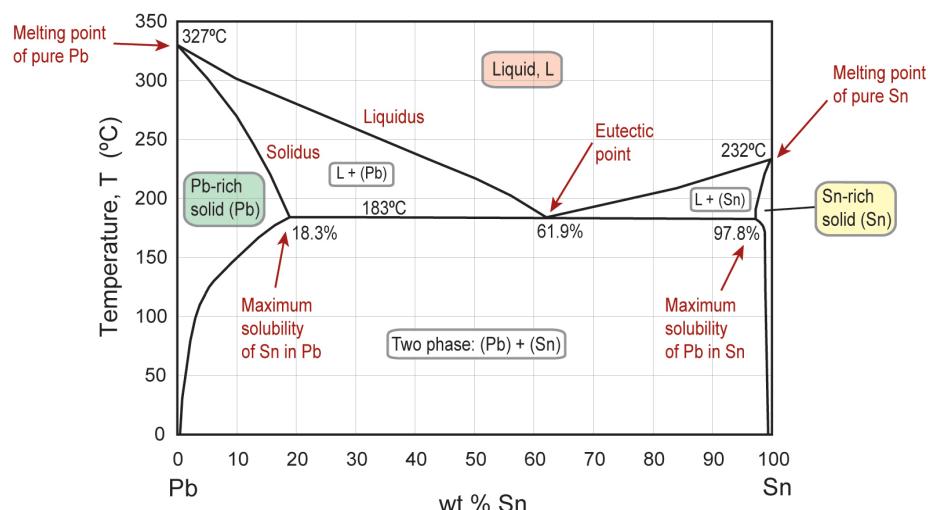


Figure 7: the completed phase diagram for the Pb-Sn system, showing the eutectic point closing the liquid field.

## 2.5. Reading Binary Phase Diagrams

### Identifying Phases

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 there are at most two). Figure 8 shows phase diagrams for Cu-Ni (Figure 8a) and Pb-Sn (Figure 8b) with the single phase fields shaded. Single phase regions are always labelled, either with the notation in Figure 8, with (Pb) for Pb-rich solid and so on, or with a Greek character ( $\alpha$ ,  $\beta$ ,  $\gamma$  etc). Note that 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 8). In the two-phase regions, the phases present are identified by following a horizontal line through the constitution point to the adjacent phase boundaries: the two phases are the single phases beyond those boundaries. This line is called a *tie-line* (see below).

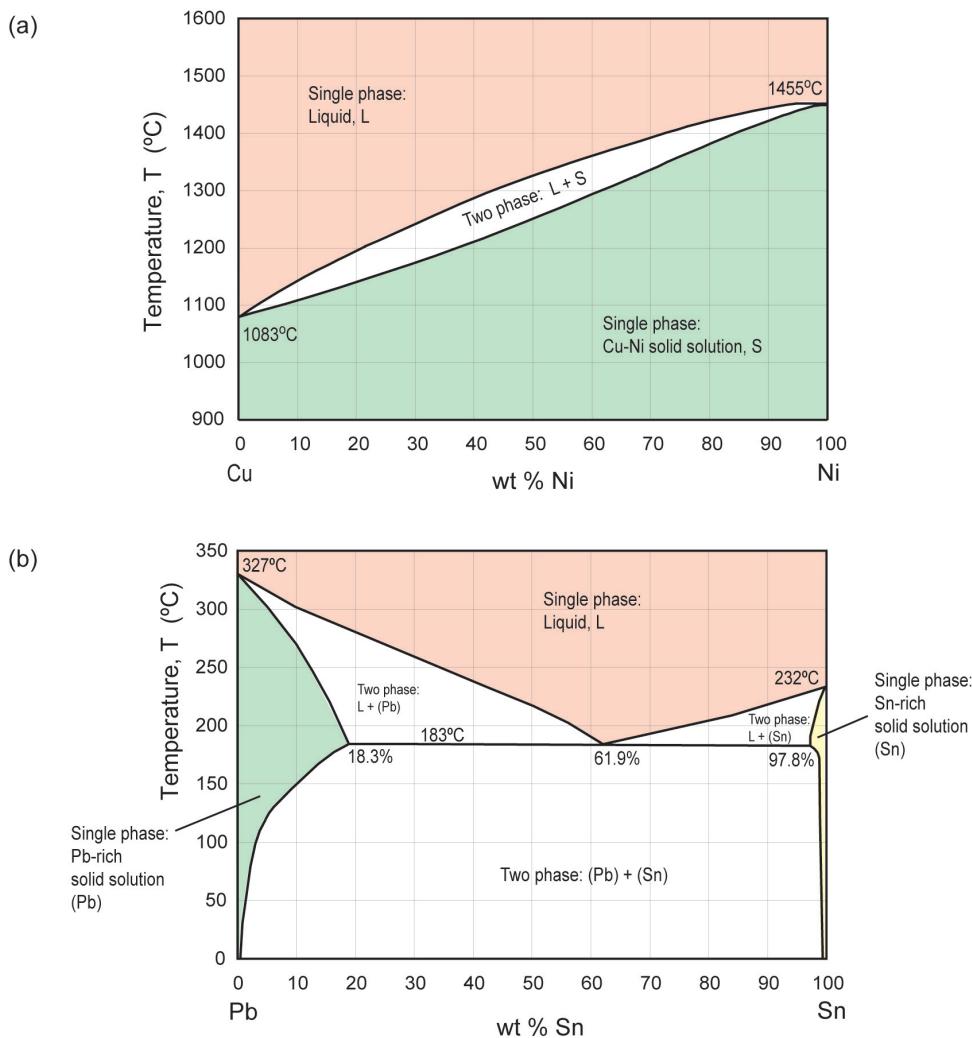


Figure 8: phase diagrams for (a) the Cu-Ni system and (b) the Pb-Sn system showing the single phase fields (shaded), separated by two-phase fields.

### Identifying Phase Compositions

Consider points A and B on the Pb-Sn phase diagram in Figure 9. At a constitution point in a single-phase region, the *phase composition* is simply the composition of the alloy itself. Constitution point A (temperature 300°C, alloy composition Pb-30wt% Sn) lies in the single-phase liquid field; the phase composition is also Pb-30wt% Sn.

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. Recall that these are the saturation limits of the single-phase fields on the other sides of the boundaries. Constitution point B (temperature 130°C, alloy composition C = 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.

**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.

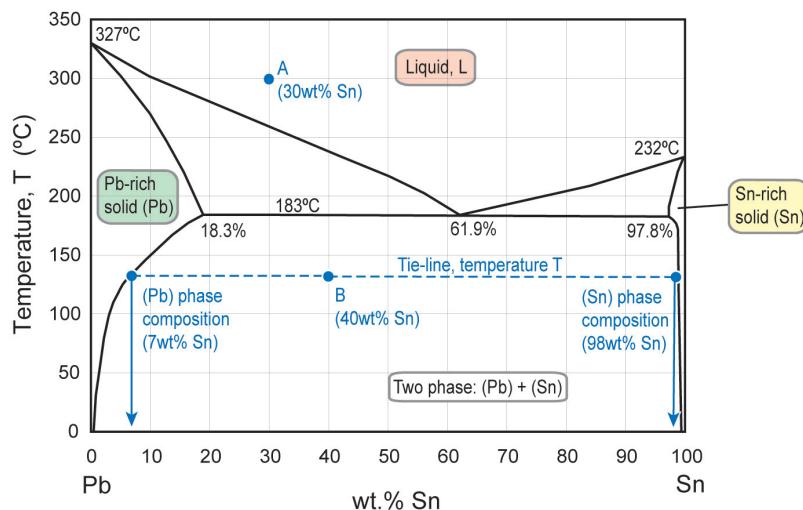


Figure 9: Phase diagram for the Pb-Sn system, illustrating constitution points in single (A) and two-phase (B) fields, and the tie-line defining the phases and compositions in the two-phase field.

*Now do Examples Paper 1, questions 6 - 7.*

### ***The Lever Rule: 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. As a result, 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 full derivation is given as an exercise in the Examples Paper.

Consider the alloy with composition  $W_{Sn} = 20$  wt% Sn at 250°C in Figure 10, 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 (Pb)* with composition  $W_{Sn}^{(Pb)} = 12$  wt% Sn; *Liquid L* with composition  $W_{Sn}^L = 34$  wt% Sn.

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

$$\ell = W_{Sn}^L - W_{Sn}^{(Pb)} = 34 - 12 = 22 \text{ wt% Sn}$$

$$a = W_{Sn} - W_{Sn}^{(Pb)} = 20 - 12 = 8 \text{ wt% Sn}$$

$$b = W_{Sn}^L - W_{Sn} = 34 - 20 = 14 \text{ wt% Sn}$$

The *weight fractions* of liquid and solid in the alloy are:  $F^L = a/\ell$  and  $F^{(Pb)} = b/\ell$ . Hence:

$$F^L = 8/22 = 36\% \quad \text{and} \quad F^{(Pb)} = 14/22 = 64\%$$

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).

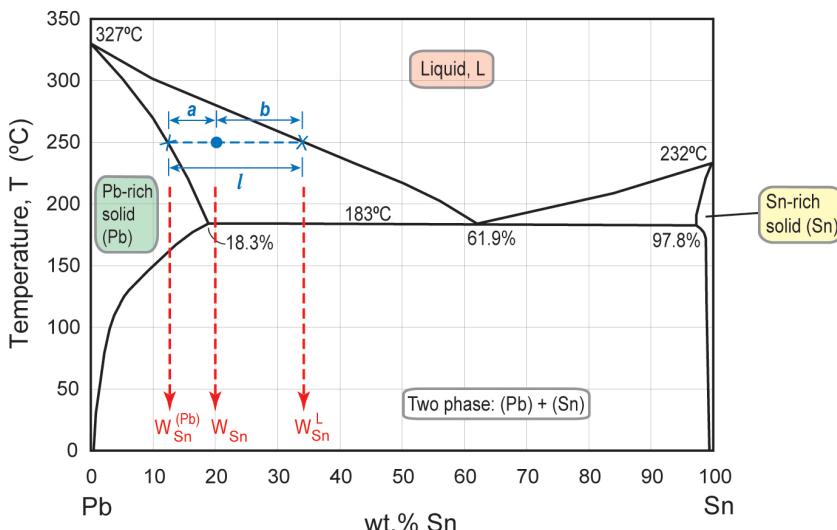


Figure 10: Phase diagram for the Pb-Sn system, illustrating the lever rule for finding the weight fractions of the phases in a two-phase field.

Note the following:

- $F^{(\text{Pb})} + F^L = a/\ell + b/\ell = (a+b)/\ell = 1$  (as expected, the two fractions sum to unity)
- At the left-hand end of the tie-line,  $F^{(\text{Pb})} = 1$  ( $a=0, b=\ell$ )
- At the right-hand end of the tie-line,  $F^L = 1$  ( $a=\ell, b=0$ )
- If the densities of the phases are known, the volume fractions  $V^{(\text{Pb})}$  and  $V^L$  can be calculated from the weight fractions.

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  $a$ ,  $b$  and  $\ell$  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 reading off the three compositions (in wt%) and evaluating  $a$ ,  $b$  and  $\ell$ , 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.

**Now do Examples Paper 1, questions 8 – 9.**

## 2.6. Intermediate Compounds

Many systems show *intermediate phases*: compounds which form between components. Examples are CuAl<sub>2</sub>, Al<sub>3</sub>Ni and Fe<sub>3</sub>C. 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 having lower free energy than, say, a mixture of two phases. 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.

### Composition

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<sub>3</sub>C 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 e.g. 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).

Compounds are inherently more stable, and in some respects behave like pure elements. For example, for compositions on both sides of a compound the liquid field often shows falling liquidus lines, with eutectics forming between the compound and a solid solution (or between two compounds, if the system shows more than one). Figure 11 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 5 separate phase diagrams back-to-back: the Ag-Ag<sub>5</sub>Sr diagram, the Ag<sub>5</sub>Sr-Ag<sub>5</sub>Sr<sub>3</sub> 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. And in all the two-phase fields the compositions of the solid phases are fixed, and do not vary with temperature.

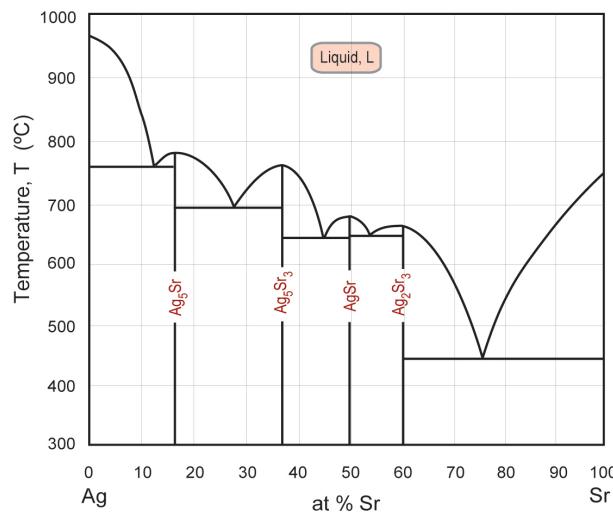


Figure 11: Phase diagram for the silver–strontium (Ag-Sr) system showing intermediate compounds.

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 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 in between the two-phase fields, it is one of the compounds – but the field has just collapsed to a single line.

### Solubility

A more typical example with engineering significance is illustrated in Figure 12, 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<sub>2</sub> (given the name  $\theta$ -phase, to signify that it is a single phase). The liquidus boundaries fall to a eutectic point at 33 wt% Cu and 548°C.

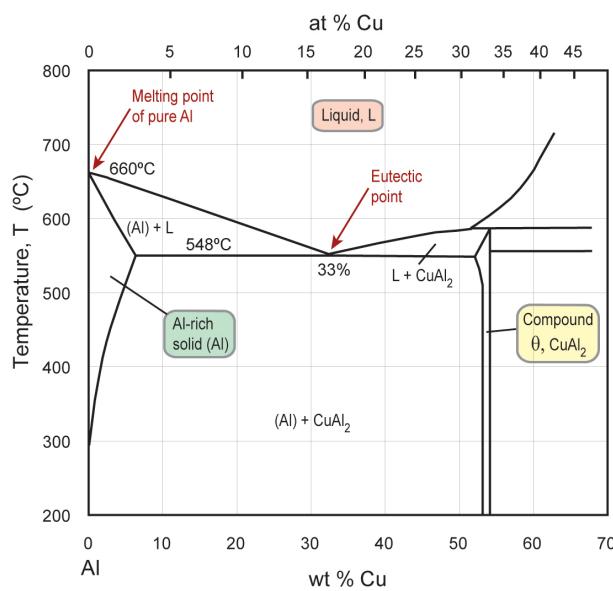


Figure 12: Phase diagram for part of the aluminium–copper (Al-Cu) system.

Now in contrast to the silver-strontium diagram, the  $\theta$  field is not a single vertical line, but a tall thin region with a small spread in composition. In other words  $\text{CuAl}_2$  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  $\text{CuAl}_2$ . 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 next examples paper question illustrates the problem.

*Now do Examples Paper 1, question 10.*

## PART 3: The Iron-Carbon Diagram

### 3.1. Introduction

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. For structural and mechanical applications, steels and other alloys based on iron (the ferrous alloys) are the dominant engineering alloys. They are intrinsically stiff, strong and tough, and mostly low cost. High density is a drawback for transport applications, allowing competition from light alloys, wood and composites. The wide range of applications reflects the many classes of ferrous alloy – different chemistries combined with different process histories. Here, we focus on ferrous alloys which are predominantly iron and carbon alone. Examples of typical applications of iron-carbon alloys are:

- *Cast iron brake discs.* Brake discs use sliding friction on the brake pads to decelerate a moving vehicle, generating heat in the process. The key material properties are therefore hardness (strength) for wear resistance, good toughness and a high maximum service temperature. Casting is the cheapest way to make the moderately complicated shape of the disc. Cast irons contain typically 2-4 wt % carbon, giving a lot of the hard compound iron carbide, giving excellent precipitation hardening.
- *Plain carbon steel: I-beams, cars and cans.* If we had to single out one universally dominant material, we might well choose mild steel – iron containing 0.1-0.2 wt % carbon. Almost all structural steels, automotive alloys and steel packaging (beer and food cans) are made of mild steel (or a variant enhanced with a few other alloying additions). All of these applications are wrought – the alloy is deformed extensively to shape. The excellent ductility of plain carbon steel enables this, while the deformation process exploits their work hardening to give the required product strength. Ductility, toughness and decent strength are vital in a structural material.

### 3.2. Pure Iron

#### Phase Changes with Temperature

First, we consider pure iron. Figure 13a shows the phases found in pure iron (i.e. the phase diagram becomes a single temperature axis). The low temperature form of iron is called *ferrite* (or  $\alpha$ -iron), which has a BCC lattice (body-centred cubic). On heating pure iron changes to *austenite* (or  $\gamma$ -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  $\delta$ -iron, before melting at 1534°C, and boiling at 2860°C.

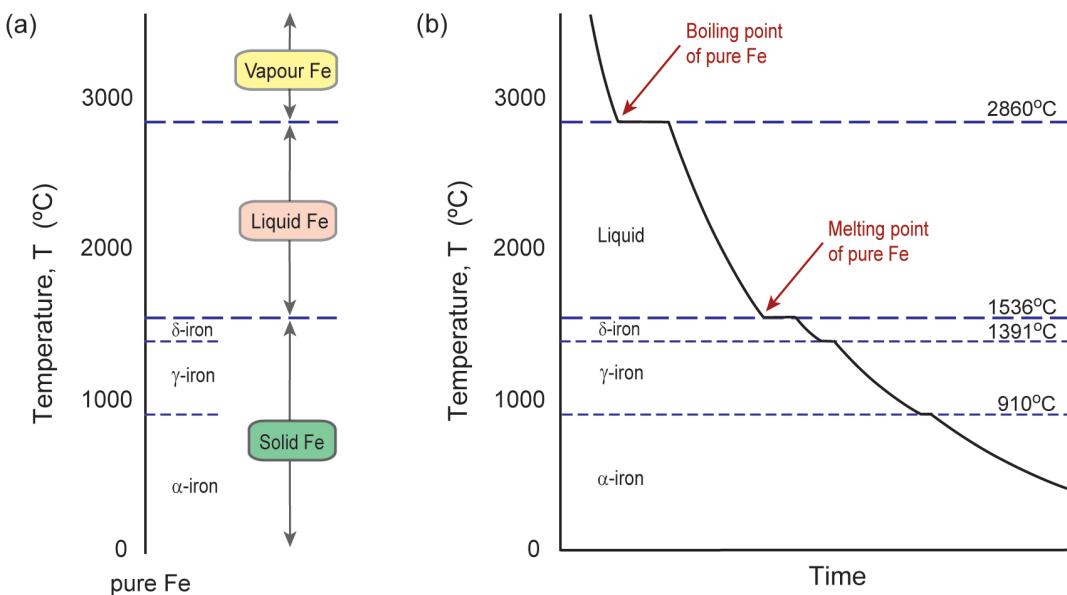


Figure 13: (a) one-dimensional phase diagram for pure iron; (b) corresponding cooling curve for condensing then solidifying iron from vapour to liquid to solid.

### Cooling Curve and Latent Heat

If we cool iron slowly from above its boiling point, the temperature as a function of time – Figure 13b – shows two shelves in the cooling curve (*arrest points*) at the boiling and melting points. As with pure copper (Section 2.3), these arrest points during cooling are due to the release of *latent heat* at each temperature where there is a phase change (recall that on heating, the latent heat is absorbed instead at these arrest points). Pure iron solidifies initially to BCC  $\delta$ -iron, but undergoes further solid-state phase transformations on cooling, first to FCC  $\gamma$ -iron at 1391°C, and then back to BCC  $\alpha$ -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 13b. The mechanisms of these solid state changes are considered later.

### 3.3. Features of the Fe-C Phase Diagram

The Fe-C phase diagram is shown in Figure 14. The key features of this diagram are described in turn below.

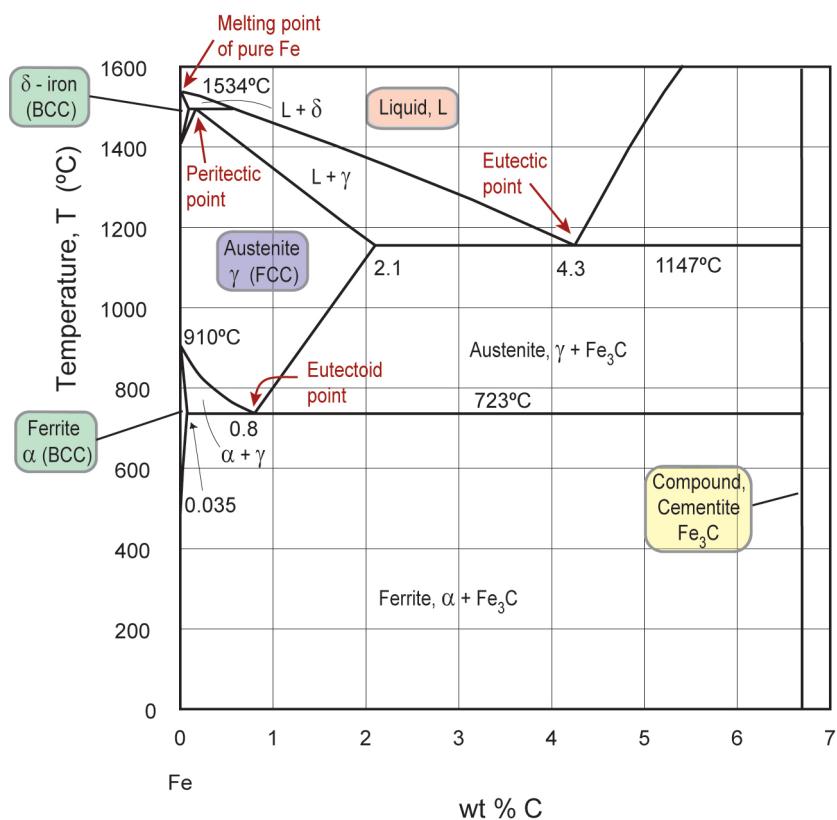


Figure 14: The iron-carbon phase diagram up to 6.7wt% carbon, the region covering cast irons and carbon steels.

### Ferrite, Austenite and $\delta$ -Iron Solid Solutions

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. The *interstitial holes* are larger in FCC than in BCC. This leads to low solubility of carbon in BCC ferrite and  $\delta$ -iron, and much higher solubility in FCC austenite. Note that the same names (ferrite, austenite and  $\delta$ ) 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.

### Cementite

Figure 14 shows the iron-carbon diagram, up to 6.7 wt% carbon. This upper limit corresponds to 25 at% C, at which composition the compound *iron carbide*  $\text{Fe}_3\text{C}$  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. Figures 15-17 show expanded extracts to clarify the diagram.

### Eutectoid Point

First consider the Fe-C phase diagram below 1000°C, up to 2.0wt% carbon (shown in expanded view in Figure 15). This shows the low solubility of carbon in ferrite, with a maximum of 0.035wt% 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 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*.

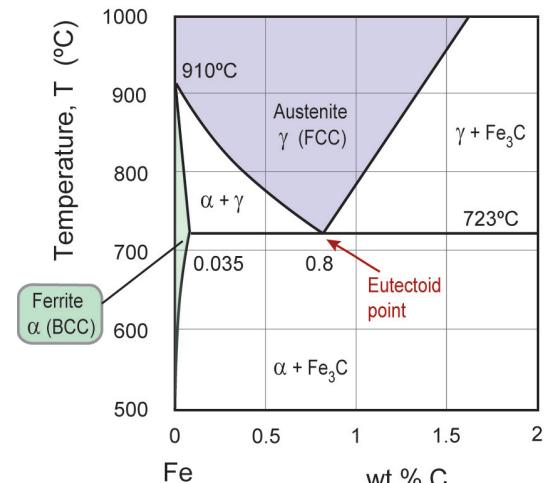


Figure 15: Fe-C phase diagram for low temperature and low wt% C: the eutectoid point.

### Eutectic 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 16 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 other two-phase regions indicate mixtures of the compound, iron carbide, with liquid and austenite respectively.

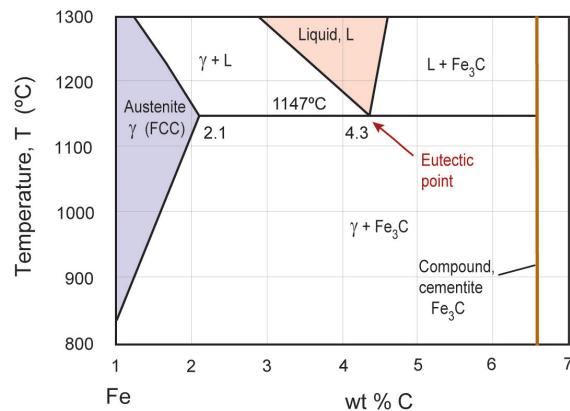


Figure 16: Fe-C phase diagram for high temperature and high wt% C: the eutectic point.

### Peritectic Point

Completing the austenite field introduces another new feature, a *peritectic point*. Figure 17 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 ( $\gamma$ ) to the left of the peritectic, and  $\gamma$  + liquid to the right.

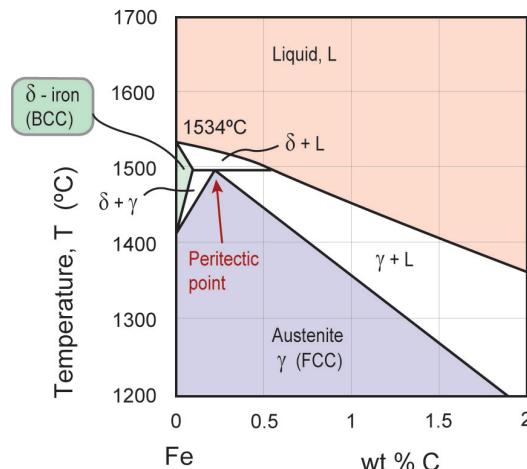


Figure 17: Fe-C phase diagram for high temperature and low wt% C: the peritectic point.

***Fe-C Phase Diagram: Summary***

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

- *Ferrite*:  $\alpha$ -iron (BCC) with up to 0.035 wt% C dissolved in solid solution
- *Austenite*:  $\gamma$ -iron (FCC) with up to 2.1 wt% C dissolved in solid solution
- *$\delta$ -iron*: (BCC) with up to 0.08 wt% C dissolved in solid solution
- *Cementite*:  $\text{Fe}_3\text{C}$ , a compound (iron carbide), with 6.7 wt% C.

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 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.

***Now do Examples Paper 1, question 11.***

## 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.

### 4.1. 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:

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

Figure 18 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.

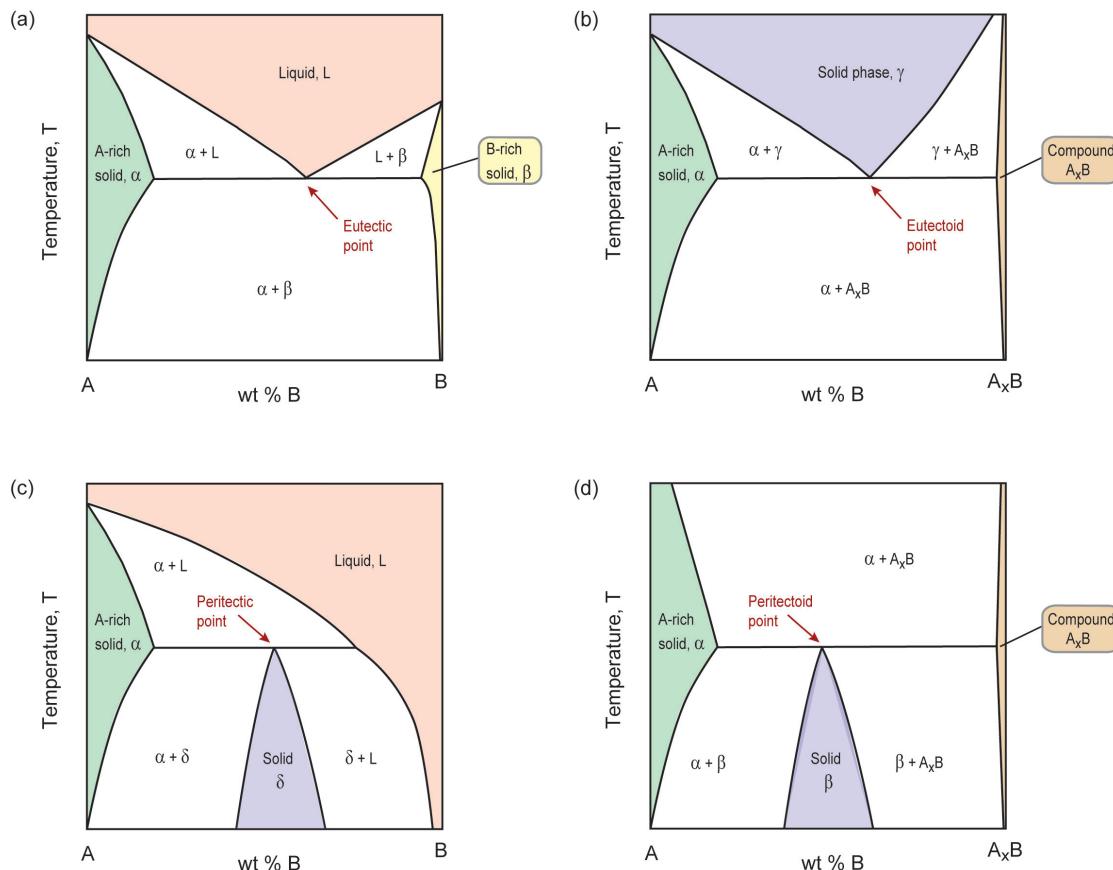


Figure 18: Schematic views of: (a) eutectic point; (b) eutectoid point; (c) peritectic point; (d) peritectoid point.

**Worked Example: Copper-Zinc (Brass)**

These key points may be found on a number of practical phase diagrams. One such example is the copper-zinc system (which includes brasses), shown in Figure 19. To help with the interpretation, the single phase regions have been shaded.

One *eutectoid point* (circled with a dashed line) can be identified: its composition and temperature is  $W_{Zn} = 73\text{wt\%}$ ,  $T = 555^\circ\text{C}$ .

There are 5 *peritectic points* (circled with solid lines):

- (i)  $W_{Zn} = 37\text{wt\%}$ ,  $T = 900^\circ\text{C}$
- (ii)  $W_{Zn} = 60\text{wt\%}$ ,  $T = 825^\circ\text{C}$
- (iii)  $W_{Zn} = 73\text{wt\%}$ ,  $T = 700^\circ\text{C}$
- (iv)  $W_{Zn} = 79\text{wt\%}$ ,  $T = 600^\circ\text{C}$
- (v)  $W_{Zn} = 99\text{wt\%}$ ,  $T = 420^\circ\text{C}$

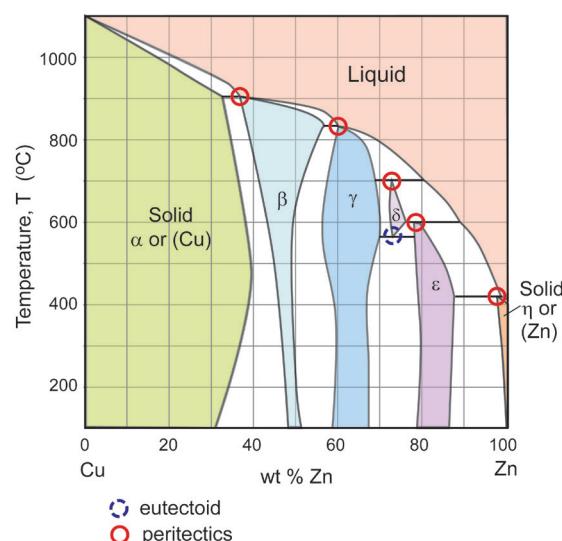


Figure 19: Phase diagram for the copper-zinc (Cu-Zn) system.

**4.2. 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  $\text{Al}_2\text{O}_3$ . In some cases, we are interested in mixtures of ceramics (or ceramic alloys). An example was mentioned earlier, *spinel* is made of Magnesia ( $\text{MgO}$ ) and Alumina ( $\text{Al}_2\text{O}_3$ ). 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 20 shows the silica-alumina ( $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ ) system. It forms an intermediate single phase, known as *mullite*. Note that the top of this single phase field closes in a peritectic point, while above this point, the two phase field is liquid +  $\text{Al}_2\text{O}_3$ .

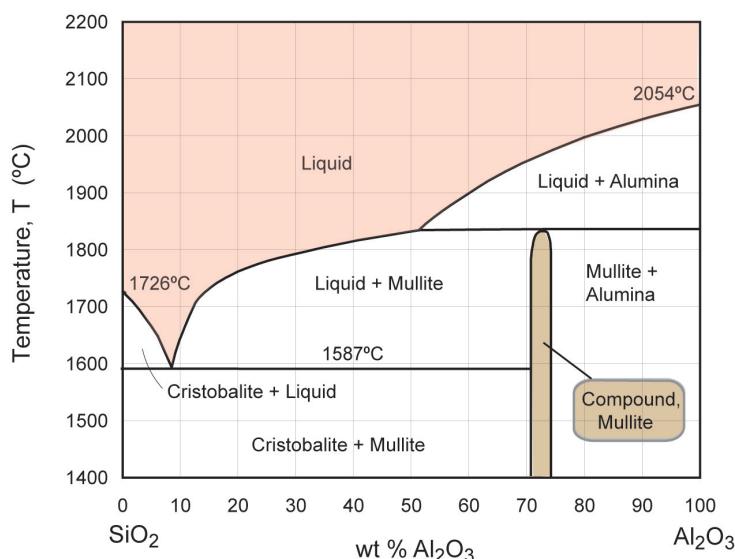


Figure 20: Phase diagram for the binary ceramic silica-alumina ( $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ ) system.

**Now do Examples Paper 1, questions 12 - 16.**

## PART 5: Phase Transformations and Microstructure Evolution (for Slow Cooling)

### 5.1. Introduction

After completing Parts 1–4 you should be able:

- To recognise 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.

Part 5 (and the associated lectures) 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 mould 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.

### Phase Diagrams and Microstructure

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. Here we consider slow cooling, when it is reasonable to assume that the microstructure can always evolve to maintain equilibrium. In lectures, we will look at cases where we deliberately cool quickly to bypass equilibrium and achieve a different microstructural outcome.

### Experimental Techniques for Microstructure Evaluation

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 1 summarises the various methods and their physical basis:

Optical and electron microscopy have been revolutionised 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 are 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, utilising 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 temperature *differences* between the samples. These are amplified to reveal the phase change temperatures, and the extent of transformation.

Technique	Physical Basis
<b>Dilatometry</b>	Measurement of dimensional changes at high resolution to detect changes of density and symmetry caused by phase change.
<b>Electrical Resistivity</b>	Measurement of electrical resistivity changes associated with difference in electron mean free path before and after phase change.
<b>Calorimetry: Differential Thermal Analysis</b>	Sensitive differential measurement of release or take-up of latent heat associated with phase change.
<b>Optical Microscopy</b>	Differential reflection of light, either in colour or intensity, by phases or by a surface film created by chemical or electro-etching.
<b>X-ray Diffraction</b>	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.
<b>Scanning Electron Microscopy (SEM)</b>	Differential back-scattering of electrons by differing phases giving both an image and compositional information
<b>Transmission Electron Microscopy (TEM)</b>	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 1: Techniques for observing phases and microstructures

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.

### 5.2. Solidification of Pure Metals

The mechanism of solidification is illustrated in Figure 21.

For *homogeneous nucleation*, solid colonies form spontaneously within the melt (Figure 21a). 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 21b) – the interface advancing in the opposite direction to the atomic transfer.

Growth continues until *impingement* of the solid regions occurs (Figure 21c). 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 21d). 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 22 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 which change the polarity of the reflected light (see Figure 22b). 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!

So grain structure is our first example of a microstructure formed by a phase transformation. Let’s emphasise 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 more detail in lectures.

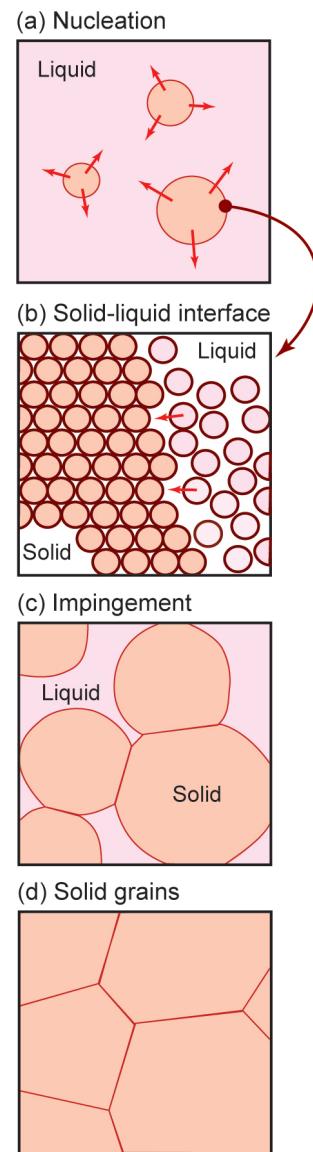


Figure 21: Solidification mechanism.

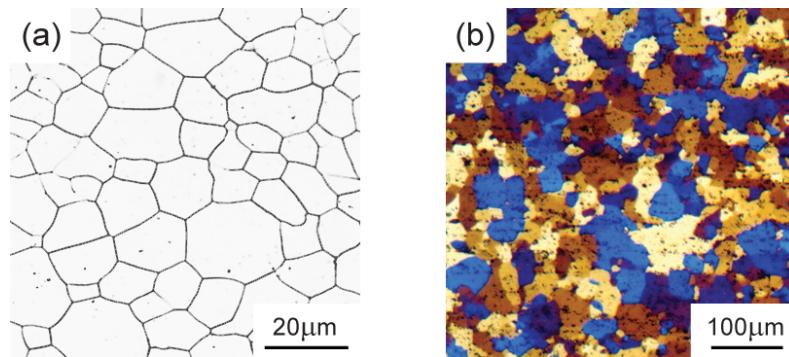


Figure 22: Optical micrographs of grains in (a) pure Fe and (b) pure Al. In (b) the etching technique produces colour contrast between different crystal orientations – but it is still all one phase. (*Images courtesy of ASM Micrograph Center, ASM International, 2005*)

### 5.3. Simple Binary Alloys

#### Cooling through a Two Phase Region

Alloys show a freezing range, between the liquidus and solidus lines. Consider solidification of Cu-30wt% Ni on the phase diagram shown in Figure 23a. Solidification starts at 1240°C – nuclei form as shown in image A in Figure 23b. 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 image B in Figure 23b. To reach 100% solid (image C in Figure 23b) 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.

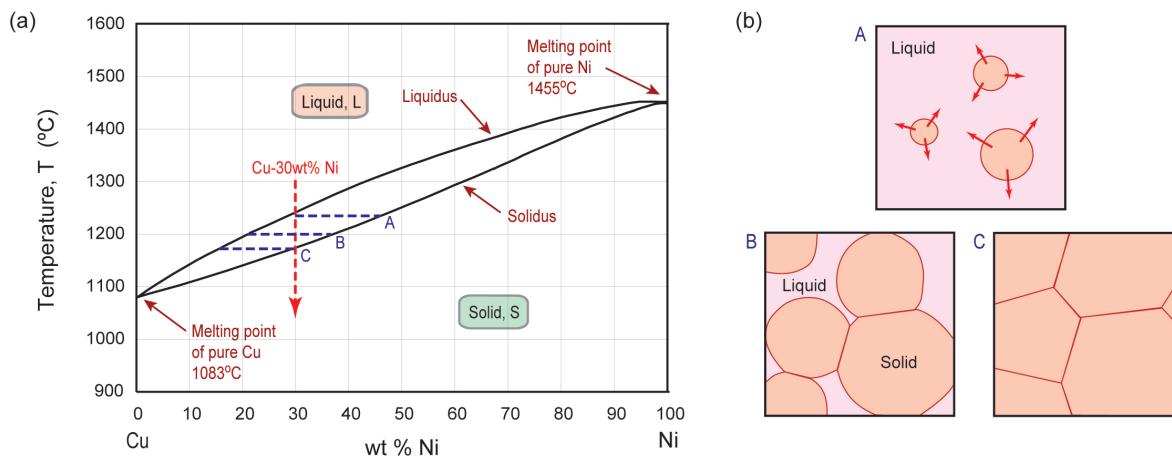


Figure 23: Cooling through the two-phase region in Cu-Ni, showing the microstructural changes taking place at selected points, A-C.

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 11).

### Dilute Alloys with Solubility Limits

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 24 – alloy A).

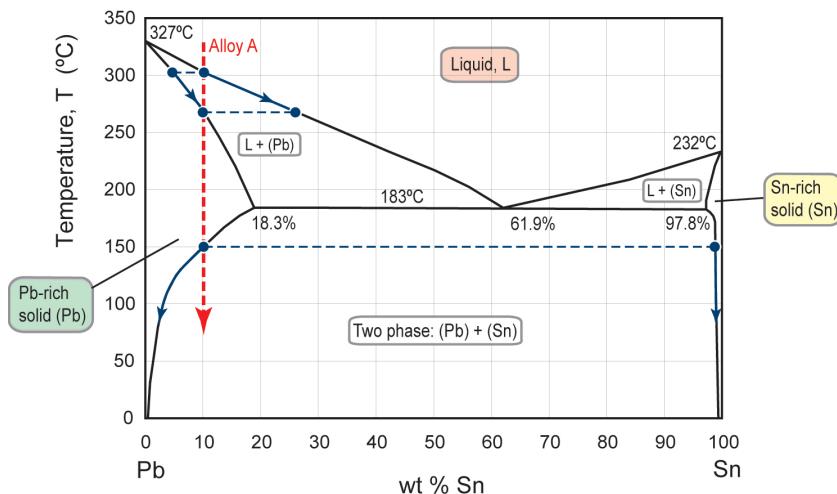


Figure 24: The Pb-Sn phase diagram: solidification of a dilute alloy A.

The transformations and reactions are as follows, leading to the microstructure evolution shown in Figure 25.

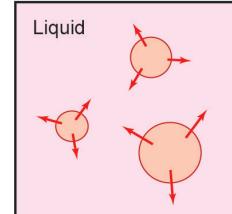
(i) *Solidification stage:*

- *Above 305°C:* Single-phase liquid of composition identical to that of the alloy; no phase reaction.
- *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).
- *From 270°C to 150°C:* Single-phase solid of composition identical to that of the alloy; no phase reaction.

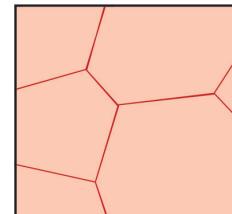
(ii) *Precipitation stage:*

- *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.

Nucleation of (Pb), below 305°C



Grains of (Pb), 270°C to 150°C



Precipitation of (Sn) within (Pb) grains, below 150°C

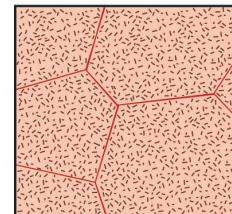


Figure 25: Schematic microstructure evolution in solidification of a dilute Pb-10wt% Sn alloy.

The formation of the Sn-rich phase takes place by *precipitation* from the solid solution. This mechanism too involves nucleation and growth: 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. Note that the scale of precipitation shown in Figure 25 is much smaller than the grain size. This is another example of how the kinetics of the phase transformation influence microstructure – many small particles form, since the mechanism involves diffusion in the solid state. The phase diagram only tells us what is expected to form (two phases in a given proportion) – predicting the dispersion and length-scale of the two phases requires additional knowledge.

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 25).

**Now do Examples Paper 1, question 17.**

### Eutectic Solidification

Next consider the solidification of the eutectic composition itself in the Pb-Sn system (Figure 26 – 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  $\alpha$  + Solid  $\beta$ .

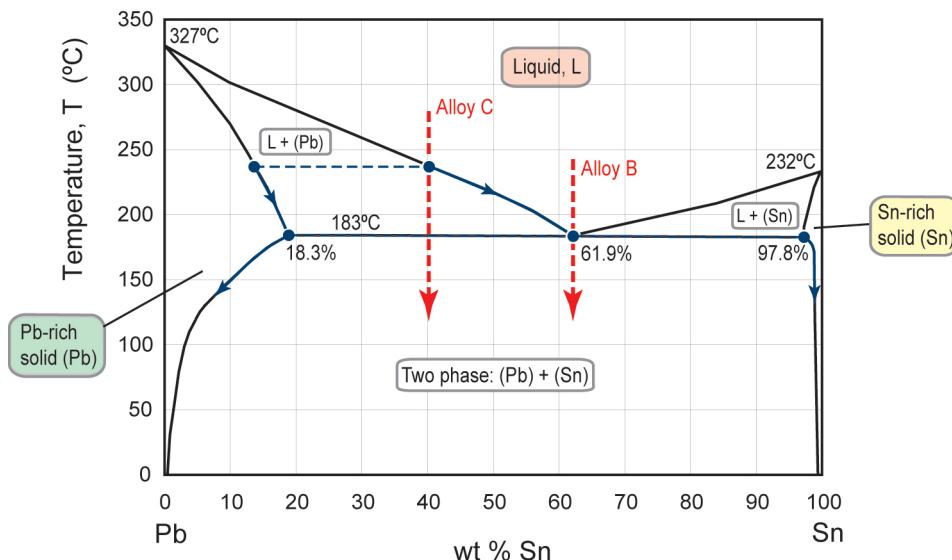


Figure 26: Pb-Sn phase diagram: solidification of eutectic alloy (B) and an off-eutectic alloy (C).

**Now do Examples Paper 1, question 18.**

So how does the eutectic reaction 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 (solid) regions in which each dominates. This must happen at the interface between the liquid and the resulting 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 27a shows a micrograph of eutectic Al-Si (the phase diagram for this system is investigated in the Examples Paper).

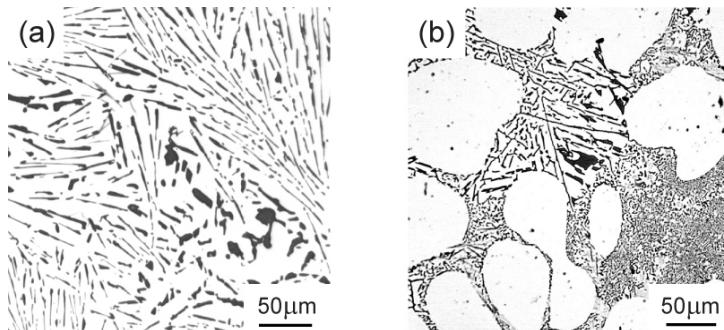


Figure 27: Optical micrographs of (a) eutectic Al-Si alloy;  
 (b) off-eutectic Al-Si alloy, showing grains of primary (Al) (white).  
 (Images courtesy of ASM Micrograph Center, ASM International, 2005)

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 the Pb-Sn system. 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 the Al-Si system (see Examples Paper).

Note in Figure 27a 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 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 (Figure 26) 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.

***Off-Eutectic Solidification***

*The section in the text box below is also covered online with a step-by-step animation to help your understanding.*

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 temperature, 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-40wt% Sn (see Figure 26 – alloy C). The transformations and reactions are as follows, leading to the microstructure evolution illustrated in Figure 28.

- *Above 235°C:* Single-phase liquid; no phase reactions.
- *From 235°C to 183°C:* The *liquidus line* is reached at 235°C and nuclei of Pb-rich solid solution appear. 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 %* (40) is roughly half way between that of the new (Pb) solid (18.3wt%) and the residual liquid (61.9wt%); so the alloy is about half liquid, half solid, by weight (and very roughly by volume, neglecting the difference in phase densities).
- *At 183°C:* The remaining liquid has reached the *eutectic point*, and this liquid undergoes solidification exactly as described before. 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.
- *From 183°C to room temperature:* The two types of microstructure each evolve:
  - (a) The primary 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.

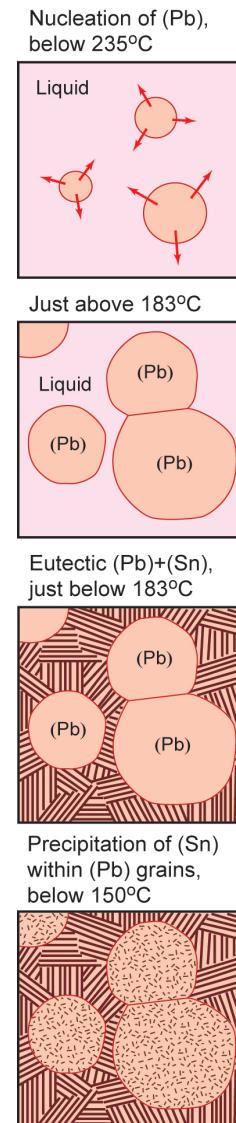


Figure 28: Schematic microstructure evolution in solidification of a dilute Pb-40wt% Sn alloy.

The final microstructure combines all of the features discussed so far. Note that in this final microstructure there are still 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 27b shows a micrograph of an off-eutectic Al-Si alloy – note how this compares with the 100% eutectic microstructure in Figure 27a. Now we have primary Al grains, 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).

**Now do Examples Paper 1, questions 19-22.**

#### 5.4. 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 29 shows the relevant section of the Fe-C phase diagram.

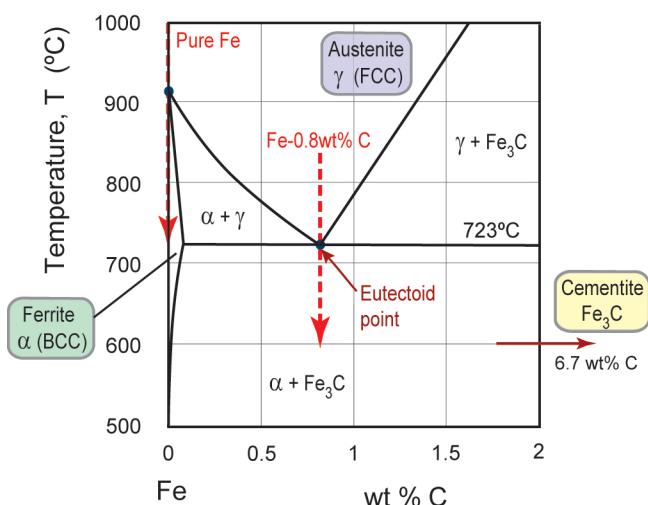


Figure 29: Fe-C phase diagram for compositions of carbon steels below 1000°C, showing cooling of pure Fe and a plain carbon steel of eutectoid composition, Fe-0.8wt%C.

#### Cooling of Pure Iron

First consider cooling of pure iron, starting with FCC  $\gamma$ -iron at 1000°C (Figure 29). At 910°C, a solid-state change to BCC  $\alpha$ -iron occurs (at constant temperature). *Nucleation* starts at the grain boundaries, where there is more space for BCC nuclei to form. The  $\alpha$  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 30b). The interface migrates in the opposite direction to the atomic jumps. Figures 30a,c show the solid-solid transformation underway and complete at 910°C. When the growing  $\alpha$  colonies impinge, new  $\alpha$ - $\alpha$  grain boundaries are formed. Since there is typically more than one  $\alpha$  nucleus per  $\gamma$  grain, the average grain size is reduced by this transformation.

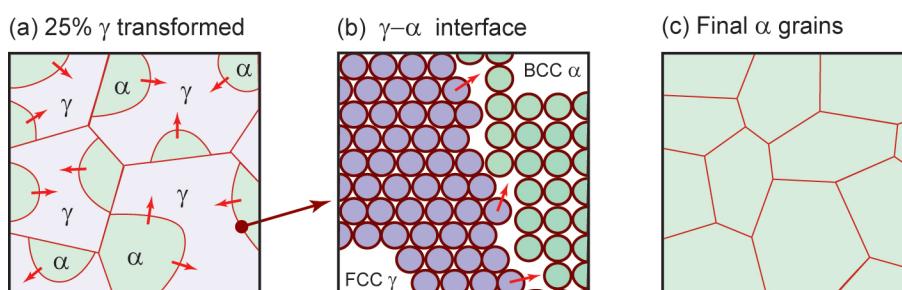


Figure 30: Schematic illustration of the transformation from FCC  $\gamma$ -iron to BCC  $\alpha$ -iron in pure iron:  
 (a)  $\gamma$ - $\alpha$  grain structure after 20% transformation;  
 (b) atomic transfer mechanism at the phase interface;  
 (c) final  $\alpha$ -iron grain structure.

### The Eutectoid Reaction

The eutectoid point in the Fe-C system was introduced in Part 3. Cooling austenite of eutectoid composition (0.8wt% C) is also highlighted on the phase diagram of Figure 29 – it leads to complete transformation to ferrite and cementite, at the (constant) eutectoid temperature, 723°C.

More generally we can 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  $\beta$ .

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, FCC austenite containing 0.8wt% C changes into BCC ferrite (containing almost no carbon) and cementite, with its own lattice structure ( $\text{Fe}_3\text{C}$ , containing 6.7wt% C, or 25 atomic % carbon). The transformation mechanism must therefore enable changes in the lattice structures of the three phases, together with a redistribution of carbon atoms into phases of high and low concentration. Figure 31 illustrates the eutectoid transformation in carbon steels.

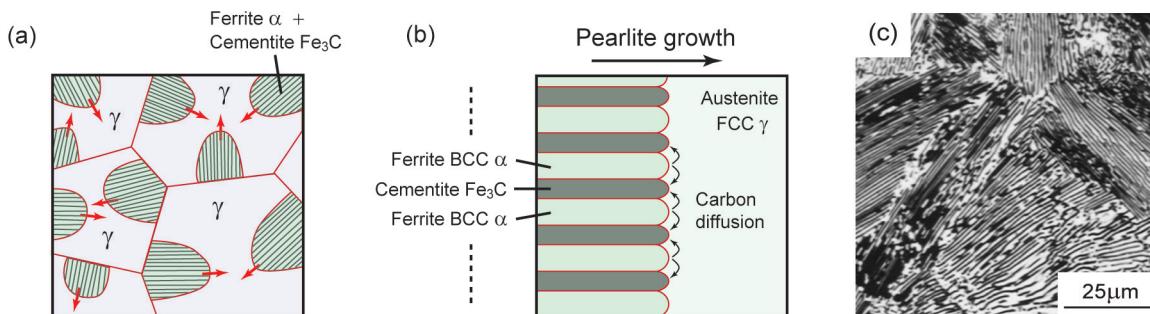


Figure 31: The eutectoid transformation from austenite to pearlite in carbon steel.

- (a) nucleation of pearlite on austenite grain boundaries;
- (b) schematic view of austenite-pearlite interface;
- (c) micrograph showing grains of 100% pearlite.

(Image courtesy of ASM Micrograph Center, ASM International, 2005)

Nuclei of small plates of ferrite and cementite form at the grain boundaries of the austenite. The plates of ferrite and cementite grow in tandem, consuming the austenite as they go (Figure 31a). The transformation is complete when the ferrite-cementite regions impinge, forming grain boundaries. Just ahead of the interface between the austenite and the growing phases, carbon diffusion takes place on a local scale (Figure 31b), to enable the ferrite and cementite to form with their respective carbon contents.

This 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 32c shows 100% pearlite, at high magnification, revealing the alternate plates of ferrite (white) and cementite (black).

Note that the lamellar (plate-like) pearlite structure again has a very large area of phase boundary between ferrite and cementite, with associated surface energy penalty. However, it is the kinetics that 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. Once again, the phase diagram just tells us what phases should form – not how they do it.

The length scale of the plates in pearlite is also much finer than in a eutectic, being formed by solid-state diffusion. At low magnification, pearlite may just appear as dark etching grains. This is easily mistaken for a single phase, which 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

The section in the text box below is also covered online with a step-by-step animation to help your understanding.

Some commercial steels have a eutectoid composition – the steel used for a 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 32). 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 0.8wt% 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 33 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.

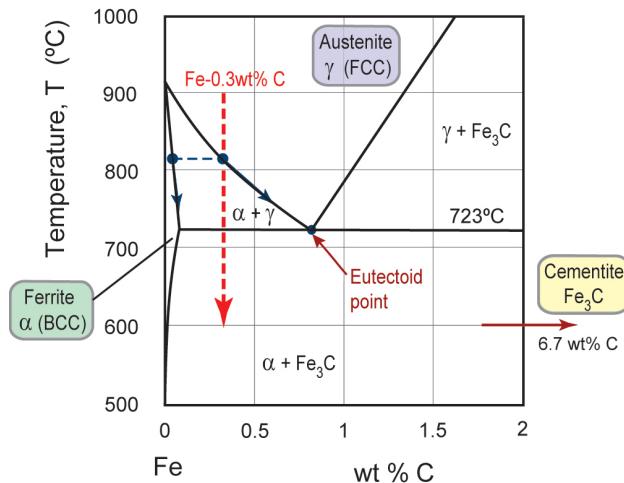


Figure 32: Fe-C phase diagram for compositions of carbon steels below 1000°C, showing cooling of a hypo-eutectoid carbon steel, Fe-0.3wt%C.

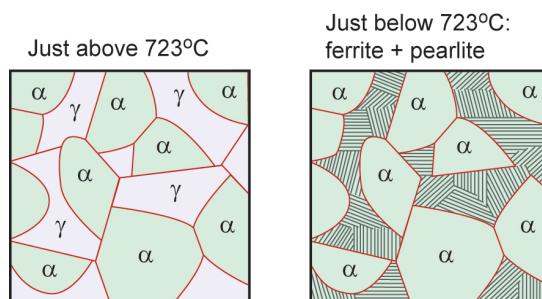


Figure 33: Schematic illustration of microstructure evolution in a 0.3wt% C hypo-eutectoid steel, from austenite to ferrite + pearlite.

***Strength and Toughness of Carbon Steels***

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 (more on this in labs and lectures).

*Now do Examples Paper 1, questions 23-25.*

***Further Reading***

Ashby M.F., Shercliff H.R. and Cebon D. (2010, 2014, 2019) Materials: Engineering, Science, Processing and Design, Butterworth-Heinemann, 2<sup>nd</sup>, 3<sup>rd</sup> or 4<sup>th</sup> edition. ISBN 978-0-08-102376-1 (*Design-led treatment of materials and processes, starting from applications and drilling down into the relevant science. Chapter 19 and a longer version of this document extend the coverage of phase diagrams to thermodynamics and non-equilibrium phase transformations.*)

Ashby, M.F. and Jones, D.R.H. (2013) Engineering Materials II: An Introduction to Microstructures and Processing, Butterworth-Heinemann, 4th edition. ISBN 978-0-08-096668-7 (*Popular treatment of material classes, and how processing affects microstructure and properties.*)