

TALAT Lecture 1203

Phase Diagrams

14 pages, 13 Figures

Basic Level

prepared by **M H Jacobs** *
Interdisciplinary Research Centre in Materials
The University of Birmingham, UK

(Based on approach adopted by Dr D J Stratford of The School of Metallurgy & Materials at the University of Birmingham)

Objectives

To develop a qualitative understanding of binary phase diagrams by reference to the model systems Cu-Ni, Ni-Pt, Au-Ni and Ag-Cu, and also by reference to the Phase Rule.

To apply the basic concepts of phase diagrams to binary aluminium alloys.

To extend the discussion to an outline of ternary phase diagrams, and to show how a so-called pseudo-binary section can be applied with benefit to the Al-Mg-Si system for alloys balanced in Mg_2Si .

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1203 Phase Diagrams

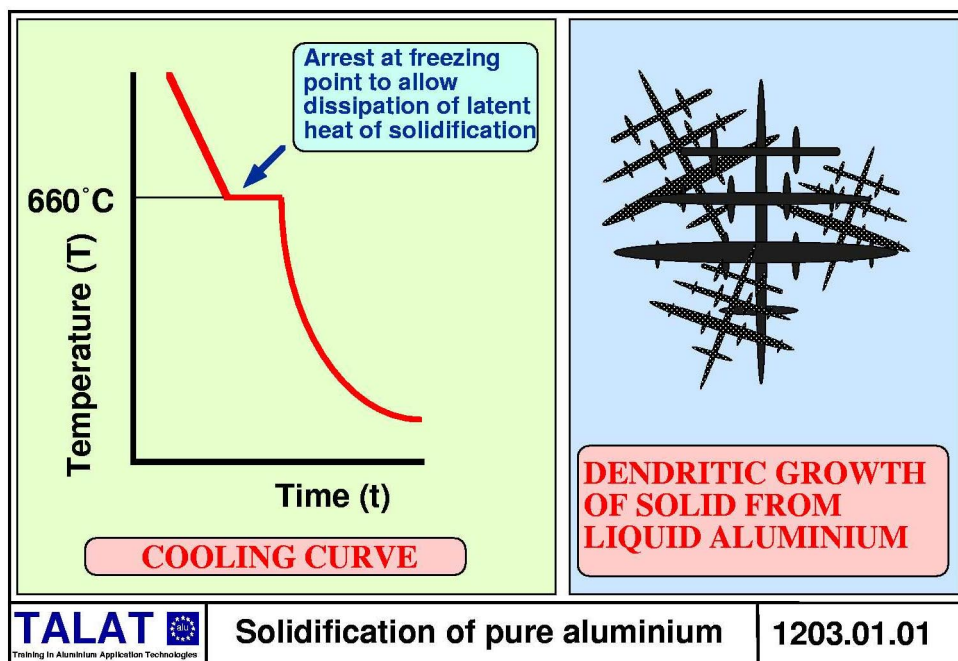
Contents

1203 Phase Diagrams	2
1203.01 Introduction to binary and ternary phase diagrams	3
1203.01.01 Background - single and two component systems	3
1203.01.02 Model binary systems	5
(a) <u>Cu-Ni</u>	5
(b) <u>Ni-Pt</u>	7
(c) <u>Au-Ni</u>	8
(d) <u>Ag-Cu</u>	9
1203.01.03 Some important aluminium-rich binary systems	9
1203.01.04 Ternary phase diagrams	11
1203.02 Pseudo-binary diagrams (particularly Al- Mg₂Si)	12
1203.03 References	14
1203.04 List of Figures	14

1203.01 Introduction to binary and ternary phase diagrams

1203.01.01 Background - single and two component systems

Super-pure aluminium is a single component material, that is, the only material is aluminium: below its melting point it is a single phase solid (crystalline aluminium with a face-centred cubic structure - see [lecture 1201](#)); above its melting point it is a single phase liquid; and at atmospheric pressure it has a unique melting point at 933°K (660°C) which is co-incident with its freezing point when solidifying from liquid to solid. Experimentally, the freezing point may be determined by measurement of a cooling curve from liquid to solid, as shown schematically in [Figure 1203.01.01](#). The transformation from liquid to solid during solidification at the freezing point is accompanied by the evolution of latent heat. This causes a temporary arrest in the cooling curve at the freezing point.



Solidification occurs by the nucleation and growth of dendrites of solid aluminium, [Figure 1203.01.01](#) (see also [lecture 1201](#) and [Figure 1201.03.06](#)). During the growth of dendrites, two phases are present; the solid dendrites and the remaining liquid. According to **Gibb's Phase Rule**, see box below, at a constant pressure of one atmosphere the temperature of solidifying aluminium remains constant until solidification is complete (pure aluminium is a single component system ($c = 1$), two phases are present during solidification ($p = 2$); hence, $f = 0$ and there are no degrees of freedom, so the temperature cannot be a variable according to the phase rule and is constant).

Gibb's Phase Rule

This states that if a system containing c components and p phases is in equilibrium then the number of degrees of freedom f is given by the relationship:

$$p + f = c + 2$$

A degree of freedom is a variable such as temperature (T), pressure (P) or composition (X_a , X_b , etc).

For the purposes of this lecture, the pressure (P) is constant at one atmosphere; hence, one degree of freedom is lost and the Phase Rule for this special case becomes

$$p + f = c + 1 \quad (\text{at constant pressure})$$

The above argument assumes that the pressure environment is inert. In practice this probably will not be true, and is more likely to be air. In one atmosphere of air, oxygen reacts immediately with aluminium at the air / aluminium interface to produce a second phase, aluminium oxide. This reaction applies not only to pure aluminium but to all of its alloys - we shall take it 'as read' in the presentation below in which we concentrate on the interactions between the metallic components in aluminium alloys.

In general, engineering materials are composed of a system of more than one component and more than one phase. This applies to aluminium alloys. A phase is a region of system that is separated from the remainder by a mechanical interface. Again in general, each different phase will have a characteristic composition and crystal structure.

Let us take as an example the system of aluminium and iron. Atoms of aluminium have a diameter of 0.29nm, which is much larger than the diameter of an iron atom at 0.25nm [1] (see also [Figure 1201.03.02](#) in lecture 1201). At a high temperature, in the liquid state, atoms are far apart; consequently, liquid aluminium will readily mix with liquid iron to produce a system composed of a single phase - a solution of liquid aluminium and iron.

The situation is very different at around room temperature in the solid state. The large atomic size difference and the fact that solid aluminium is face-centred cubic and solid iron is body-centred cubic at low temperatures mean that there is extremely low solubility between aluminium and iron in the solid. Consequently, iron is regarded as an 'impurity' in 1xxx type wrought alloys of 'commercially pure' aluminium, in which it appears as particles of an 'intermetallic phase' FeAl_3 .

A phase diagram (often also called an equilibrium diagram) is a convenient way of representing the phases present in an alloy system at equilibrium as a function of composition and temperature (remember, pressure is one atmosphere). A system of two components is known as a 'binary system' ; one with three components as a 'ternary system', and so on.

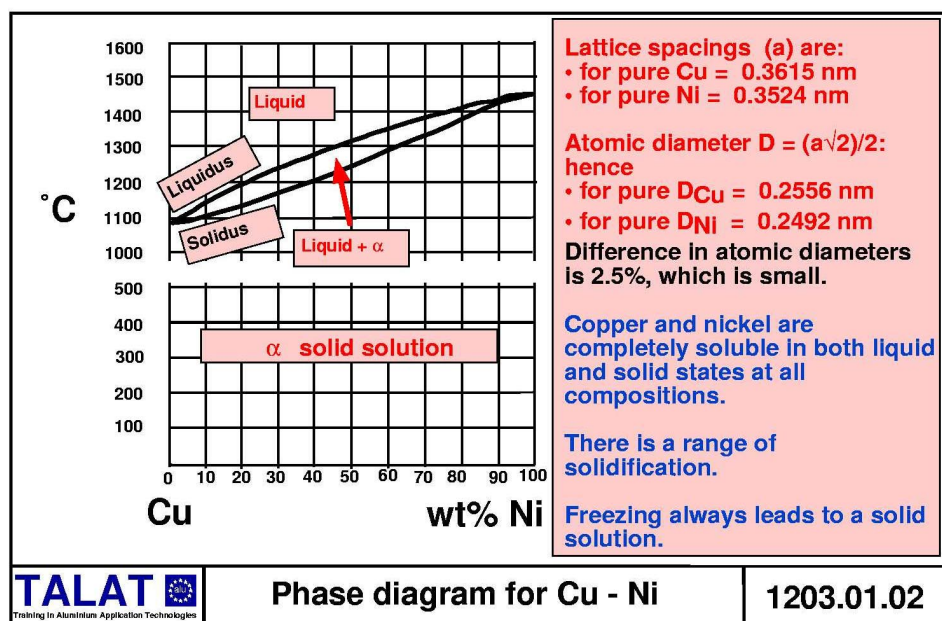
Clearly, the aim of this lecture is to demonstrate how phase diagrams can be used to

aid the appreciation and interpretation of how aluminium alloys respond to mechanical processing and heat treatment, topics of great importance to the understanding of the metallurgy of aluminium alloys. Unfortunately, phase diagrams of aluminium alloys are not of the simplest type and their interpretation requires some prior knowledge. This prior knowledge is developed in the next section, where the principles for simple systems of Cu-Ni, Ni-Pt, Au-Ni and Ag-Cu are presented. This will put us in the position, later in this lecture, to look at binary and ternary diagrams for aluminium alloys.

1203.01.02 Model binary systems

(a) Cu-Ni

Let us begin with the simplest of all metallic binary systems; one in which there is complete solubility (mixing and complete miscibility of atoms) in both the liquid and solid states. Alloys of copper (Cu) and nickel (Ni) are an example of such a system. The phase diagram for Cu-Ni is shown in **Figure 1203.01.02**, where the diagram follows the normal presentation, with the ordinate as temperature and the abscissa is composition, plotted in this case as wt% Ni (Note: an abscissa in atomic % is an alternative presentation, but we will use weight % in this lecture).

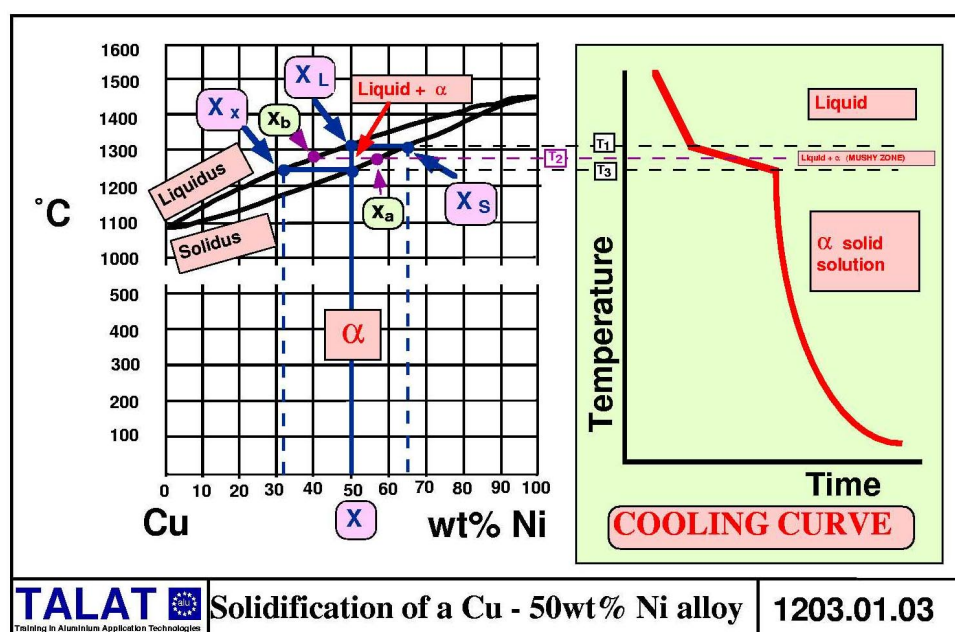


The first point to note is that pure solid copper and pure solid nickel both have face-centred cubic crystal structures (see **Figure 1201.02.05**) with closely similar lattice spacings, see **Figure 1203.01.02** (here, the lattice spacing a is defined as the length of the cube edge of the unit cell). For pure copper $a = 0.3615$ nm and for pure nickel $a = 0.3524$ nm [1]. Furthermore, the atomic diameter for each metal may be defined as the nearest neighbour distance, which for a fcc structure is given by $(a\sqrt{2})/2$. Hence the atomic diameter for pure copper is 0.2556 nm and for pure nickel is 0.2492 nm. The difference in atomic diameters is small at 2.5%. For all of these reasons, together with other thermodynamic and electron structure reasons which are outside the scope

of this lecture [2,3], copper and nickel are fully soluble (miscible) in the solid state - they form a continuous solid solution at all compositions - this is represented on the phase diagram of the system, **Figure 1203.01.02**. Note that, apart from the pure elements, all alloys of Cu and Ni have a range of temperatures over which solidification (freezing) occurs - the field is defined by the liquidus and solidus lines on the phase diagram. We now need to look more closely at the consequences of this.

In **Figure 1203.01.03** consider an alloy X composed of Cu + 50wt% Ni, initially at some high temperature, say 1,400°C; the liquid is a uniform solution X_L of Cu and Ni. Next, consider what happens if this liquid is slowly cooled. When the temperature has fallen to T_1 and just below, the liquidus line is intersected and solidification begins. The first solid that forms is of composition X_S , approximately 65wt% Ni in the example, **Figure 1203.01.03**. As cooling proceeds under equilibrium conditions, the compositions of the solid formed and the remaining liquid follow precisely those defined by the solidus and liquidus lines (this, in fact, is how the phase diagram is determined experimentally in the first place). For example, at a temperature T_2 , the composition of the solid is X_a and of the liquid, X_b ; the relative amounts of solid phase (α solid solution) and liquid are given by the **lever rule**, as follows:

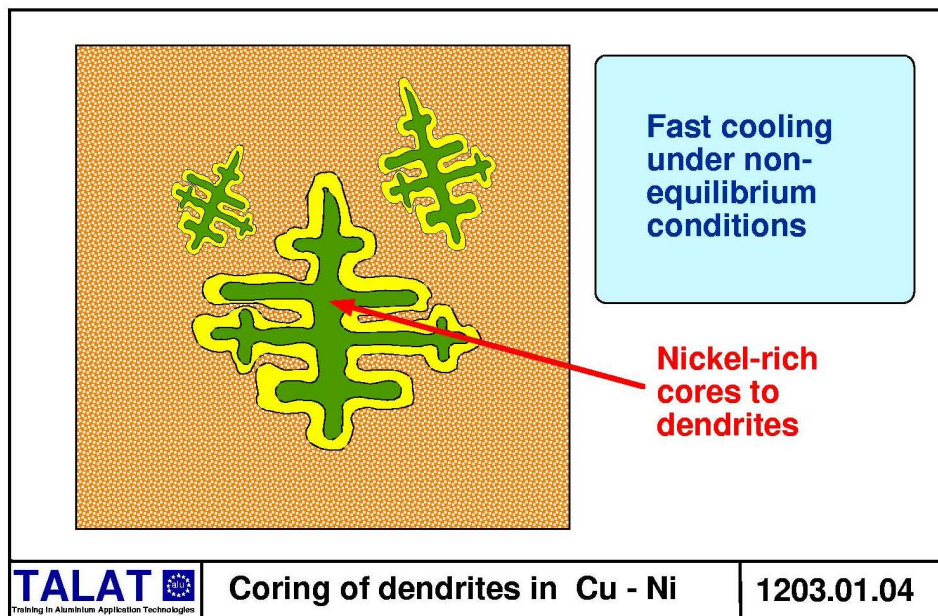
$$\frac{\text{amount of } \alpha \text{ phase}}{\text{amount of liquid}} = \frac{X_b - X}{X - X_a}$$



Clearly at temperature T_2 , indeed at any temperature between T_1 and T_3 , two phases are present in equilibrium - α solid solution and liquid. According to Gibb's phase rule, we have a two component system, with Cu and Ni ($c = 2$) and two phases, with solid and liquid ($p = 2$), hence there is one degree of freedom ($f = 1$), which allows temperature to be a variable. In physical terms, this means that solidification takes place over a range of temperature, as indicated in **Figure 1203.01.03**. The mixture of solid and liquid is often referred to as 'mushy material'. When the temperature has fallen to T_3 , the alloy emerges from the mushy zone and the last solid to freeze will have composition, X.

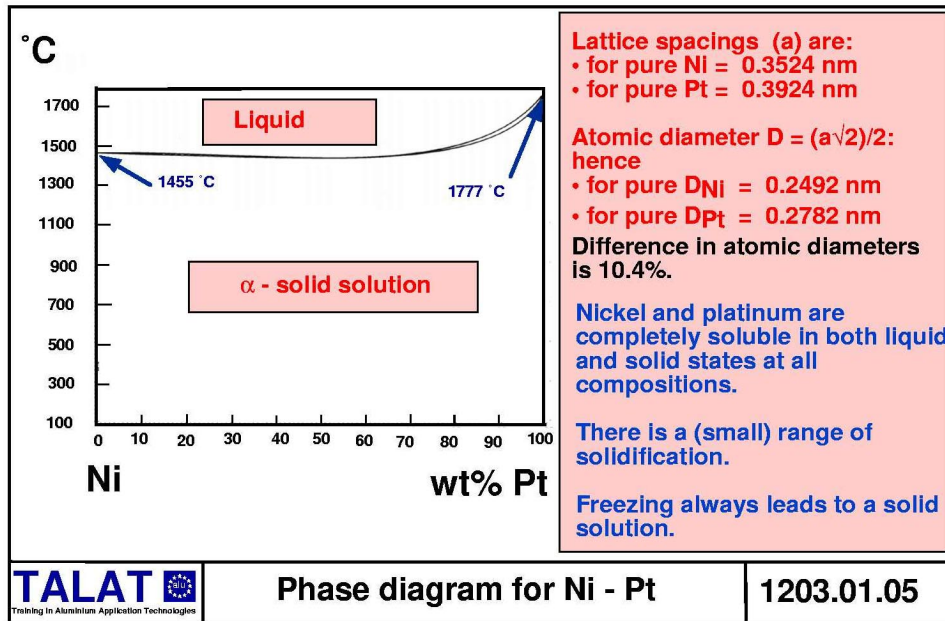
Under true equilibrium conditions (that is, extremely slow cooling) the solid solution constantly changes its composition by diffusion such that, upon reaching T_3 , the material is 100% solid and of uniform composition X (Cu + 50wt% Ni in [Figure 1203.01.03](#)).

In practice, the solidification of alloys during industrial processing is never at a sufficiently slow cooling rate for equilibrium to be maintained. Time is not available for composition gradients to be removed by diffusion and dendrites with spines rich in the first solid solution to be solidified are retained. In the case of Cu-Ni, the spines are rich in nickel. This leads directly to coring of the α - solid solution dendrites, [Figure 1203.01.04](#), where the core of each dendrite is rich in Ni. As indicated above, coring is common place at commercially used cooling rates and this leads directly to variations in composition - **microsegregation**. Microsegregation is usually on a relatively large scale of distance - many μm - and, because of the large diffusion distances involved, a long homogenisation treatment is required at a high heat treatment temperature in order to obtain an α -solid solution of uniform composition.



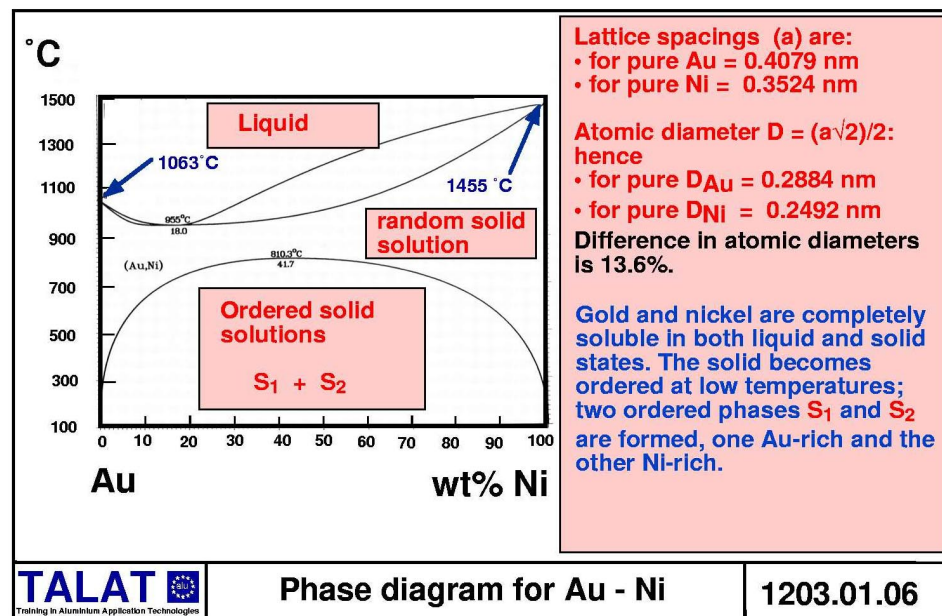
(b) Ni-Pt

Let us now move on to another binary system, Ni-Pt, see [Figure 1203.01.05](#), where again both pure elements are fcc but the difference in atom diameters is larger at 10.4%. The larger atomic size difference depresses the solidification temperature, but it is not too big to prevent the atoms in the solid state from existing at random sites on the same crystal lattice at temperatures down to room temperature - the diagram is spanned by a complete series of random α - solid solutions.



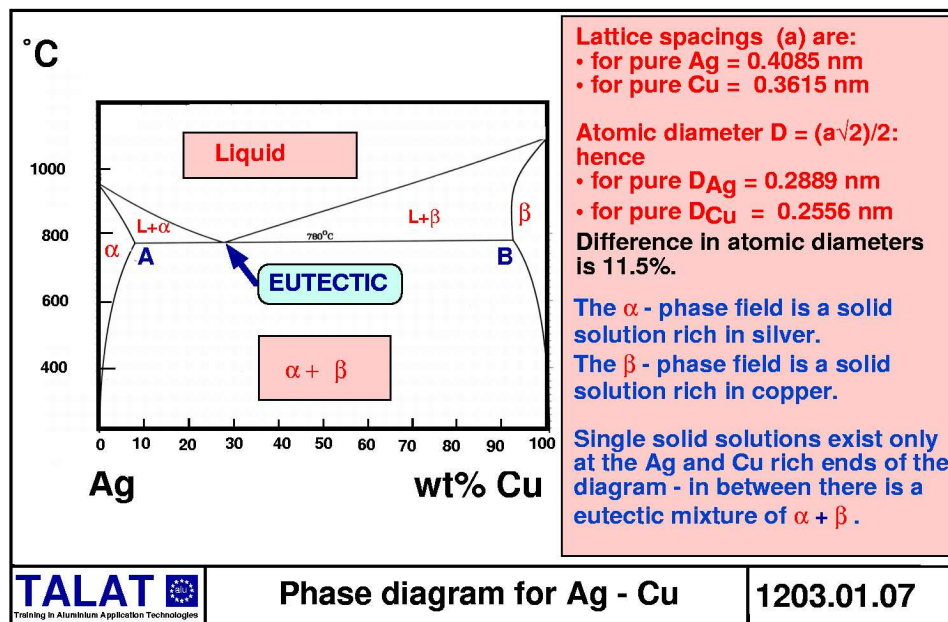
(c) Au-Ni

Figure 1203.01.06 is the phase diagram for Au-Ni, again both fcc but with an even bigger atomic size difference of 13.6%. There is still mutual solubility in the solid state, but at low temperatures the size difference is accommodated by random mixing being replaced by clustering via diffusion of higher compositions of atoms of similar type [2]. Two distinct phases, S_1 rich in Au and S_2 rich in Ni are formed, whose composition depends on the alloy composition and the temperature and cooling rate.



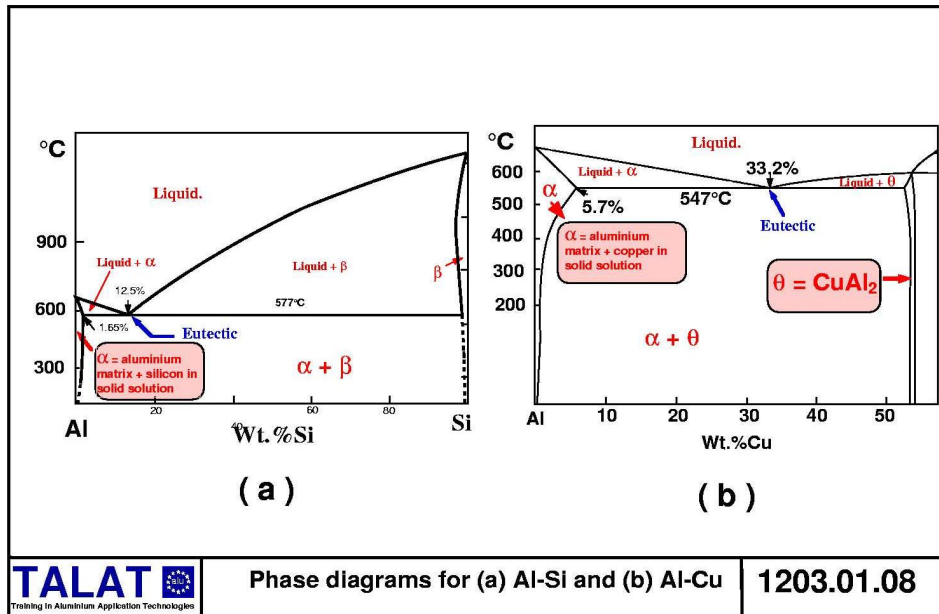
(d) Ag-Cu

Figure 1203.01.07 shows the phase diagram for Ag-Cu, again both fcc and with a large difference in atom size at 11.5%. In this case, there is no single solid solution across the whole wide of the diagram; only end members α and β , which are characterised by increasing solid solubilities up to maxima A and B at the so-called eutectic temperature (780°C in the specific case of Ag-Cu). It is emphasised at this point that this feature of increasing solid solubility with temperature will be extremely important when we come to look at aluminium alloys, because it is central to the topic of precipitation hardening. Solid alloy between the end member solid solutions consists of a so-called eutectic mixture of two phases α and β .



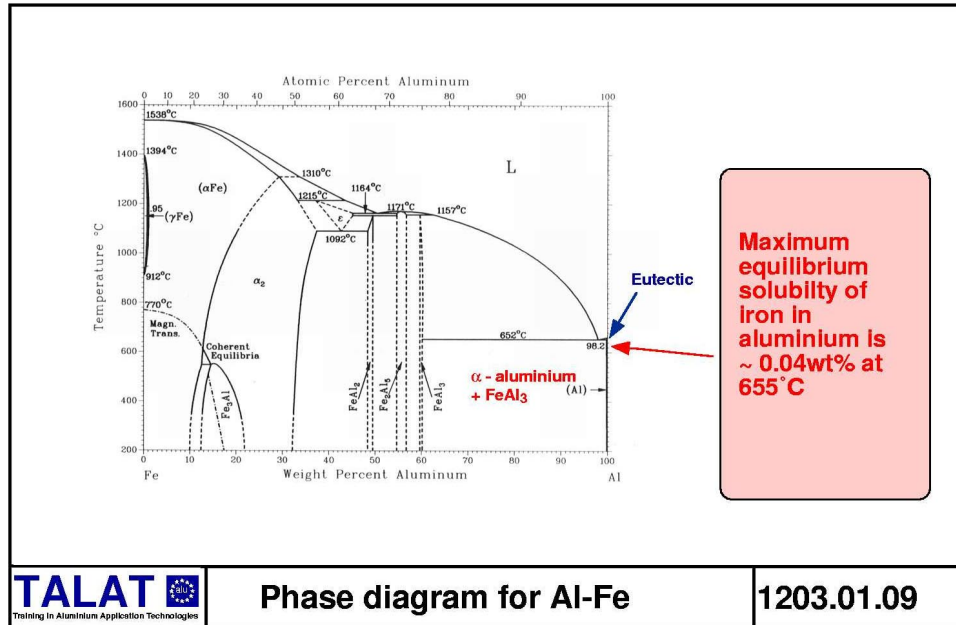
1203.01.03 Some important aluminium-rich binary systems

Figure 1203.01.08 shows two important systems, Al-Si and Al-Cu. Both are eutectic systems. Al-Si is a classical eutectic system, with a phase diagram with characteristics similar in that of the Ag-Cu phase diagram presented above. Alloys of Al and Si are important as casting alloys and we will return to this system in **lecture 1205**.



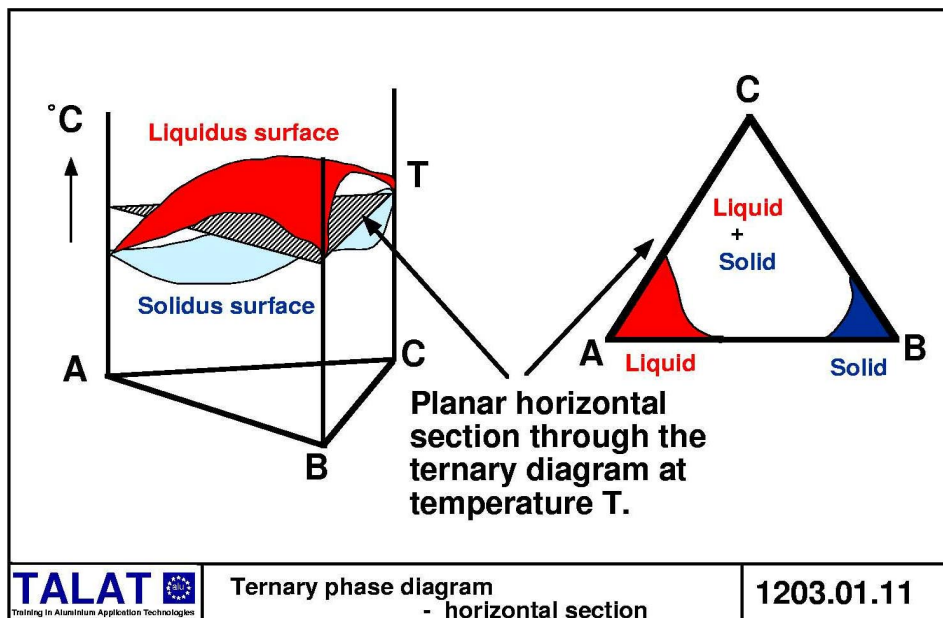
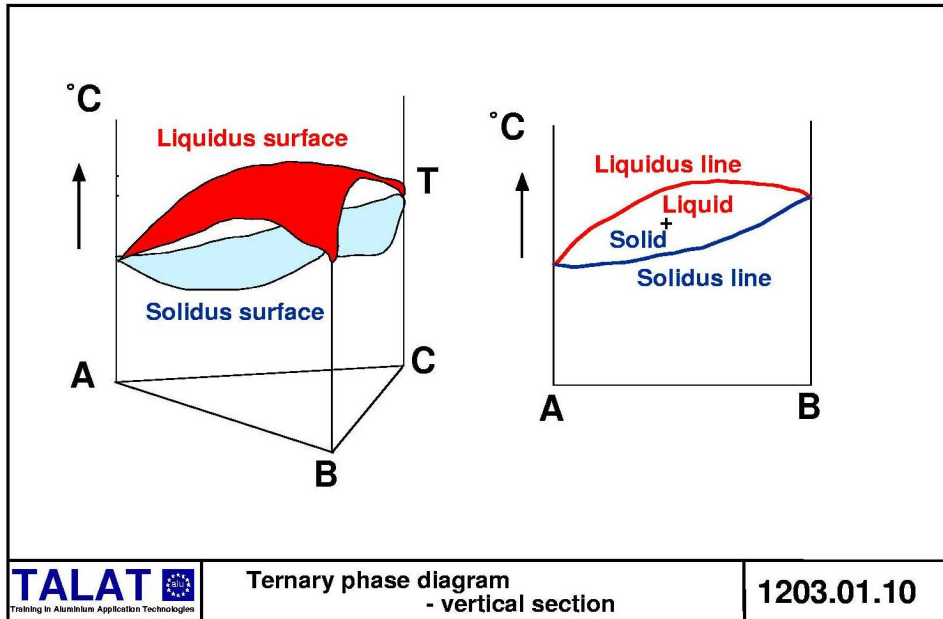
The Al-Cu system is important as a classical precipitation hardening system for alloys of up to $\sim 4\text{wt}\%$ Cu, and we will look in much more detail at this system in the next [lecture 1204](#). It is to be noted that the equilibrium eutectic phases are α and θ , where θ is the intermetallic phase CuAl_2 .

Finally, let us return to where we began with the Al-Fe system. The phase diagram for Al-Fe is shown in [Figure 1203.01.09](#). Two points are to be noted: (1) the solubility of Fe in Al is extremely small, only $0.04\text{ wt}\%\text{Fe}$ at 655°C and decreasing to virtually zero at room temperature; and (2) the second equilibrium eutectic phase is the intermetallic phase FeAl_3 . Hence, the problem associates with iron as an impurity in aluminium that we looked at the beginning of this lecture. At this point, however, it must be emphasised that phase diagrams deal with equilibrium situations and, for example, rapid quenching can and does introduce quite different metallurgical considerations - in fact, novel alloys based on very rapidly quenched Al- $8\text{wt}\%\text{Fe}$ contain interesting non-equilibrium structures with potentially valuable mechanical properties - this is discussed in [lecture 1254](#).



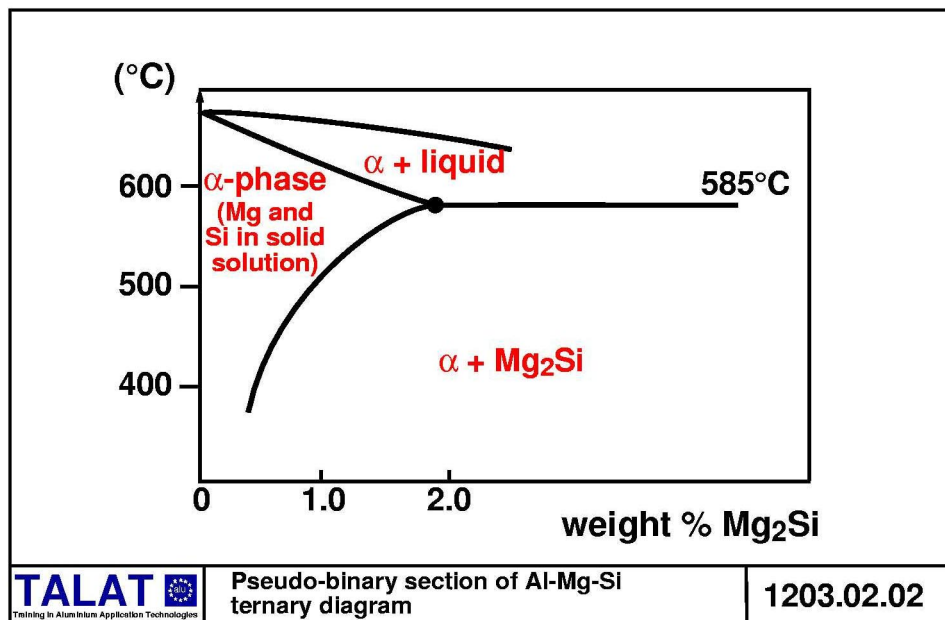
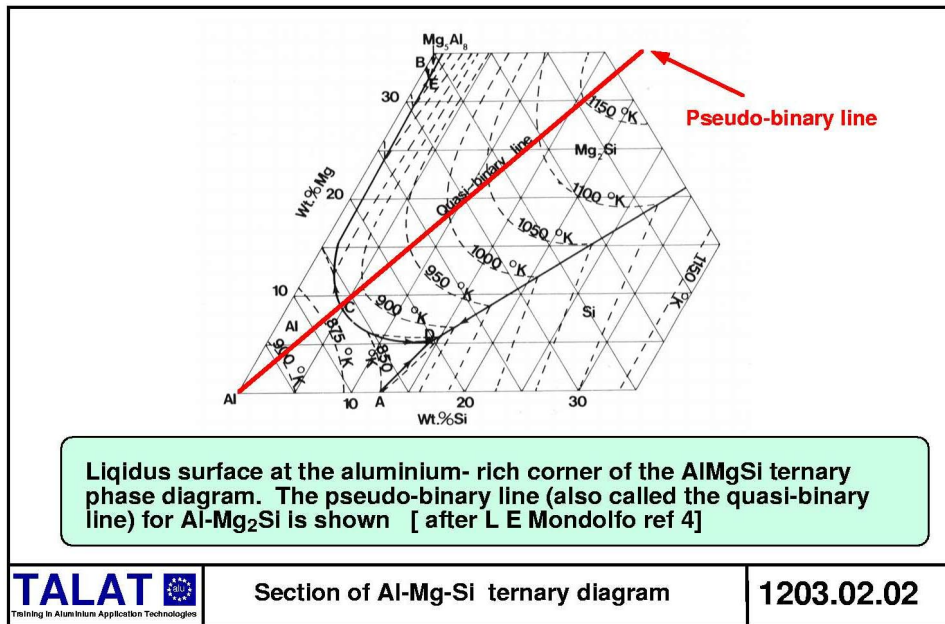
1203.01.04 Ternary phase diagrams

The concepts presented above for binary systems may all be extended to three component systems (and indeed higher order systems), the main problem being in the complexity of presenting the data on paper. The situation is illustrated in [Figure 1203.01.10](#) which is a three-dimensional representation of a hypothetical system of three components A, B and C, all alloys of which exhibit solid solubility. A vertical binary section for A and B components will be as we have discussed above. Similar vertical sections could be drawn for binary alloys A + C and B + C. A planar horizontal section of such a ternary diagram shows equilibrium phases present at the temperature T selected; this is demonstrated in [Figure 1203.01.11](#). It is also common practice to show non-planar horizontal sections in the form of contour maps where, for example, isotherms of temperature are displayed. This is illustrated below for an example of great importance to the metallurgy of commercial aluminium alloys - for the AlMgSi system.



1203.02 Pseudo-binary diagrams (particularly Al- Mg_2Si)

Figure 1203.02.01 shows the liquidus surface at the aluminium-rich corner of the AlMgSi ternary phase diagram [4]. Also shown is the pseudo-binary line (also called the quasi-binary line) for the composition Al- Mg_2Si . The pseudo-binary section of the AlMgSi system is extremely important because a series of commercially-important engineering alloys are based on the composition Al- Mg_2Si . The equilibrium phase in these alloys is Mg_2Si - hence, a pseudo-binary section, similar to the Al- $CuAl_2$ binary for Al-Cu, **Figure 1203.01.08**, is of value and is shown in **Figure 1203.02.02**. This diagram forms the starting point, in lecture 1204, for a detailed presentation of precipitation hardening in Al- Mg_2Si alloys.



1203.03 References

1. Smithells Metals Reference Book, 7th edition, edited by E A Brandes and G B Brook, Butterworth Heinemann, 1992
2. B Chalmers, Physical Metallurgy, John Wiley & Sons / Chapman & Hall, 1959.
3. D A Porter and K E Easterling, Phase Transformations in Metals and Alloys, 2nd edition, Chapman & Hall, 1992.
4. L E Mondolfo, Aluminium Alloys - Structure and Properties, Butterworths, 1976.

1203.04 List of Figures

Figure Nr.	Figure Title (Overhead)
1203.01.01	Solidification of pure aluminium
1203.01.02	Phase diagram for Cu- Ni
1203.01.03	Solidification of a Cu – 50 wt% Ni Alloy
1203.01.04	Coring of dendrites in Cu-Ni
1203.01.05	Phase Diagram for Ni-Pt
1203.01.06	Phase Diagram for Au-Ni
1203.01.07	Phase Diagram for Ag - Cu
1203.01.08	Phase diagrams for (a) Al-Si and (b) Al-Cu
1203.01.09	Phase diagram for Al-Fe
1203.01.10	Ternary phase diagram – Vertical Section
1203.01.11	Ternary phase diagram – horizontal section
1203.02.01	Section of Al-Mg-Si ternary diagram
1203.02.02	Pseudo-binary section of Al-Mg-Si ternary diagram