TALAT Lecture 3204

The Freezing of Castings

22 pages, 20 figures

Basic Level

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Objectives:

− To provide an introduction to solidification theory.
− To achieve an essential background understanding of solidification and cast
 structures.

Prerequisites:

− Basic knowledge of the solidification of metals.

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3204 The Freezing of Castings

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Introduction

The purpose of this lecture is to introduce the theories of solidification of simple alloys under equilibrium and non-equilibrium conditions. These form the scientific foundation for all aspects of the production of castings. We shall also consider nucleation and grain refinement in casting and the modification of the Al-Si eutectic.

Simple Case Analysis

We shall start by considering the movement of a planar solidification front along a bar of liquid metal which contains a solute with an initial concentration of C_O. This type of solidification can be achieved in practice by using a special furnace to impose a steep temperature gradient on a crucible holding the metal.

We shall now consider three limiting cases:

a) Equilibrium Solidification

The first of these is equilibrium solidification (**Figure 3204.00.01**). This assumes that total mixing takes place in both the liquid and the solid. This requires complete diffusion to take place in the solid, which is usually impossible! However, it does apply when solutes have a high diffusion rate, examples being hydrogen or carbon in cast irons and steels, or hydrogen in copper. We then allow the liquid metal to start to solidify so that, at a particular temperature, a certain volume fraction of solid has formed, f_S, leaving a certain volume fraction of liquid, f_L, where $f_S + f_L = 1$.

Solidification under Equilibrium Conditions 3204.00.01
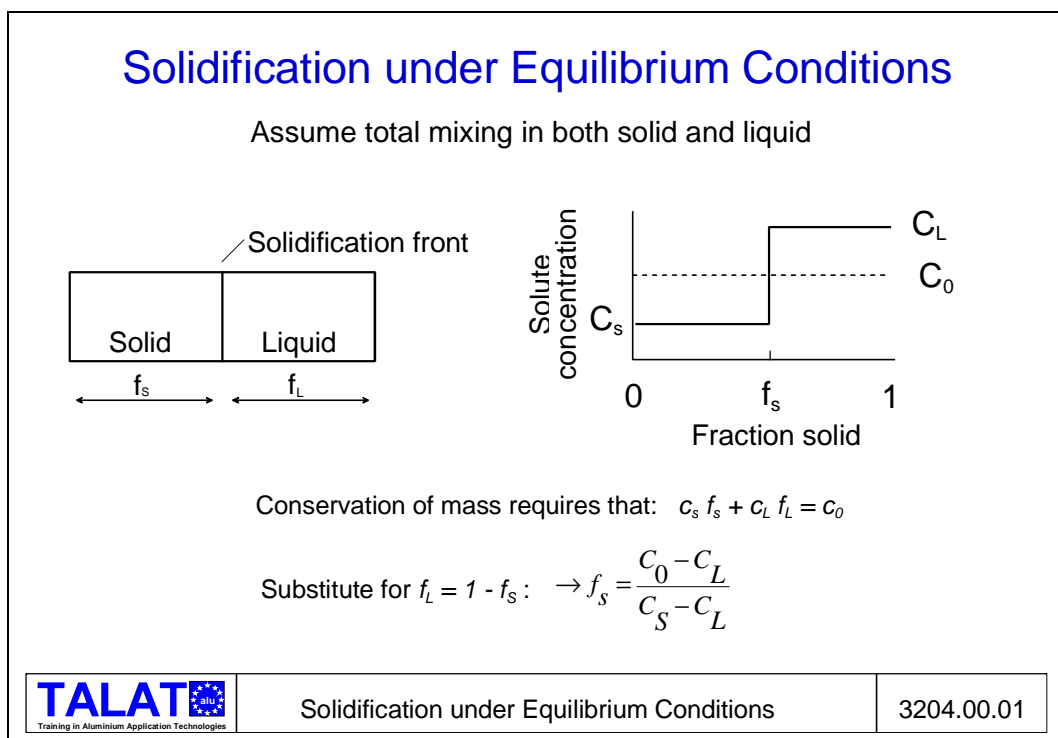
The law of the conservation of mass requires that:

(Solute in solid) + (Solute in liquid) = (total solute)

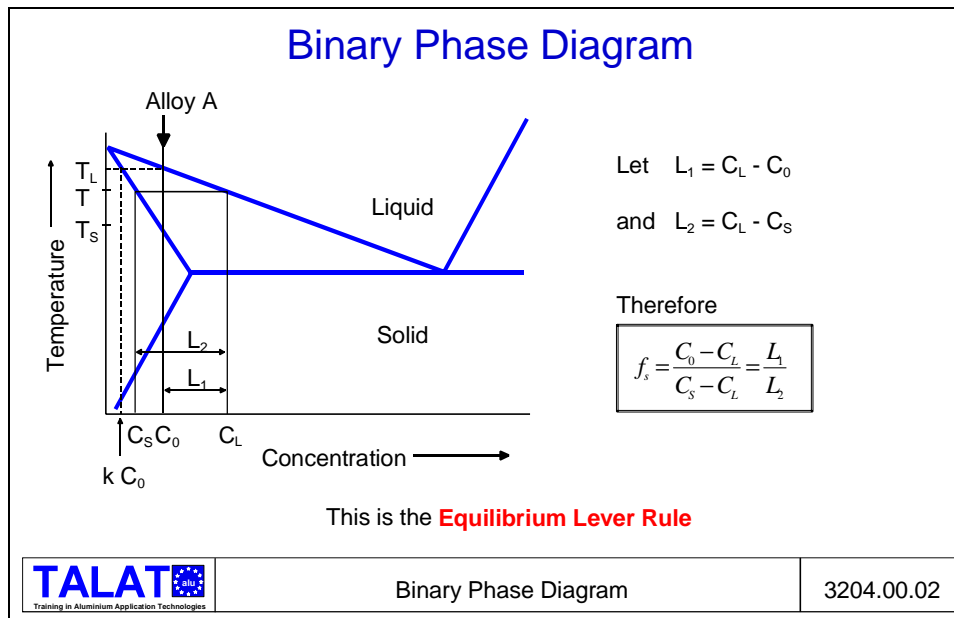and so $\qquad C_S f_S \quad + \quad C_L f_L \quad = \quad C_O \qquad$ (1)

where C_S and C_L are the concentrations of the solute in the solid and liquid respectively.

The above equation can be shown to be merely a re-statement of the lever rule by substituting for f_L. Equation (1) then becomes:

$$C_S f_S \quad + \quad C_L (1 - f_S) \ = \ C_O$$

hence

$$f_S = \frac{C_O - C_L}{C_S - C_L} \qquad (2)$$

Binary Phase Diagram

Alloy A

T_L
T
T_S

Temperature

Liquid

Solid

$C_S\,C_O \qquad C_L$

$k\,C_O$

Concentration

Let $\ L_1 = C_L - C_0$

and $\ L_2 = C_L - C_S$

Therefore

$$f_s = \frac{C_0 - C_L}{C_S - C_L} = \frac{L_1}{L_2}$$

This is the **Equilibrium Lever Rule**

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Binary Phase Diagram | 3204.00.02

Figure 3204.00.02: Reference to this phase diagram shows the cooling of molten Alloy A having an initial solute concentration of C_O, a liquidus temperature of T_L and a solidus temperature of T_S. At a temperature T where the fraction solid is f_S,

$$L_1 \ = \ C_L - C_O \quad \text{and} \quad L_2 \ = \ C_L - C_S$$

and substitution of these values in equation 2 gives:

$$f_S = \frac{L_1}{L_2}$$

which is the equilibrium lever rule.
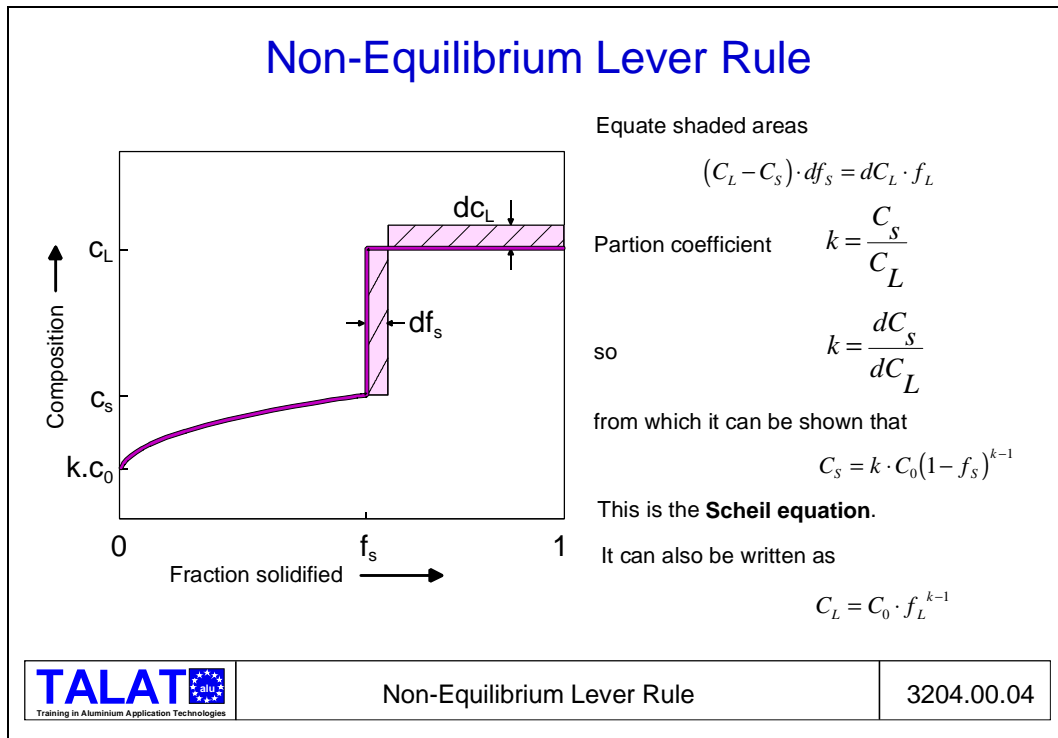
b) Non-equilibrium Analysis

Moving onto the second limiting case, we shall now consider non-equilibrium solidification and derive the Scheil equation which is widely used to describe the solidification behaviour. The top part of **Figure 3204.00.03** again shows the progression of solidification with a front between solid and liquid moving from left to right. The bottom half shows solute concentration as a function of the fraction solid.
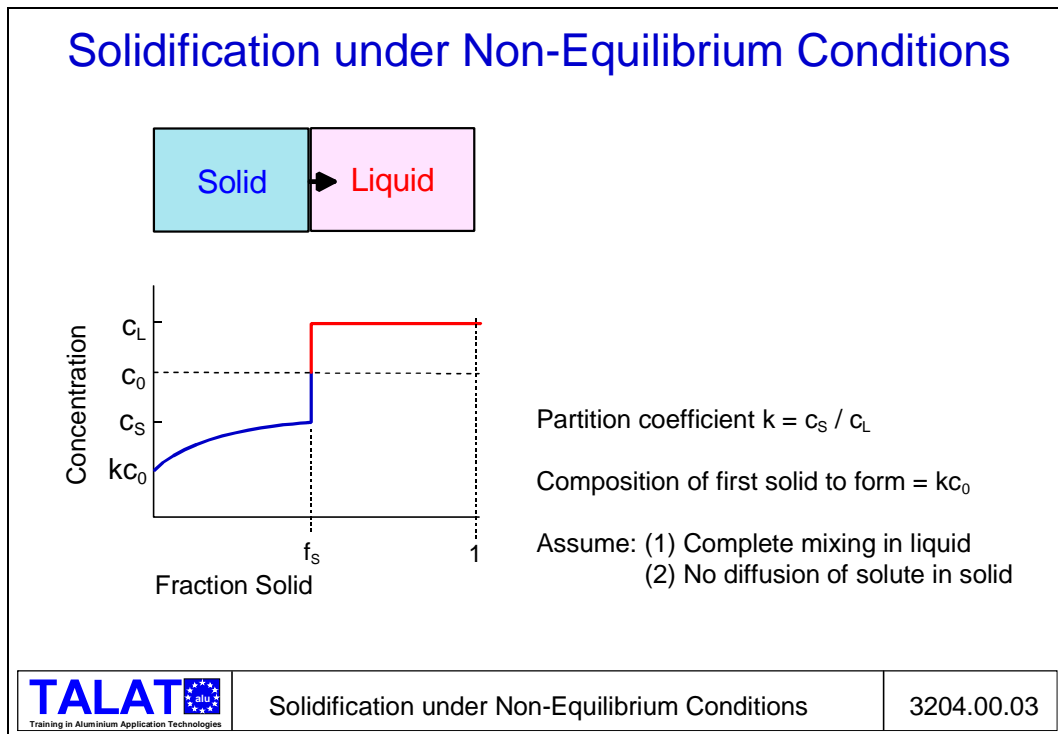
The initial uniform solute concentration in the liquid is C_O. The first solid to form has a composition of $k \cdot C_O$, where k is the partition coefficient and defines how the solute partitions between the solid and liquid phases, i.e. $k = C_S / C_L$. High values of k (close to 1) indicate that the solute is evenly distributed between liquid and solid (i.e. there is little tendency to segregation). As k becomes small (for instance, 0.05 for oxygen in iron), so more and more solute is concentrated in the liquid, i.e. segregation increases (for instance, by a factor of 20 for oxygen in iron).

When the initial solid is formed, the excess solute is rejected ahead of the advancing front. The following assumptions are then made:

1. there is efficient mixing in the liquid so that there is a uniform solute distribution, giving a uniform concentration C_L;
2. there is no diffusion of solute in the solid phase, which can arise if the rate of cooling is high or if the rate of diffusion is low. This is usually quite a good approximation for most substitutional solutes, such as Mn in Fe, or Cu in Al.

Non-Equilibrium Lever Rule

Equate shaded areas

$$(C_L - C_s) \cdot df_s = dC_L \cdot f_L$$

Partion coefficient $\quad k = \dfrac{C_s}{C_L}$

so $\quad k = \dfrac{dC_s}{dC_L}$

from which it can be shown that

$$C_s = k \cdot C_0 (1 - f_s)^{k-1}$$

This is the **Scheil equation**.

It can also be written as

$$C_L = C_0 \cdot f_L^{\,k-1}$$

Figure 3204.00.04 shows the solute concentrations of C_S in the solid and C_L in the liquid. We then allow the solid-liquid interface to advance by a small amount df_S, with the rejected solute increasing the solute concentration in the liquid by dC_L. The shaded areas can be equated, so that

$$(C_L - C_S) \, df_S = dC_L \cdot f_L \tag{3}$$

By definition, $k = C_S / C_L$, hence $k = dC_S / dC_L$.

Eliminating C_L and integrating leads to:

$$C_S = k \cdot C_O (1 - f_S)^{k-1} \tag{4}$$

This is the Scheil equation which is also known as the non-equilibrium lever rule. It can also be written in terms of the liquid:
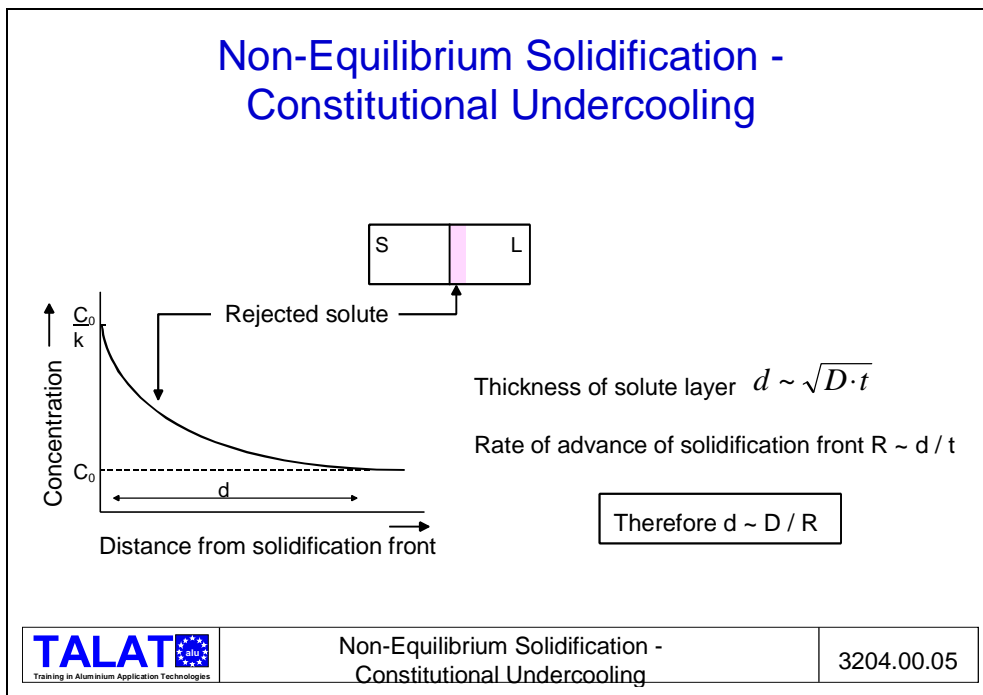
$$C_L = C_O \cdot f_L^{\,k-1} \tag{4}$$

or

$$f_L = \left(\frac{C_L}{C_O}\right)^{\frac{1}{k-1}} = \left(\frac{C_O}{C_L}\right)^{\frac{1}{1-k}}$$

It applies with reasonable accuracy to all substitutional solutes, such as Cu, Zn and Mg in Al, and Cu, Cr and Mn in Fe.

Where higher accuracy is required, there are computational methods which analyse the situation where a limited amount of back-diffusion is occurring in the solid. These techniques give results which are intermediate between perfect equilibrium and perfect non-equilibrium (the Scheil equation). In general, however, the results are closer to the Scheil solution. These approaches are outside the scope of these lectures.

c) Solute Rejection Model

So far, it has been assumed that perfect mixing occurs in the liquid. We shall now consider the third case: in this, as solute is rejected ahead of the advancing front, it diffuses away in the liquid to give a steady-state profile. We again assume that there is no diffusion in the solid. Under these conditions, the solute rejected into the liquid builds up to a peak concentration of C_0/k ahead of the moving front, the effect being like that of a snowplough (**Figure 3204.00.05**).

Non-Equilibrium Solidification - Constitutional Undercooling

Thickness of solute layer $d \sim \sqrt{D \cdot t}$

Rate of advance of solidification front R ~ d / t

Therefore d ~ D / R

| TALAT | Non-Equilibrium Solidification - Constitutional Undercooling | 3204.00.05 |

Solid Front Growth

Close to the solid front, where the liquid is stagnant in a thin boundary layer, the dispersion of the solute into the liquid is controlled by diffusion, so that the thickness of the solute layer, d, can be estimated from the order-of-magnitude relation:
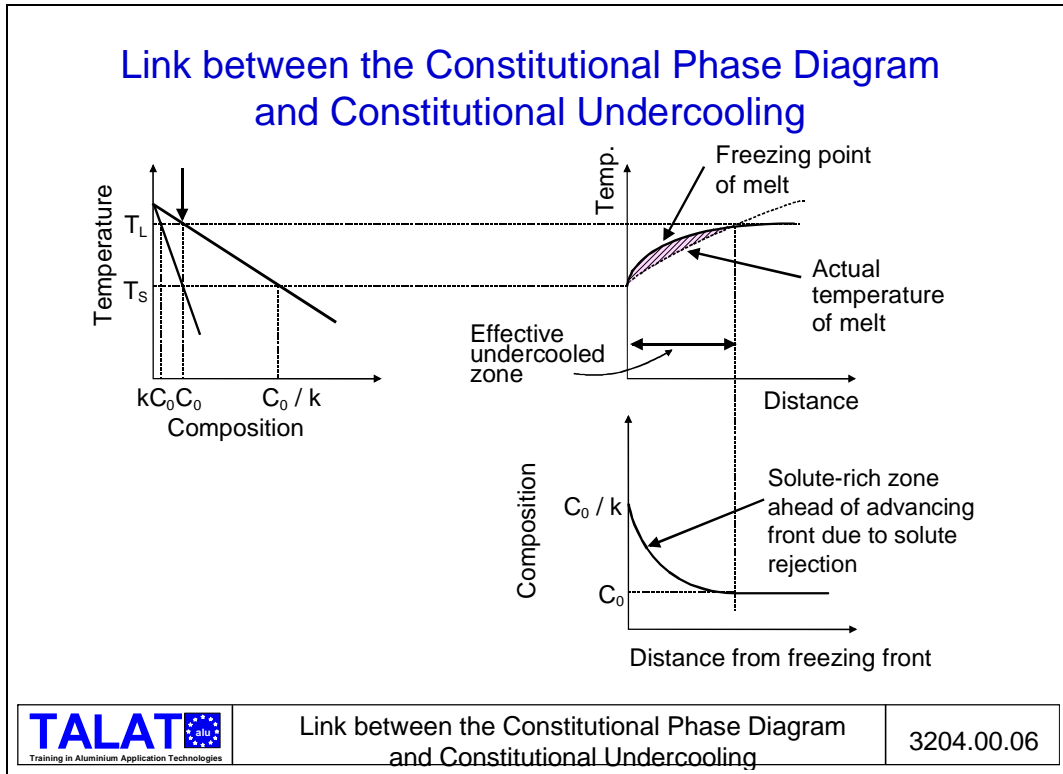
$$d \approx \sqrt{D \cdot t}$$

where D = coefficient of diffusion of the solute in the liquid.

Since R, the rate of advance of the solidification front, is given by

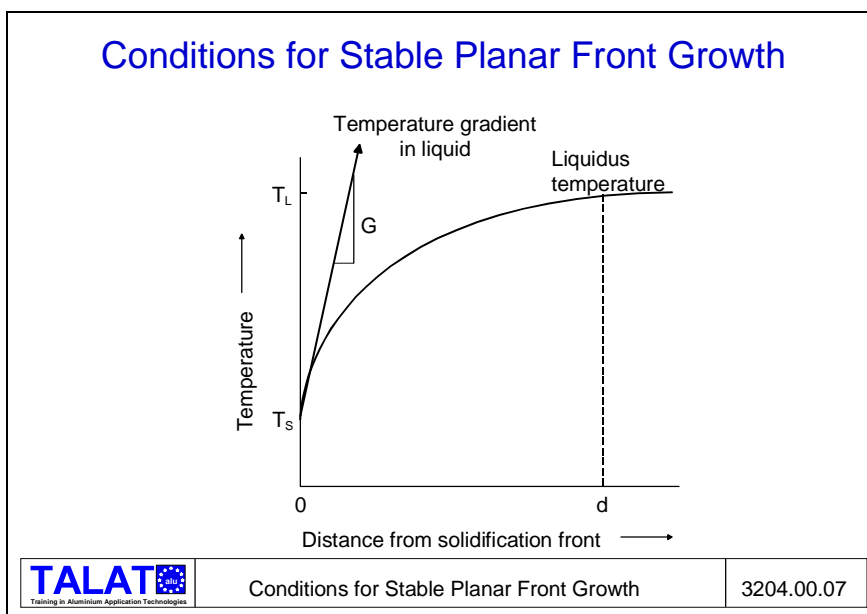$$R = \frac{d}{t}$$

it follows that $$d = \frac{D}{R}$$

Link between the Constitutional Phase Diagram and Constitutional Undercooling

| | Link between the Constitutional Phase Diagram and Constitutional Undercooling | 3204.00.06 |

Figure 3204.00.06: The rejection of solute into the liquid reduces the liquidus temperature close to the interface; the temperature increases towards its equilibrium value as the distance from the solidification front increases.

Conditions for Stable Planar Front Growth

| | Conditions for Stable Planar Front Growth | 3204.00.07 |

It is then necessary to consider the actual temperature gradient, G, applied to the liquid (see **Figure 3204.00.07**). When G is high, the temperature of the liquid ahead of the solidification front is always above the melting point. This leads to conditions for stable planar growth, i.e. there is no constitutional undercooling.

However, if the temperature gradient is lower, the liquid ahead of the front is effectively undercooled below its freezing point (**Figure 3204.00.08**). This unstable condition leads to cellular or even dendritic growth. Thus the condition for stable growth can be defined, *very approximately*, as being when
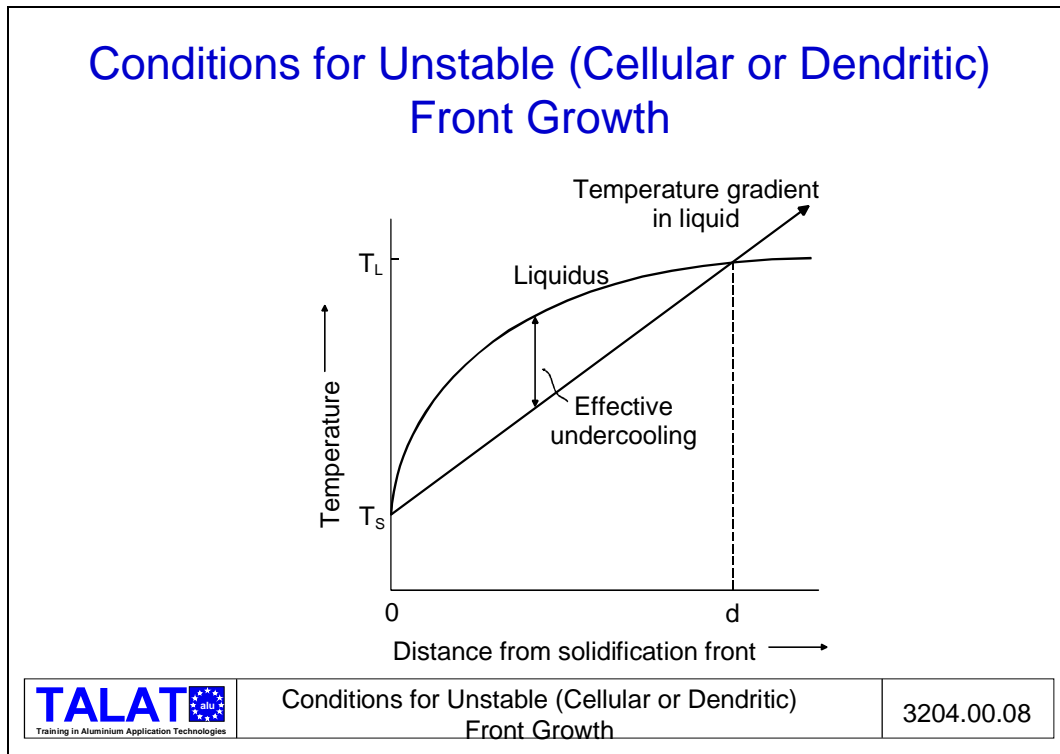
$$\text{G} \geq \frac{T_L - T_S}{d}$$

(The rough, order of magnitude approximation can be appreciated from the Figure!)

Substituting for *d* gives

$$\frac{G}{R} \geq \frac{T_L - T_S}{D}$$

This is the condition which roughly defines that there is no constitutional undercooling ahead of the interface which therefore remains stable and flat. If the equality is reversed, then the liquid ahead of the solidification front is effectively undercooled below its freezing point causing the unstable situation which leads to cellular or dendritic growth. This instability arises because any slight perturbation of the growing front causes the front to move into a region of higher effective undercooling, so growth is accelerated. This is of course a run-away situation, leading to the disintegration of the planar front into a series of long, finger-like growth forms such as cells or, more extremely, as dendrites.

Conditions for Unstable (Cellular or Dendritic) Front Growth

| TALAT | Conditions for Unstable (Cellular or Dendritic) Front Growth | 3204.00.08 |

Figure 3204.00.09: The condition is often written in a form using the slope of the liquidus line, *m*, where
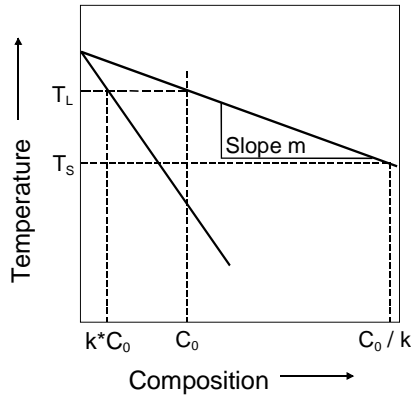
$$m = - \frac{T_L - T_S}{(C_O / k) - C_O}$$

This gives the familiar relation originally derived by Chalmers in 1953:

$$\frac{G}{R} \geq \frac{- m \cdot C_O (1 - k)}{D \cdot k}$$

The derivation of this equation marked the beginning of a revolution in solidification studies, showing how the application of **physical** principles could **quantify** observations and lead to **predictions**.

Condition to Avoid Constitutional Undercooling

Slope of the liquidus line $m = -\dfrac{T_L - T_s}{C_0/k - C_0}$
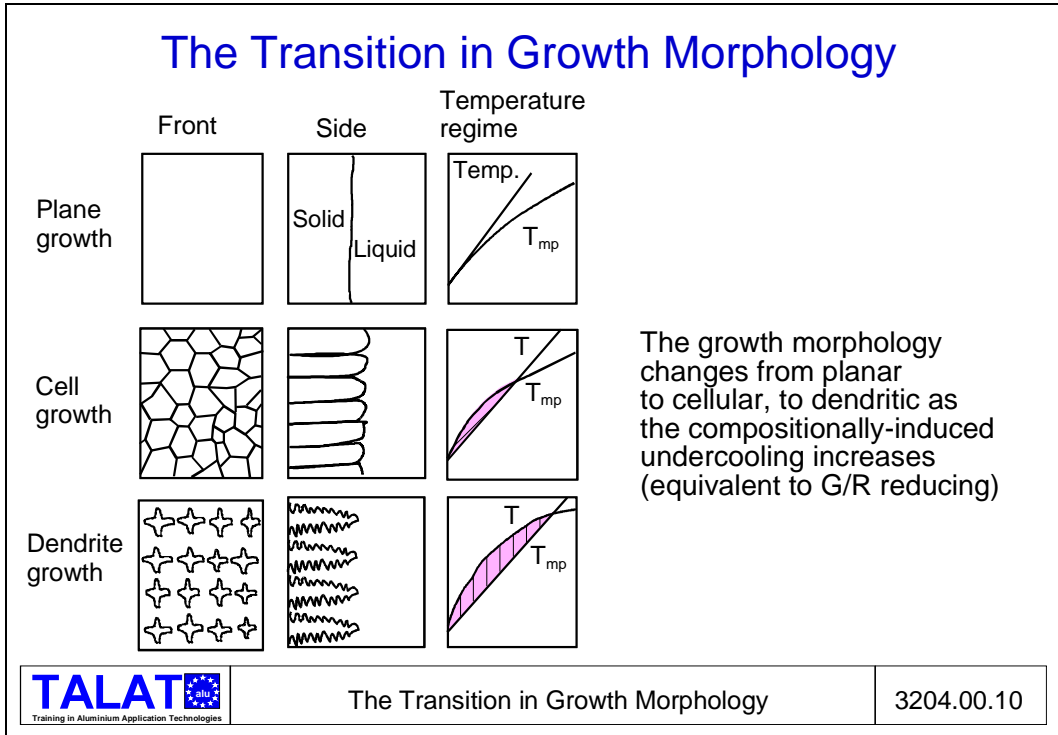
The condition for stability can now be written as:

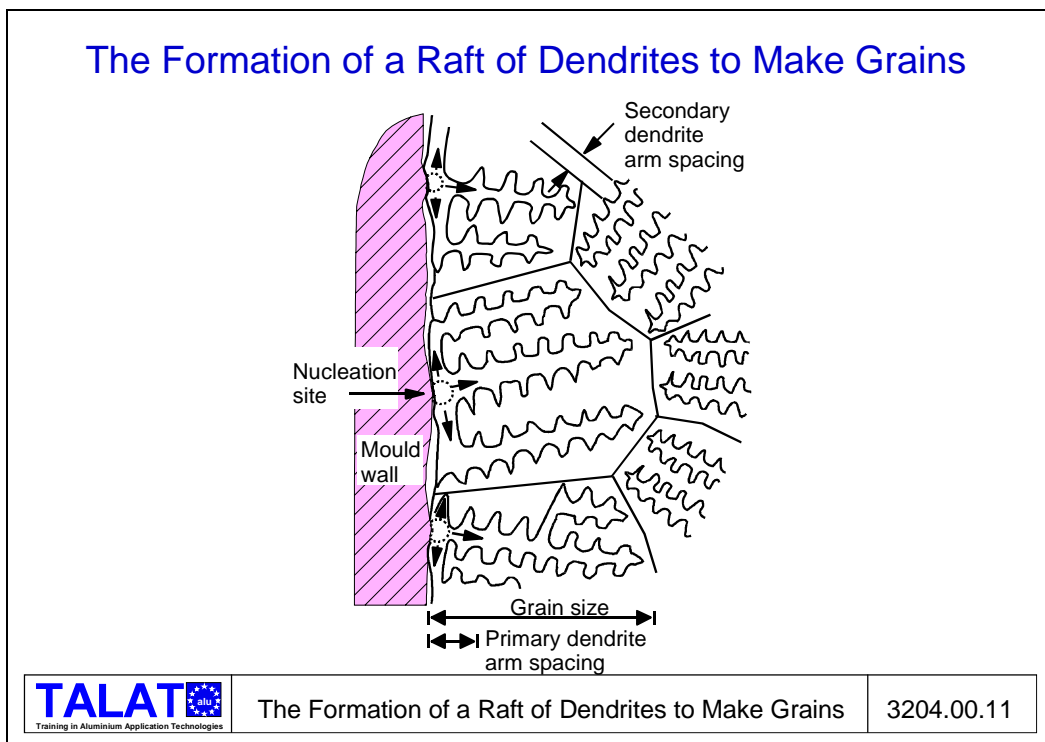$$\frac{G}{R} \geq \frac{-m \cdot C_0}{D}\left(\frac{1-k}{k}\right)$$

This was originally derived by Chalmers in 1953.

TALAT	Condition to Avoid Constitutional Undercooling	3204.00.09

Transition in Growth Morphology

Figure 3204.00.10 shows how the growth morphology changes from planar to cellular and then to dendritic as the compositionally-induced undercooling increases. Although metals can solidify in any of these modes, the most common form in real castings is dendritic solidification. A dendrite can be defined as the basic tree-like growth form of the solidification front which occurs when instability predicted by the constitutional undercooling condition is high.

The Transition in Growth Morphology

	Front	Side	Temperature regime
Plane growth		Solid / Liquid	Temp. / T_{mp}
Cell growth			T / T_{mp}
Dendrite growth			T / T_{mp}

The growth morphology changes from planar to cellular, to dendritic as the compositionally-induced undercooling increases (equivalent to G/R reducing)

TALAT Training in Aluminium Application Technologies	The Transition in Growth Morphology	3204.00.10

Dendrites normally grow from a single nucleus which may be only a few µm in diameter. The nucleus may be a foreign particle or a fragment of another grain. The dendrite grows both forwards and sideways, with the secondary arms generating more primaries (see **Figure 3204.00.11**). Although the arms grow in different physical directions, they all have the same crystallographic structure and orientation, i.e. a dendrite is a single crystal.

The Formation of a Raft of Dendrites to Make Grains

Secondary dendrite arm spacing

Nucleation site

Mould wall

Grain size

Primary dendrite arm spacing

| **TALAT** Training in Aluminium Application Technologies	The Formation of a Raft of Dendrites to Make Grains	3204.00.11

Dendrite Arm Spacing (DAS)

A grain may consist of one dendrite or of a 'raft' of thousands of dendrites, but all must have the same crystallographic orientation and will have grown from the same nucleation site. A grain boundary is formed where rafts of different orientation meet. Although grain size is used to characterise the scale of the microstructure of wrought alloys, it is often more appropriate to characterise the scale of cast microstructures by measuring the secondary dendrite arm spacing, often abbreviated to 'dendrite arm spacing', or DAS. This average length is usually measured by carrying out a line count along the length of a number of primary dendrite stems which happen to lie near to the plane of the section.

During the growth of the dendrite, the average dendrite arm spacing increases with time as a result of coarsening, in which the driving force is the reduction in surface energy achieved by reducing the surface area (**Figure 3204.00.12**). Some of the larger arms grow at the expense of smaller ones, leading to an increasing DAS as the dendrite gets older, and this process is controlled by the rate of diffusion of solute in the liquid. Thus the DAS, d, is largely a function of the solidification time, t_S, and the relationship is of the approximate form:

$$d = k \cdot t_S^{0.3}$$

The overhead shows a typical set of results for an Al-4.5%Cu alloy in which the dendrite arm spacing is plotted as a function of the solidification time (note that a log scale has been used). The above relationship can be seen to hold over an impressive 8 orders of magnitude.

Grain size is usually measured by a linear intercept method in which a fixed distance is divided by the number of grains crossed. Grains can be considerably larger than the DAS but, of course, the reverse is not possible. This is also illustrated by these results.

Relation between Dendrite Arm Spacing, Grain Size and Local Solidification Time (Al - 4.5% Cu alloy)
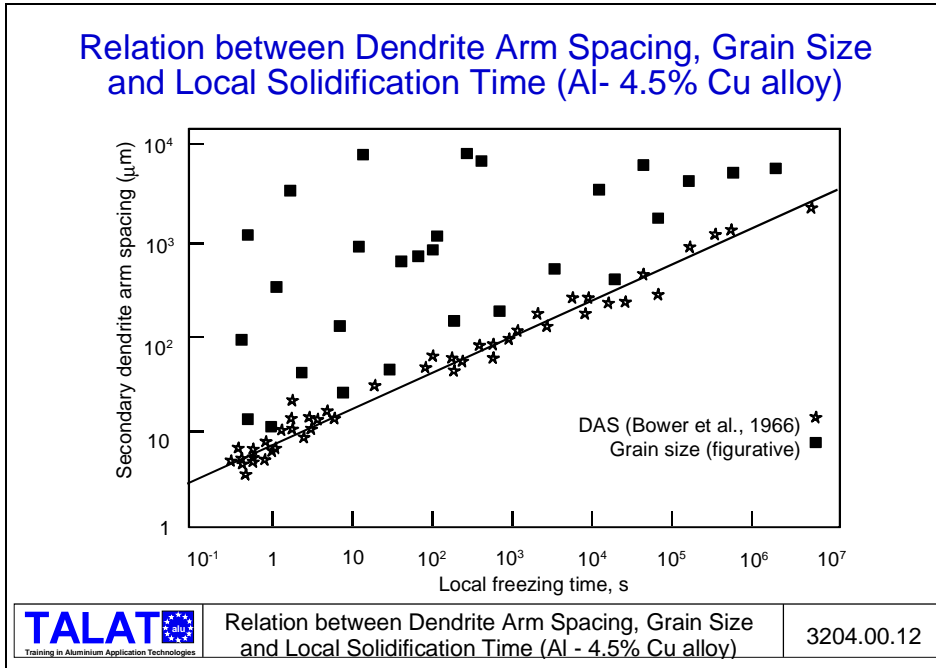
3204.00.12

Figure 3204.00.13: The mechanical properties of most cast alloys depend strongly on DAS: the tensile strength, ductility and elongation all increase as DAS decreases. A small DAS also reduces the time required for homogenisation heat treatments since the diffusion distances are shorter. It is therefore beneficial to reduce the DAS as far as possible and since this is almost exclusively a function of the freezing time, any technique to reduce this will have a beneficial effect upon the DAS.

In the case of sand casting, metal chills will help considerably in reducing the DAS. Die castings will have a finer DAS, and lower die temperatures will assist even further.

Why is Dendrite Arm Spacing Important?

3204.00.13

Grain Refinement

I would now like to consider grain refinement by reference to the graph (**Figure 3204.00.14**) that we have just seen. Although grain size does tend to reduce somewhat as freezing time is decreased, it is not closely controlled by the freezing time. This is clearly illustrated by the general scatter in grain sizes above the $d = k \cdot (t_S)^{0.3}$ line on this graph. Clearly, a number of other factors control the grain size.

Relation between Dendrite Arm Spacing, Grain Size and Local Solidification Time (Al - 4.5% Cu alloy)
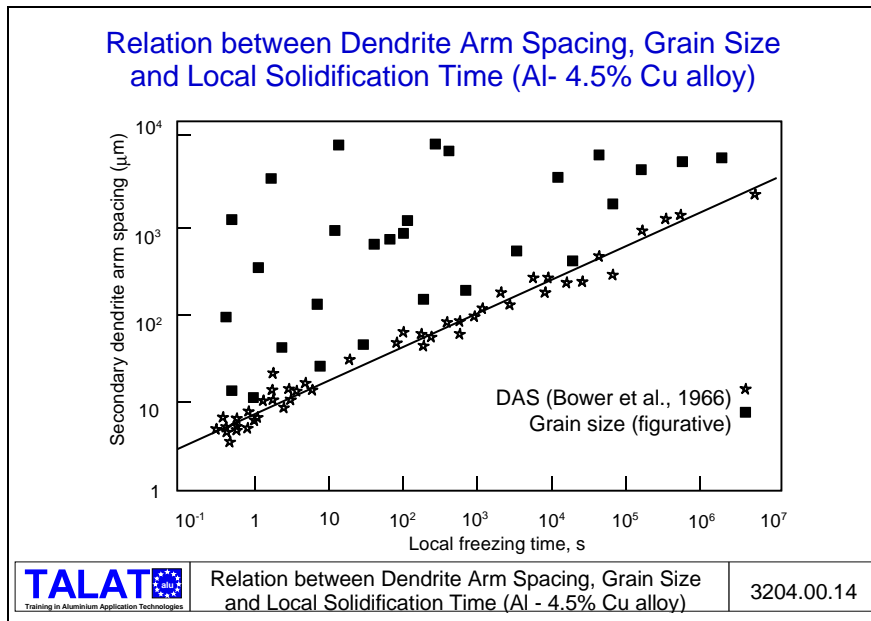
3204.00.14

Figure 3204.00.15: The first of these may be homogeneous nucleation. It can be hypothesised that microscopic regions adjacent to the mould wall may be supercooled by several hundreds of degrees K and thereby promote homogeneous nucleation. This is because an oxide skin is normally against the mould wall and the inside surface of this is not an effective nucleus for the initiation of solid. Hence, large amounts of supercooling may take place before nucleation occurs.

Next, we have heterogeneous nucleation which can be promoted by the introduction of effective foreign nuclei. Examples include Zr in some Mg alloys, Ti in Al alloys and TiC and TiN in ferritic iron.

Another possibility is to cause grain fragmentation by a variety of means. One technique is to use a low pouring temperature so that as dendrites form and are broken up in the stream of flowing metal, fragments are swept into the bulk of the casting and if they do not re-melt, they can act as efficient nuclei. Alternatively, any mechanical, thermal or solutal disturbance during freezing will assist, such as surface shower multiplication, or grain refinement by vibration or stirring, such as electromagnetic stirring. Ultrasonic vibration is also a well-known method of achieving grain refinement although there are a number of explanations of how it works. One of these is that ultrasound generates heat and re-melts the roots of the dendrite arms, allowing them to float free. Another is that ultrasound shears dendrite arms along a slip plane. A third explanation is that the dendrite arms are bent, causing work hardening and subsequent recrystallisation. This creates high angle boundaries which can be wetted by the molten alloy which can then penetrate along them and cause arms to separate.
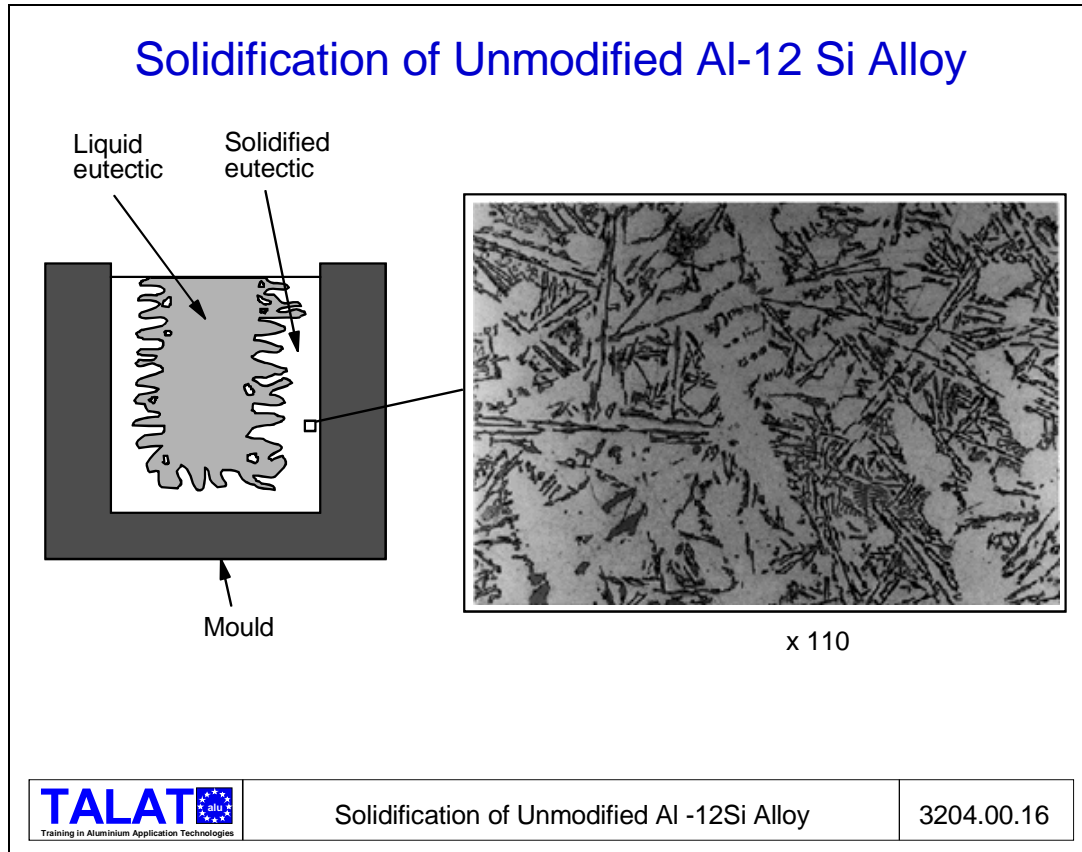
Effect of Alloying Elements

Finally, it is possible to restrict grain growth after nucleation. One way of achieving this is to use alloying elements with a low distribution coefficient, k, i.e. those solutes which segregate strongly ahead of the advancing front and so slow down diffusion and thus the rate of arrival of aluminium atoms to grow the primary aluminium dendrites. This is probably how B helps to grain refine Al alloys which contain additions of Ti.

In summary, there is widespread confusion between the concept of a grain and the concept of a dendrite. It is necessary to be on one's guard against this.

We shall now turn to the modification of the aluminium-silicon eutectic (**Figure 3204.00.16**). The Al-Si eutectic solidifies with a ragged front, as a dendritic front in which the dendrites are composed of the eutectic. This curious behaviour is shown in this overhead.

Solidification of Unmodified Al-12 Si Alloy

Liquid eutectic

Solidified eutectic

Mould

x 110

| TALAT | Solidification of Unmodified Al -12Si Alloy | 3204.00.16 |

Sodium effect

Conversely, when a minute amount of sodium is added to the alloy, the eutectic front becomes planar as shown in **Figure 3204.00.17**. These effects were noted in a discerning study by Hunt at Oxford University who found that the length of the dendritic solidification front was 17 times greater than that of the planar front. Thus, the reasoning goes, since the rate of extraction of heat from the mould is the same in both cases, the rate of advance of the dendritic front will only be 1/17th of the rate of the planar front. Thus the eutectic spacing will be coarse in the dendritic growth mode, whereas it will be fine in the planar mode because it had rapidly solidified.

This explains the action of sodium in refining the spacing of the eutectic silicon. It also explains how the action of speeding up solidification and that of sodium are both analogous and additive in practice. For instance those castings which solidify rapidly, such as die castings (especially pressure die castings) have especially fine eutectic spacing, although additions of sodium will act to refine the spacing still further.

Solidification of Al - 12Si Alloy Modified with 0.005 wt.% Na — 3204.00.17
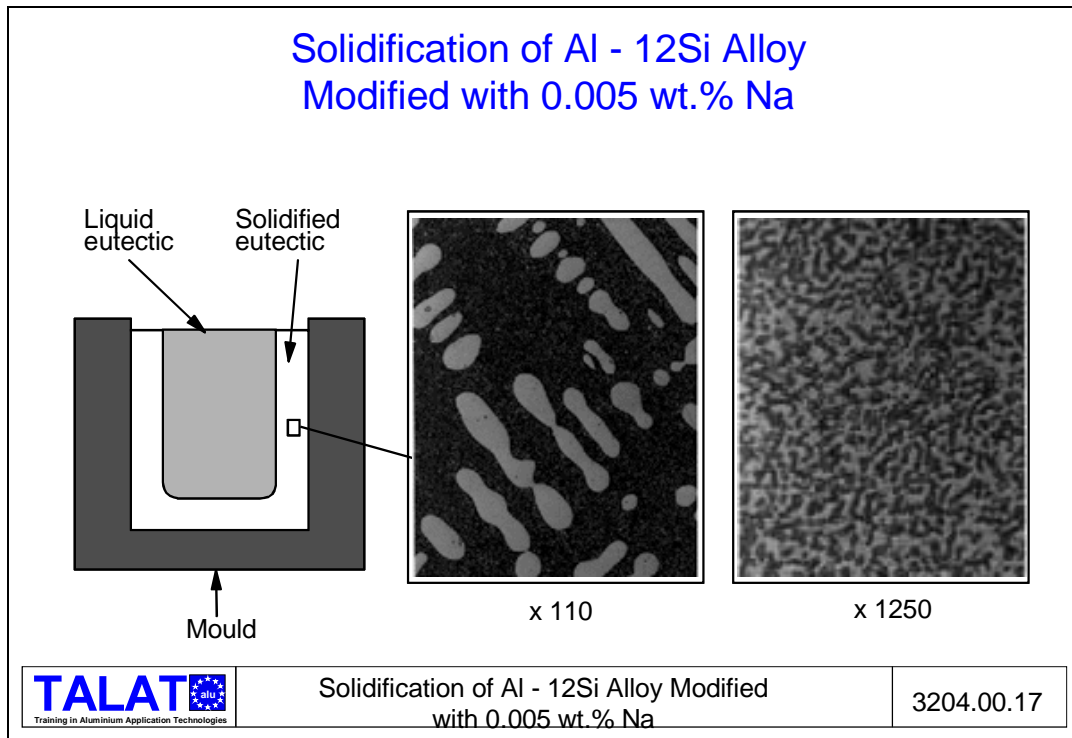
The refining of the eutectic spacing is generally carried out to enhance the strength and ductility of Al-Si alloys, particularly those alloys which contain more than about 50 per cent eutectic phase such as Al-7Si-0.4Mg and higher Si alloys such as Al-11Si etc.

In gravity die casting foundries, however, sodium is added by the caster for apparently quite different reasons. When, during a production run, the caster notices that an area of concentrated shrinkage starts to occur in a hot spot such as a re-entrant corner of the casting, he will add sodium to the melt. The effect is like magic. The surface sink disappears immediately.

The explanation of this useful effect follows from Hunt's experimental observations. Without the sodium the freezing front is ragged and thus weak and vulnerable, because of the numerous thinned parts of the solidified skin. It therefore collapses easily under the internal effects of shrinkage in the hot spot, and may actually puncture, allowing air into the shrinkage cavity which can then grow unhindered.

With the addition of sodium, the freezing front is straightened, and so becomes uniformly strong, resisting the collapsing force attempting to suck the material into the casting interior. In this situation an internal pore may form, but at least this is not visible on the outside of the casting, and is not connected to the surface. The casting is in most cases therefore acceptable to the customer and suitable for service. Often, however, an internal pore does not form. The solid therefore continues to collapse as before, but the strong, uniform skin ensures that the collapse is spread widely, and so effectively unnoticeable. (This is an effective way of solid feeding which will be described in the lecture on Feeding under the section The Five Feeding Mechanisms.)

Foundries are thinking of moving away from sodium as a modifier for the eutectic spacing. There are a number of driving forces for this change (see **Figure 3204.00.18**).

1. The addition of sodium causes a lot of fume during the period of the addition when added as sodium metal. The health and safety legislation make this aspect unpopular (although there seems to be little evidence of any hazard).

2. When sodium is added in salt form, then the residual chloride and/or fluoride salt has to be disposed of in some safe manner. Because of the danger of the pollution of ground water supplies, this procedure is also becoming less widely used.

3. The temperature at which liquid aluminium is held is above the boiling point of sodium, so that sodium is lost from the melt by evaporation. The rate of loss of sodium vapour means that most sodium is lost within 15 or 20 minutes of an addition. It is therefore not easy to ensure that the level of sodium in the melt is correct at all times. This poor chemical control is the main reason why sodium is unpopular for control of eutectic modification.

Strontium Effect

Strontium is now beginning to be used as a substitute for sodium in the modification of the Al-Si eutectic (**Figure 3204.00.19**). Its great advantages are that it is effectively permanent and it is easily and fumelessly added to the melt. It is lost slowly by oxidation. However, this is similar to the rate at which other oxidisable elements such as Mg are lost, and so can be effectively kept under good control.

Nevertheless, life is never perfect. There are, of course, disadvantages to the use of strontium:

1. The melt seems sensitised to the pickup of hydrogen gas, so that castings often display dispersed gas porosity. When the melt is allowed to remain in contact with moisture in the air, the strontium reacts with the water, forming strontium oxide on the melt surface and releasing hydrogen gas to go into the melt. This seems to happen less in low pressure die casting where holding the melt inside an enclosed pressure vessel keeps the it out of contact with air.

2. The action of strontium on straightening the freezing front of the eutectic is not quite the same as that of sodium.

Although strontium acts to smooth the front somewhat, it creates a cellular front, a kind of compromise between a planar and a dendritic condition. The cellular growth of the front sometimes causes a kind of 'orange peel' condition on the surface of poorly fed thin-walled castings, as a result of the drainage of residual liquid between the cells, thus outlining the cells and giving the appearance of crazy paving.


Strontium as a Modifier 3204.00.19

Antimony Effect

Antimony is another permanent alloying addition which has a modest effect on the refinement of the Al-Si eutectic. However, its action is different again from that of Na and Sr, and far less dramatic. In fact its effect on sand castings is sufficiently insignificant that it is usually not used for such applications. It is claimed to be reasonably useful for die castings of various sorts, and is used particularly in gravity die foundries. In addition to its relatively modest, if not poor, performance, antimony is also

somewhat toxic, and thus an addition in the foundry is not recommended. Because of its permanence as an alloying addition, it can of course be added to the alloy at the point of alloy production.

Al-Si Hypereutectic Solidification

Figure 3204.00.20: In the hypereutectic Al-Si alloys, primary silicon is the first phase to separate on solidification. This solidifies as chunky crystals of pure silicon. If there are few nuclei on which the silicon can form, then the silicon will form as large separated particles which will float out rapidly, segregating to the top of the casting.
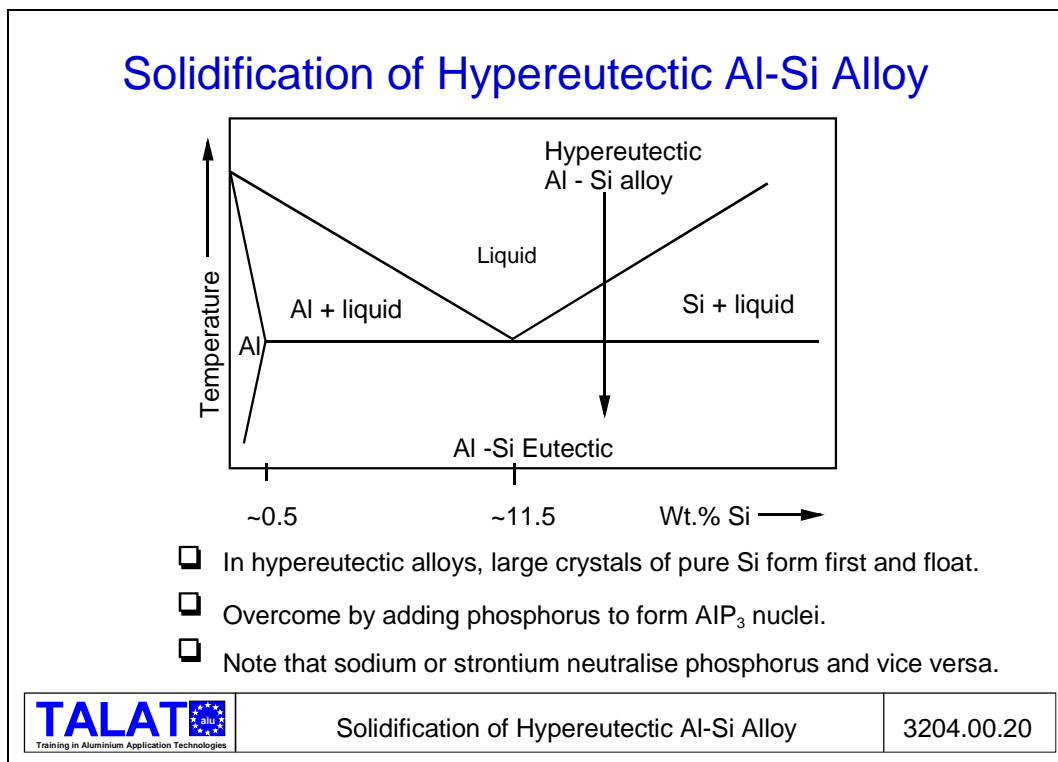
To avoid this problem, and to obtain a fine and nicely dispersed form of the primary silicon, it is necessary to make a prolific addition of suitable nuclei. This is achieved by the addition of phosphorus. It is thought that aluminium phosphide, AlP_3, is the active nucleant.

Care needs to be taken to ensure that sodium or strontium are not present when phosphorus is added. These two groups of elements are antagonistic in aluminium alloys and effectively neutralise each other. Thus if one is present, the other has to be added in sufficient amounts first to react and negate the effect of the first before any beneficial action can be gained.

Conclusions

In conclusion, this lecture has considered some of the basic scientific aspects of solidification and the formation of different cast structures. We have also seen how the cast structure of aluminium castings can be altered by the addition of small but judicial amounts of certain elements. This provides an essential foundation to future lectures in which we will see what steps are necessary to produce a sound casting (**TALAT Lecture** 3206) and the consequences of failing to achieve this (**TALAT Lecture** 3207).

Literature

Campbell, J.: Castings, Butterworth Heinemann, 1991

Flemings, M. T.: Solidification Processing, McGraw Hill, 1974.

List of Figures