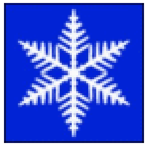
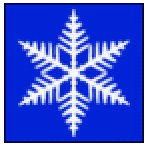
6 Structure and Structure Formation in Cast Materials

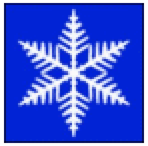


6.1 INTRODUCTION

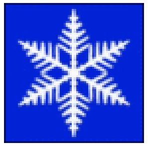


- 6.1.1 **Structures of Cast Materials**
- The crystal structure determines most of the material properties of the metal and it is therefore of greatest importance to study metal structures in detail and try to identify the relationship between structure and material properties. The formation process determines the structure of a metal.

- If metallic materials with certain specific properties need to be produced, it is necessary to understand the relationship between the method of formation and different process parameters in order to find an efficient way of controlling the structure and the properties.
- Metal and alloy components are often produced by casting. The material properties of ingots and other castings are to a great extent determined by the method of solidification and by the choice of parameters, i.e. casting method, casting temperature and rate of solidification or the cooling process.

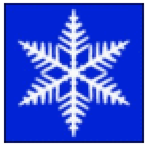


- The cooling rate determines the coarseness of the metal structure. By combining thermal conduction equations with relationships that describe coarseness of structure, it is possible to analyse the formation of the structure mathematically for different casting processes. The analysis results in predictions of the material properties *of,* for example, an ingot or of a continuously east product. Conversely the analysis can be used to control the casting process and for reducing the casting defects to a minimum.



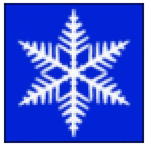
STRUCTURE FORMATION IN CAST MATERIALS

- All solidification starts by formation of so-called *nuclei* at various positions in the melt and the crystals grow from these nuclei. There is a distinction between homogeneous and heterogeneous nucleation. *Heterogeneous* nucleation implies that foreign particles in the melt or at the surface act as nuclei for subsequent growth of the solid phase. The process occurs spontaneously but may, if special measures are taken, be controlled and contribute to the required structure *of* the solidified material.



- Nucleation
  - Homogeneous Nucleation
  - Heterogeneous Nucleation
- Growth
  - Dendritic Growth (Solidification)
  - Eutectic Growth (Solidification)
  - Dendritic+Eutectic Growth (Solidification)

- The particles, so-called *embryos* that consist of several atoms ordered in a crystalline way arise spontaneously and at random. Between the embryos and the melt there is a continuous exchange of atoms. In many cases the embryos are dissolved and disappear
- If the kinetic motion is not too violent - the temperature is lower than the melting point - the attraction between the atoms may sometimes be so strong that some embryos survive in the melt. An embryo that achieves a certian critical minimum size continues to grow as a crystal.



$$-\Delta G_{\mathrm{i}} = \left[\frac{V(-\Delta G_{\mathrm{m}})}{V_{\mathrm{m}}}\right] + \sigma A \qquad (6.1)$$

where

ΔG_{i} = free energy required to form an embryo with the volume V and the area A

$-\Delta G_{\mathrm{m}}$ = change in free energy per kmole at transformation of melt into solid phase

V_{m} molar volume = M/ρ (m^3/kmole)

σ surface energy per unit area of the embryo.

For a spherical nucleus we have:

$$V = \frac{4\pi r^3}{3} = \frac{4\pi r^2 \times r}{3} = \frac{A \times r}{3}$$

$$\Delta G^* = \frac{16\pi}{3} \times \frac{\sigma^3 V_m^2}{(\Delta G_m)^2} \qquad (6.2)$$

where $-\Delta G^*$ – activation energy for formation of a nucleus of the critical size r^*.

An embryo has to grow at least to the critical size r^* to form a nucleus capable of further growth.

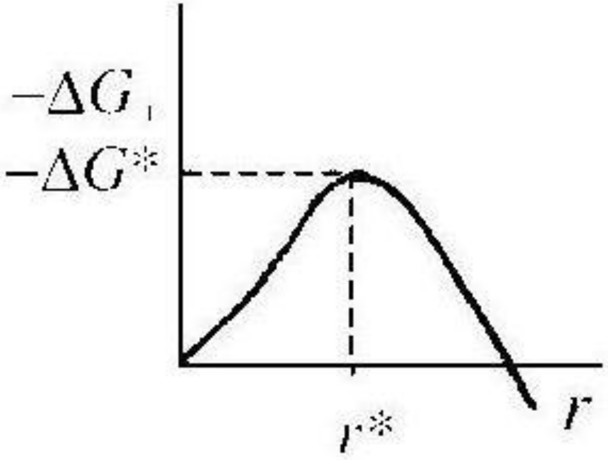


Figure 6.1 The free energy required to form an embryo as a function of its radius.

$$-\Delta G_{\mathrm{m}} = \frac{(T_{\mathrm{M}} - T)}{T_{\mathrm{M}}}(-\Delta H_{\mathrm{m}}^{\mathrm{fusion}}) \qquad (6.3)$$

where

$-\Delta G_{\mathrm{m}}$ = change in free energy per kmole at transformation of melt into solid phase
$-\Delta H_{\mathrm{m}}^{\mathrm{fusion}}$ = molar heat of fusion of the metal
T_{M} = melting point temperature of the pure metal
T = temperature of the melt
$T_{\mathrm{M}} - T$ = undercooling.

It is important to emphasize that Equation (6.3) is *not valid for alloys* as they have a solidification interval instead of a well-defined melting point. The phase diagrams of alloys have to be involved. The simple phase diagram in Figure 6.2 describes the relationship between undercooling and supersaturation. Supersaturation is an alternative variable for describing $(-\Delta G_{\mathrm{m}})$ for alloys instead of undercooling. This topic will be discussed in the next section.

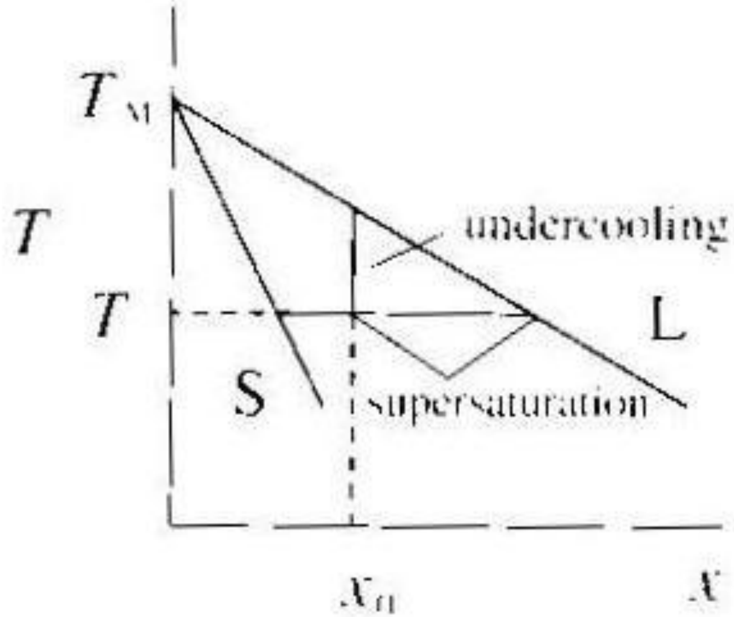
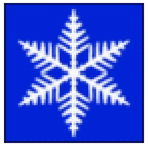


Figure 6.2 Phase diagram of a binary alloy.

- By use of Boltzmann's statistical mechanics in combination with laws that describe the capacity of the nuclei to grow and not shrink and become embryos again, it is possible to derive:



- the number of nuclei per unit volume;
- the number of nuclei formed per unit volume and unit time;
- the average activation energy, required to form a nucleus of the critical size.

The average activation energy for forming a nucleus at this temperature is calculated as:

$$-\Delta G^{*} = 60\, k_B T^{*} \qquad (6.4)$$

where k_B is Boltzmann's constant. The critical temperature T^{*}, when a large number of nuclei are formed, is found by combining Equations (6.2) and (6.4) with Equation (6.3), applied at the critical temperature (T is replaced by T^{*}). Elimination of the molar free transformation energy $(-\Delta G_{\mathrm{m}})$ gives:

$$60\, kT^{*} = \frac{16\pi}{3} \times \frac{\sigma^3 V_{\mathrm{m}}^2}{\left(\frac{(T_{\mathrm{M}} - T^{*})}{T_{\mathrm{M}}}\left(-\Delta H_{\mathrm{m}}^{\mathrm{fusion}}\right)\right)^2} \qquad (6.5)$$

The solution of this equation gives the critical temperature T^{*}.

Below the critical temperature very few nuclei per unit volume and unit time are formed. *Above* and *at* this temperature a great number of nuclei per unit time are formed. The critical temperature is also called the *nucleation temperature*. The undercooling $(T_{\mathrm{M}} - T)$ is the driving force in solidification. The lower the temperature T of a pure metal melt is, the faster will the nucleation process be.

Heterogeneous Nucleation in Metal Melts in the Presence of Small Amounts of Foreign Elements

- Nucleation occurs on foreign particles or crystals, so-called *heterogeneities, which are precipitated in the melt.*
- Often these small foreign particles nucleate homogeneously. The metal melt, including the foreign element, which i.s difficult to dissolve, constitute a two-phase system with a phase diagram such as the one in Figure 6.3.
- At the nucleation temperature *T′ small crystals precipitate with a composition .X^s that is approximately equal to 100 % of element B. These small crystals grow somewhat during continued cooling.*

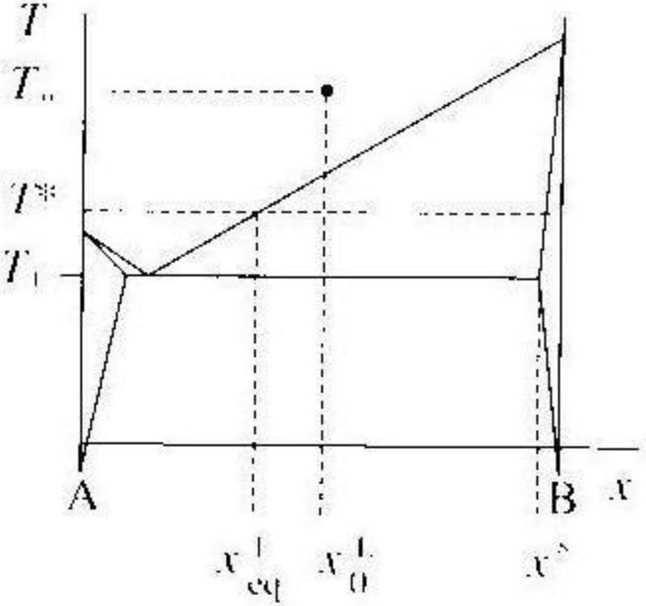


Figure 6.3 Phase diagram of a metal with a low concentration of a foreign element B that is difficult to dissolve.

For elements with very low solubility in the melt, the relationship between the change in molar free energy of the melt at nucleation (solidification) is:

$$-\Delta G_m = RT' \ln\left(\frac{x_0^L}{x_{eq}^L}\right) \qquad (6.6)$$

where $x_{\mathrm{eq}}^{\mathrm{L}}$ – equilibrium concentration (mole fraction) of the foreign element in the melt at temperature T^*, and x_0^{L} = original concentration (mole fraction) of the foreign element in the melt. In this case the critical temperature T^* is found by combining Equations (6.2), (6.4) and (6.6). Elimination of (ΔG_{m}) gives:

$$60\, k_B T^* = \frac{16\pi}{3} \times \frac{\sigma^3 V_{\mathrm{m}}^2}{\left(RT^* \ln \frac{x_0^{\mathrm{L}}}{x_{\mathrm{eq}}^{\mathrm{L}}}\right)^2} \qquad (6.7)$$

The solution of this equation gives the critical temperature T^*. It is found to be much higher than that of pure metal melts and corresponds to low undercooling. It is low enough to permit easy formation of new crystals in normal casting and solidification processes.

6.2.2 Inoculation

Calculations using Equation (6.7) show that the required concentration of foreign elements in the melt for formation of heterogeneities is very low. This fact is used in so-called *inoculation* of metals to start the solidification process. Small amounts of elements are added to the melt and small crystals are formed by homogenous nucleation. These crystals are the heterogeneities on which new crystals nucleate. The mechanism is called *heterogeneous nucleation.*

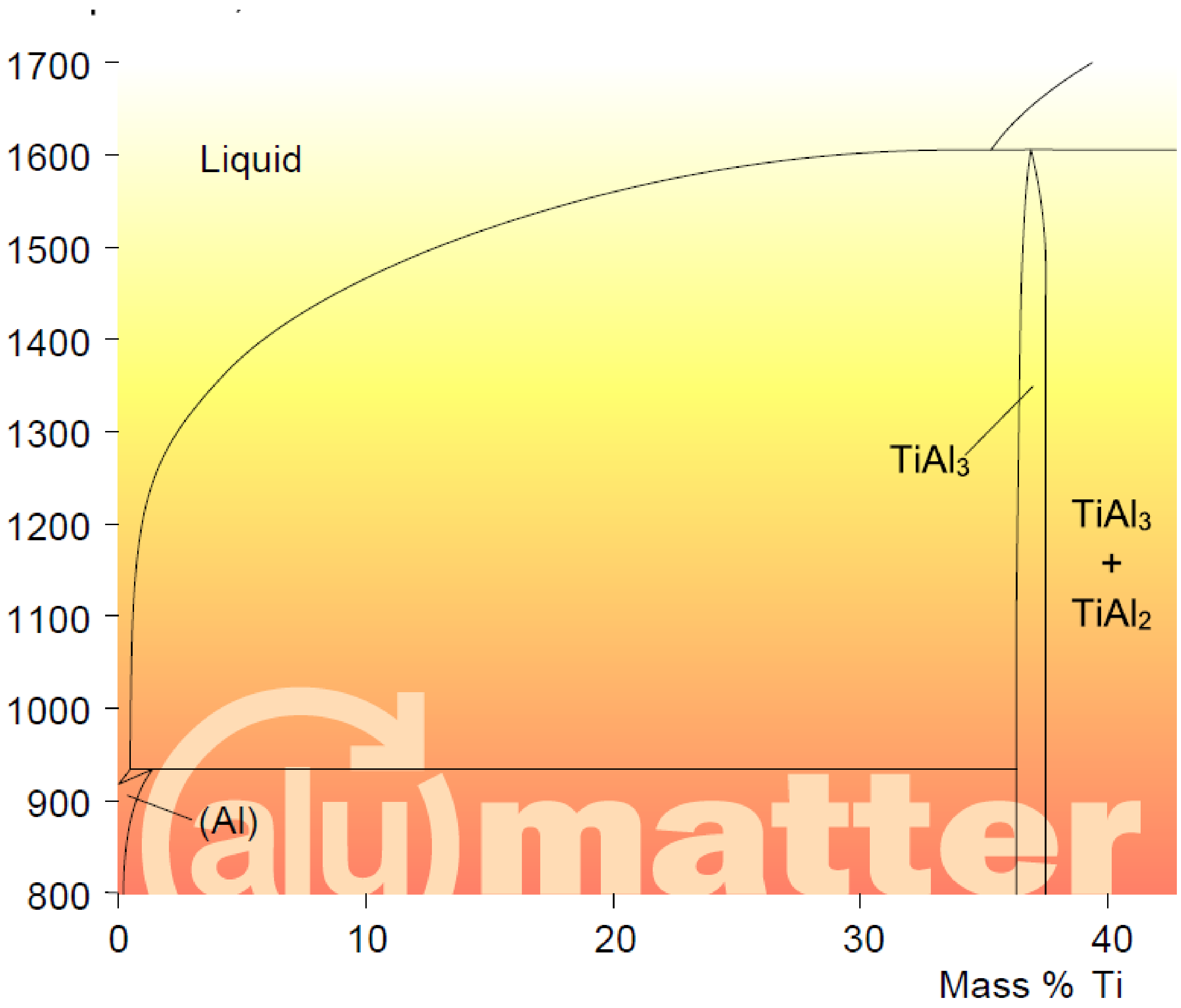
The properties of cast materials are often improved by increasing the number of formed crystals. Thus it is of great interest to increase the number of crystals during the solidification in technical processes. Inoculation is often used in casting of aluminium to get a great number of small crystals. which prevent formation of bad texture (bad plastic deformation in certain crystallographic directions) in plastic forming after casting. Inoculation is also used in casting of cast iron to reduce the risk of white solidification (page 151). In addition, in many casting processes an increase in the number of crystals occurs through so-called *crystal multiplication*, when a single crystal splits up into two or more new crystals. This phenomenon is treated in Section 6.3.3 on page 144.

At nucleation on heterogeneities in the melt it is difficult to define a specific nucleation temperature. Instead it has to be based on experimental observations. In many cases a relationship between the number of nucleated small crystals per unit volume N and the undercooling $\Delta T = T_L - T$, which is the difference between the liquidus temperature T_L and the temperature T of the melt, has been found to be:

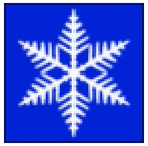
$$N = A(T_L - T)^B = A(\Delta T)^B \tag{6.8}$$

A and B are constants that are determined experimentally.

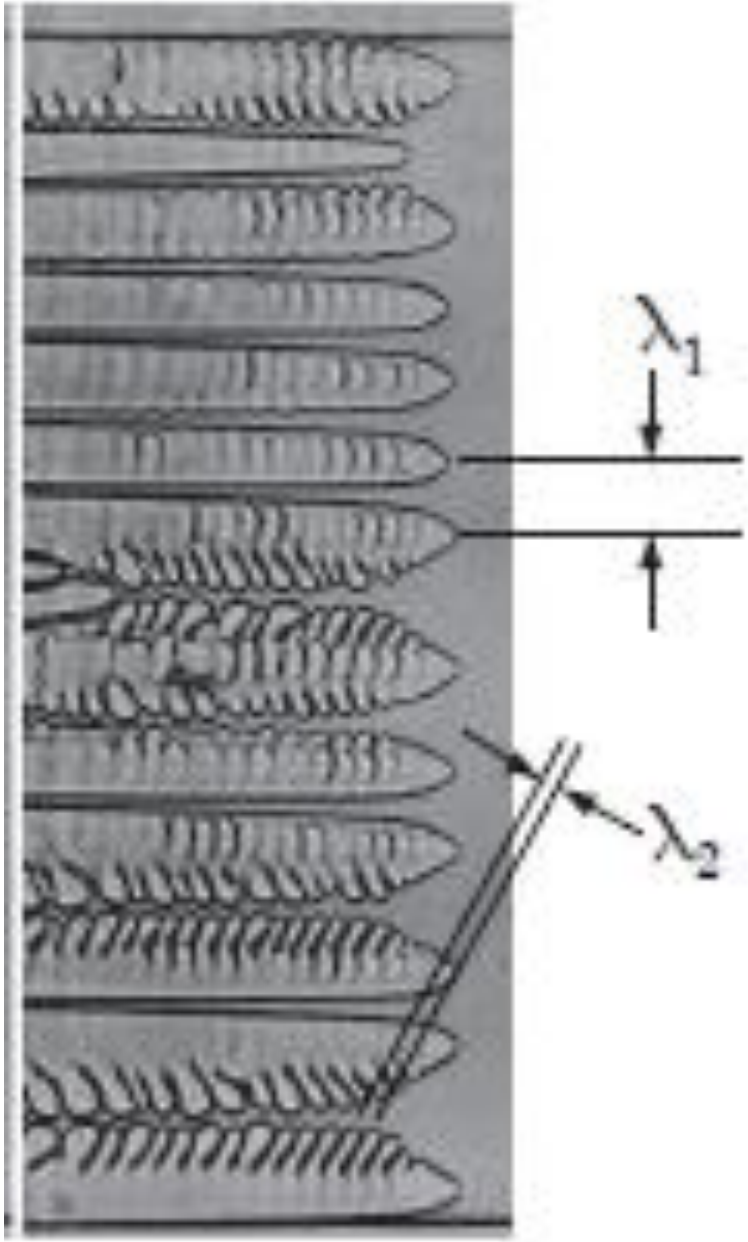
Peritectic reaction



DENDRITE STRUCTURE AND DENDRITE GROWTH

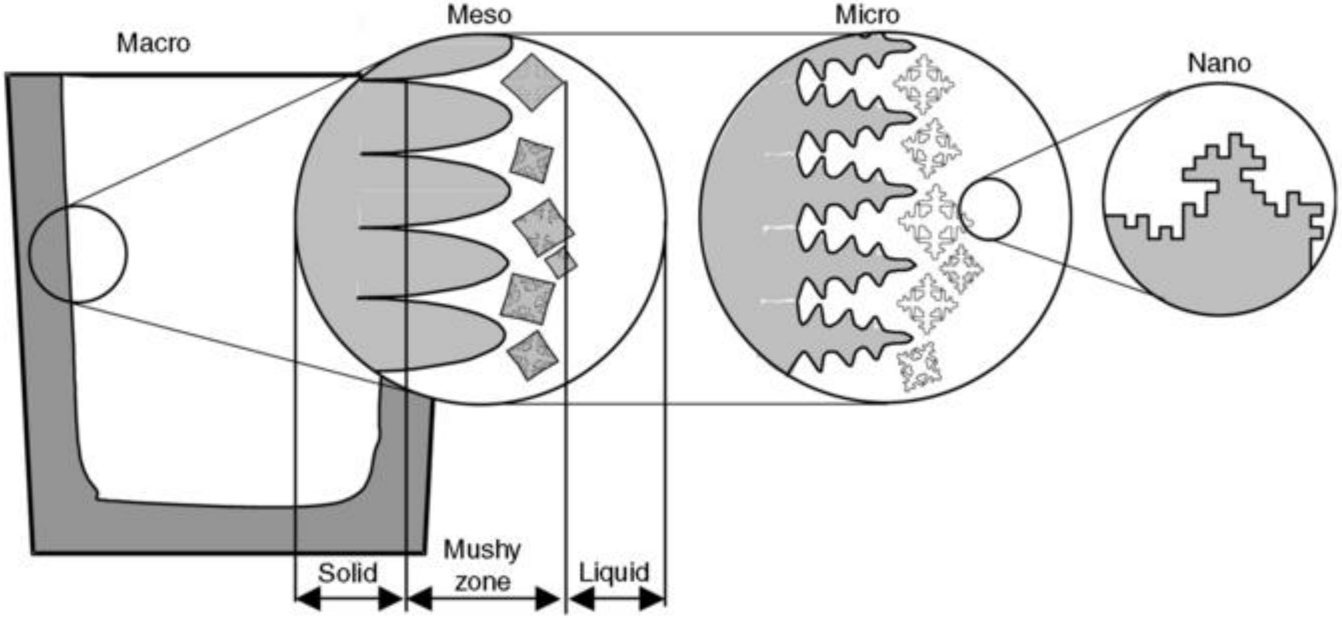


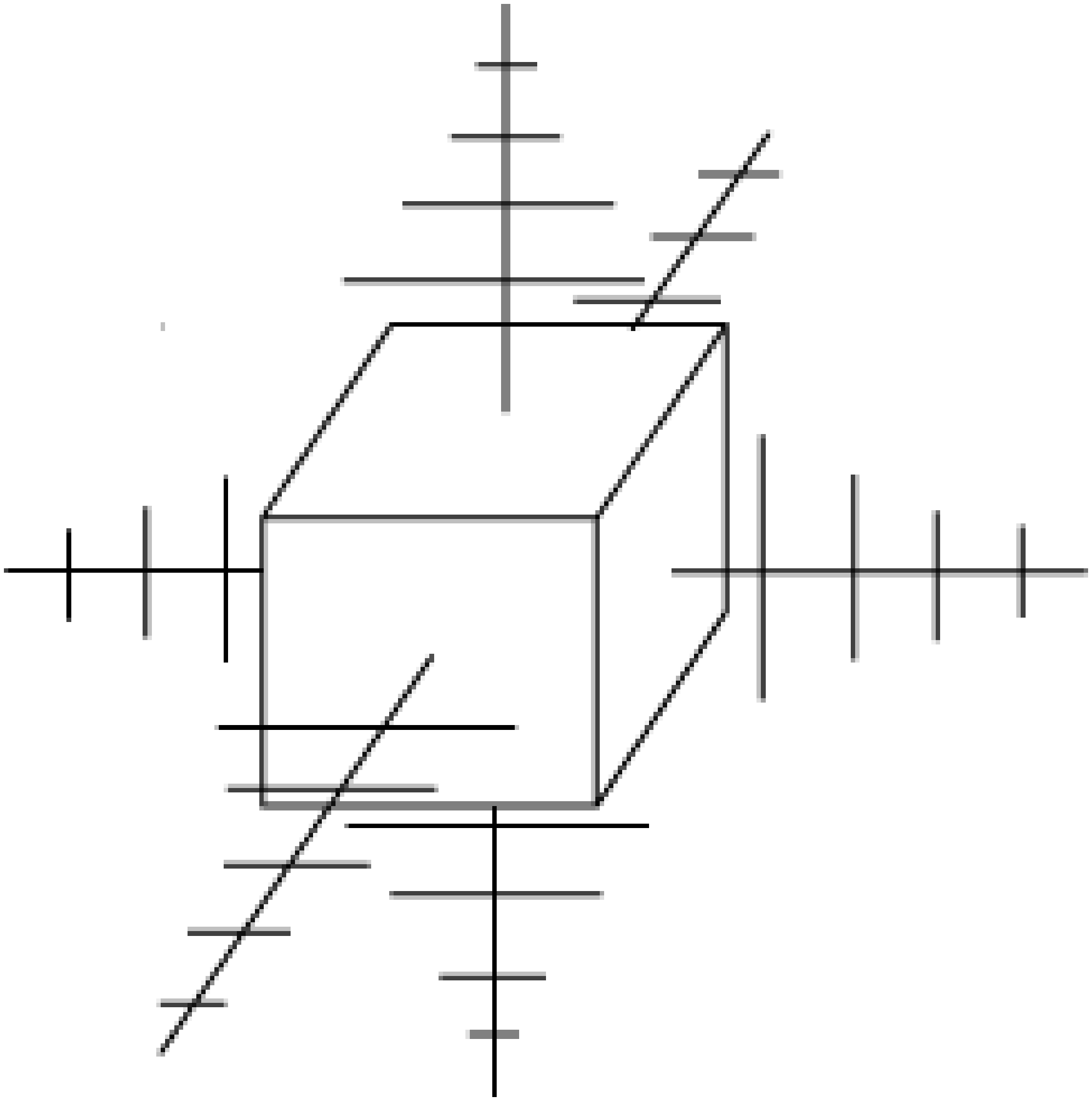
- The needle-shaped crystals that were detected in the Eighteenth century are called *dendrites. Most technically interesting alloys solidify by a primary precipitation of dendrites.*
- Its growth in certain specific crystal directions is favoured. From a crystal nucleus a dendrite tip grows, which forms the *main branch or primary* arm. *Immediately behind this tip. lateral arms or secondary dendrite arms are formed.*


λ1
λ2

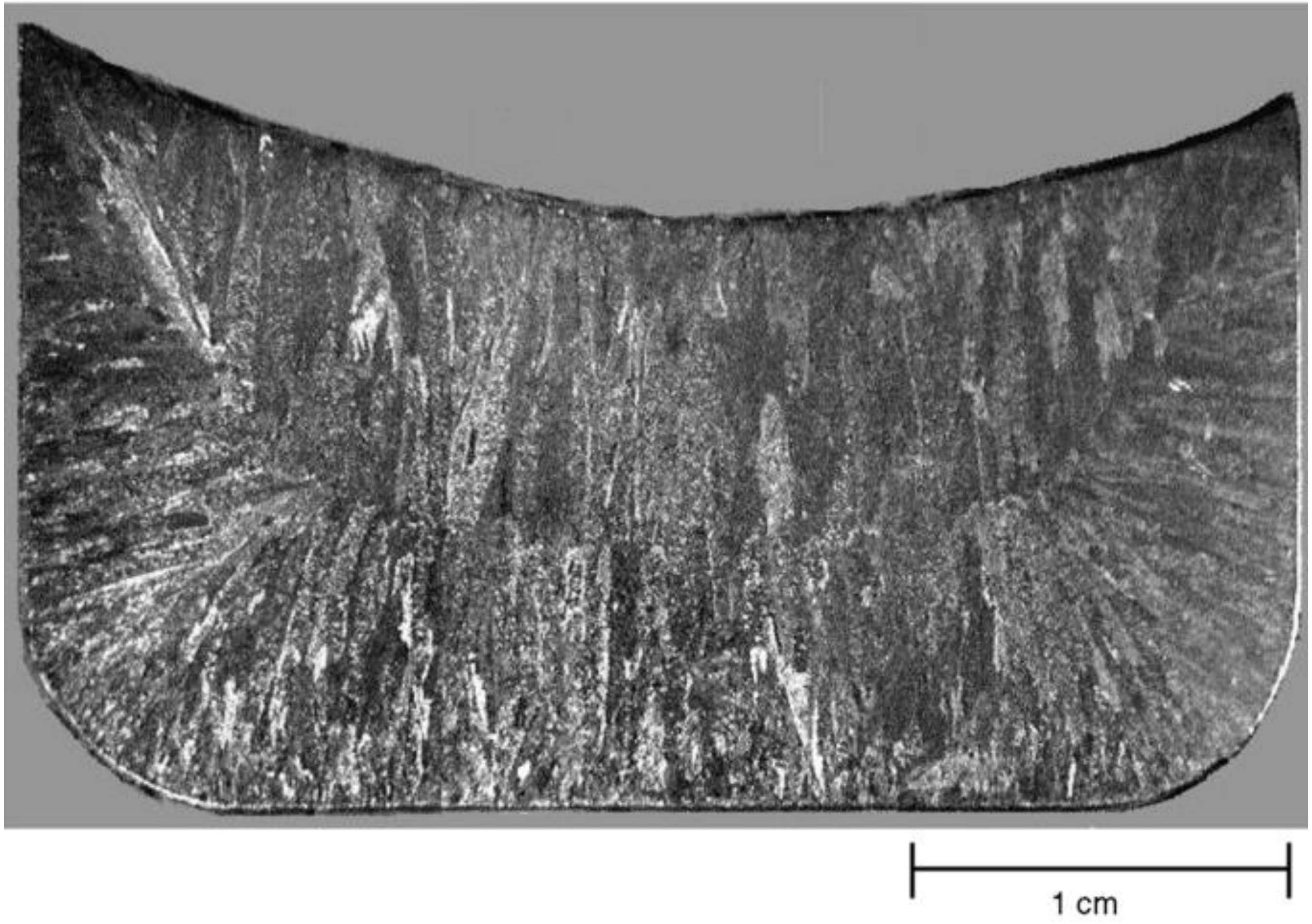
- *For metals with cubic structures they are normally* situated in two mutually perpendicular planes. The lateral arms are perpendicular to each other and the main branch. The lateral arms are successively formed behind the growing tip and reach different lengths for this reason. The oldest ones are longest.

Solidification length scale

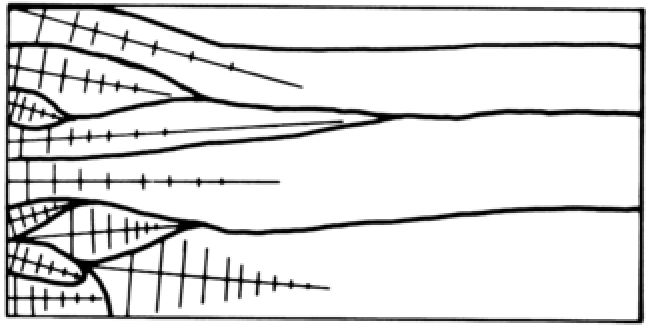




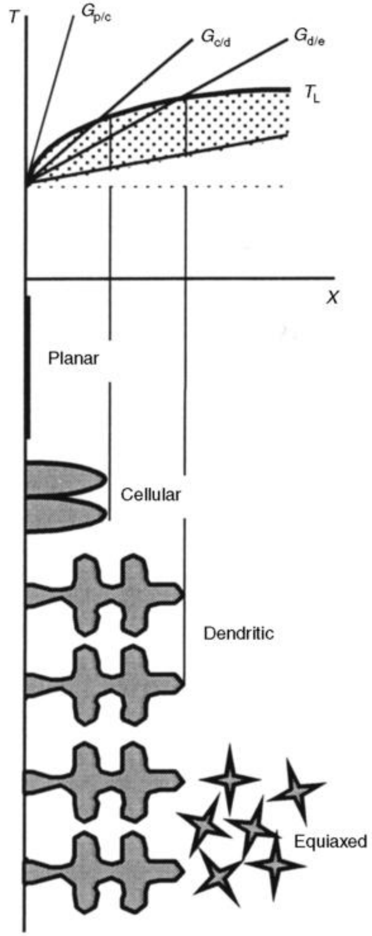
Macrostructure of a cast Ti-6Al-4V alloy specimen. Etchant: Keller's reagent



Elongated grains and preferred orientation produced by directional solidification



Correlation between the thermal gradient at the interface and the interface morphology



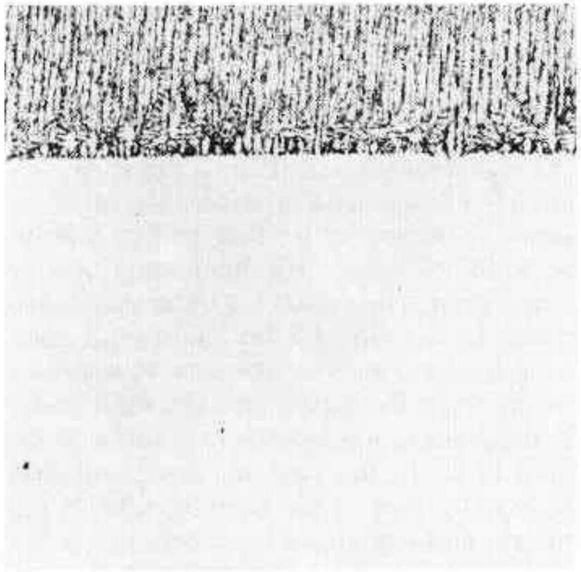


Fig. 4 Directionally solidified Sn-0.6Cd alloy. Section parallel to the growth direction shows a quenched planar liquid-solid interface, indicating the absence of constitutional supercooling. $G = 320$ K/cm, $V = 0.85$ μm/s, $\Delta T = 5.7$ K. 5 mL HNO_3, 95 mL lactic acid. 80×. (C. Brady)

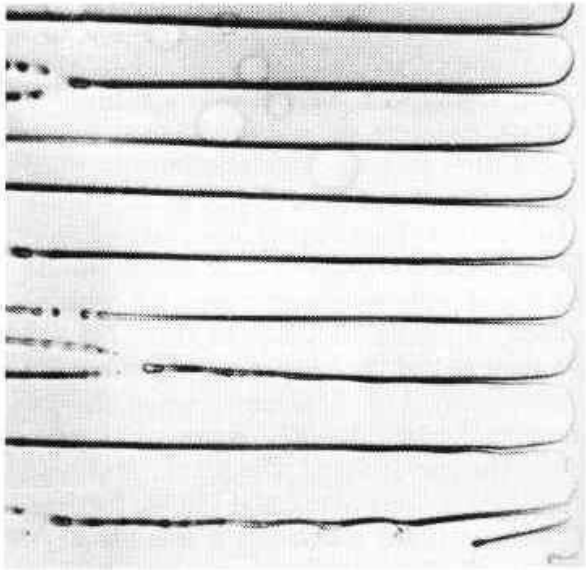


Fig. 5 Directionally solidified transparent organic "alloy," succinonitrile-5.5 mole% acetone. *In situ* observation of a growing cellular liquid-solid interface. Growth direction is shown horizontal. $G = 67$ K/cm, $V = 0.58$ μm/s, $\Delta T = 103$ K, $D \approx 10^{-5}$ cm²/s. 32×. (Ref 2)

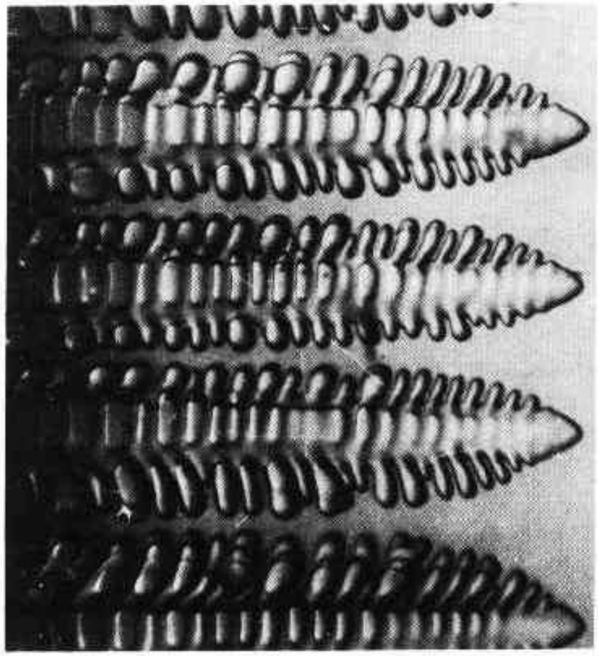
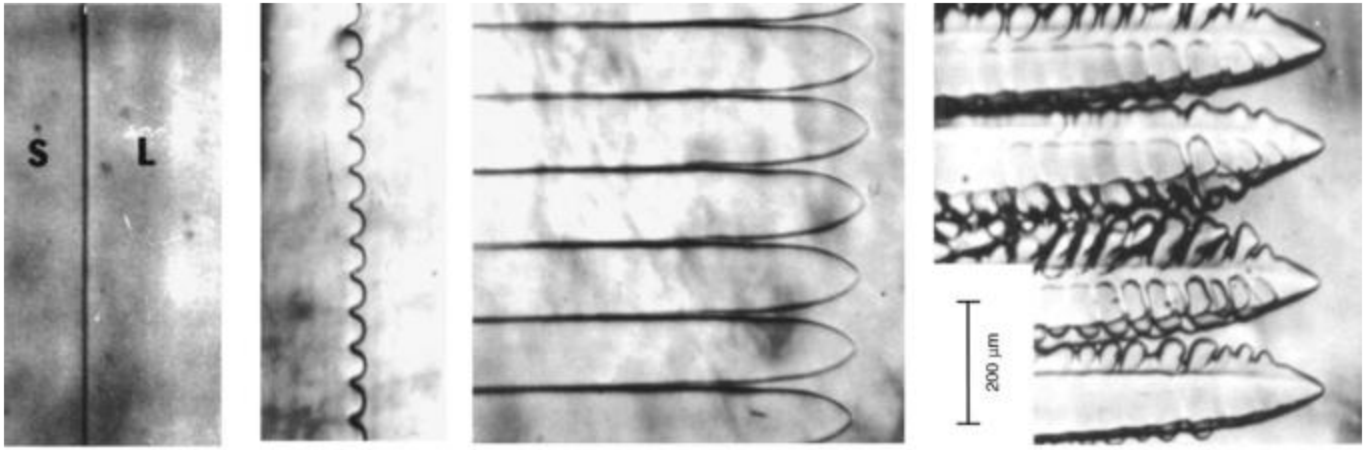


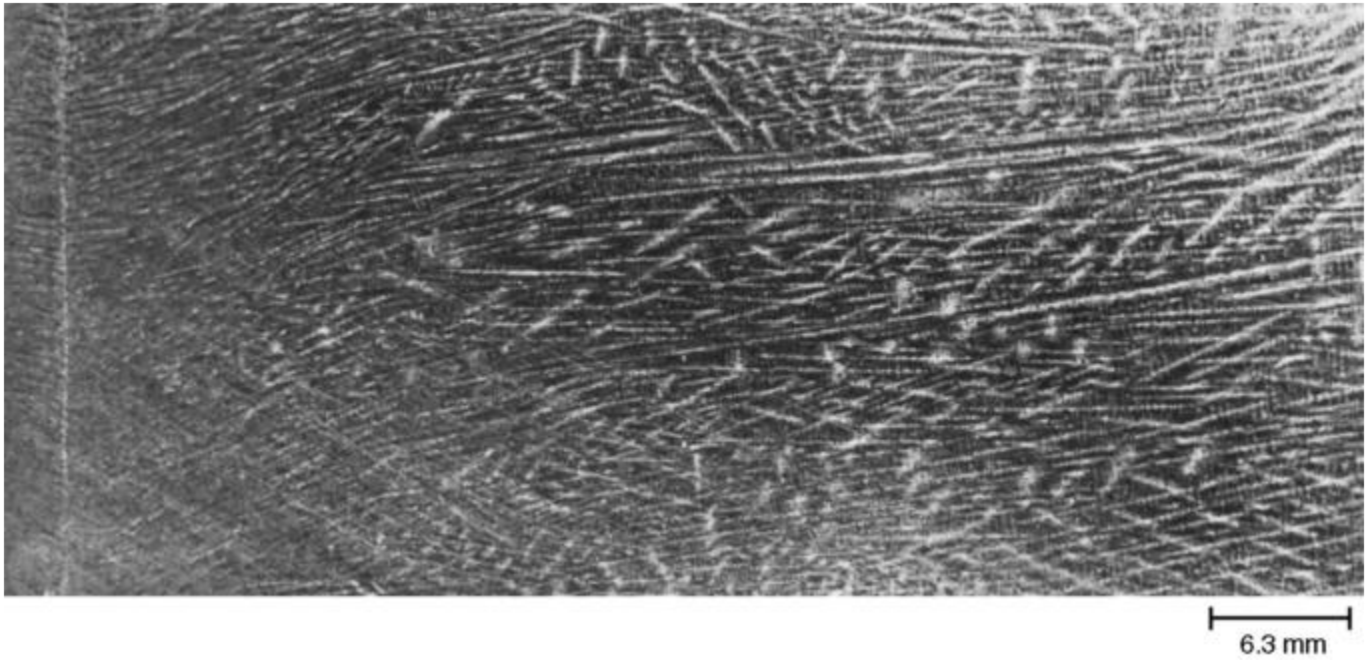
Fig. 6 Same organic compound as in Fig. 5. V was increased to 1.17 μm/s to produce a dendritic liquid-solid interface. 36×. (Ref 2)

The change of the morphology of the solid/liquid interface as a function of growth velocity (*V) in* a transparent organic system (pivalic acid, 0.076% ethanol) directionally solidified under a thermal gradient of 2.98 K/mm. (a) Planar interface, *V = 0.2 μm/s. (b) Cellular interface, V = 1.0 μm/s. (c)* Cellular interface, *V = 3.0 μm/s. (d) Dendritic interface, V = 7.0 μm/s.*

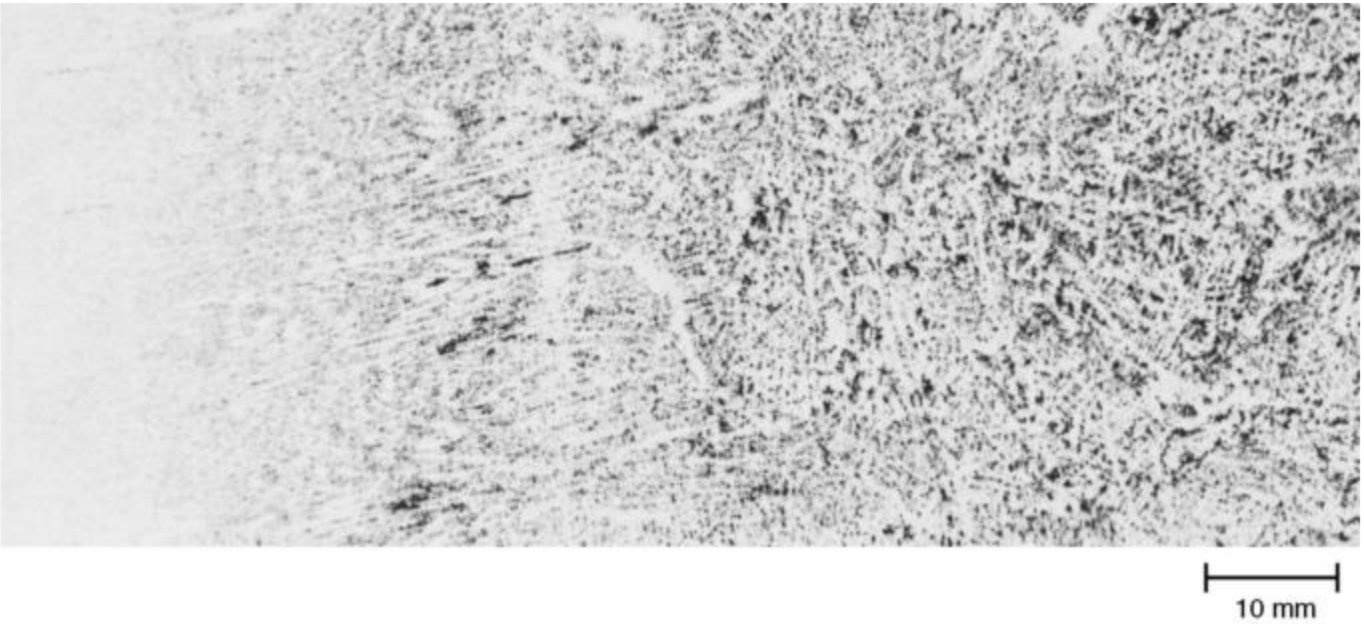


(a) (b) (c) (d)

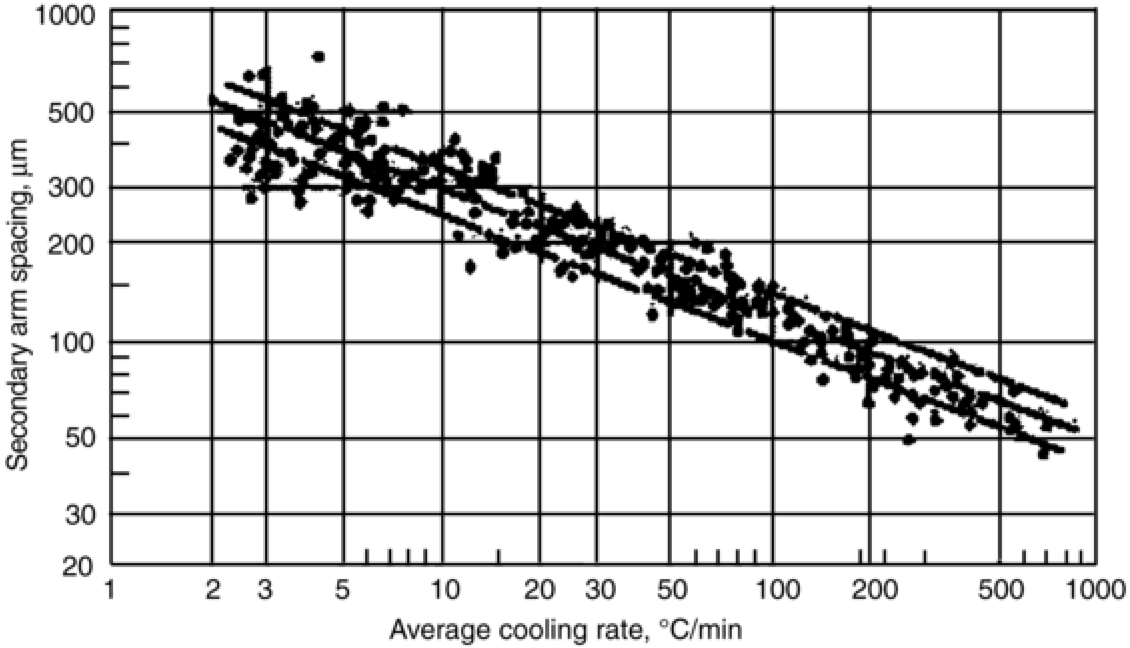
Macrostructure of UNS G10170 steel, as strand cast. Compare with Fig. 4. 10% HNO_3 in H_2O. 4.75×



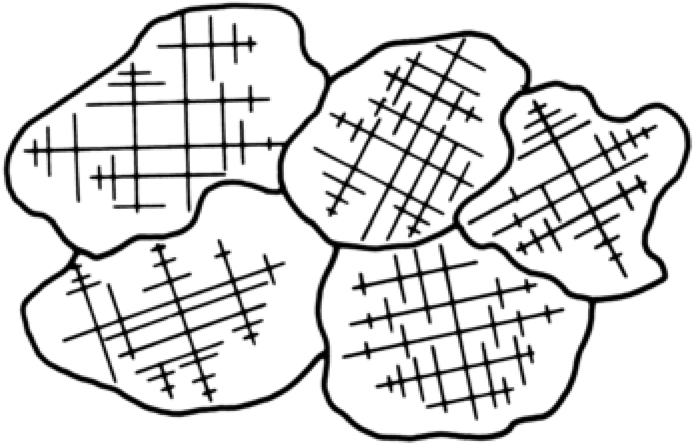
Sulfur print of UNS G10170 steel, as strand cast, Compare with Fig. 3. As-polished. 1.25×.



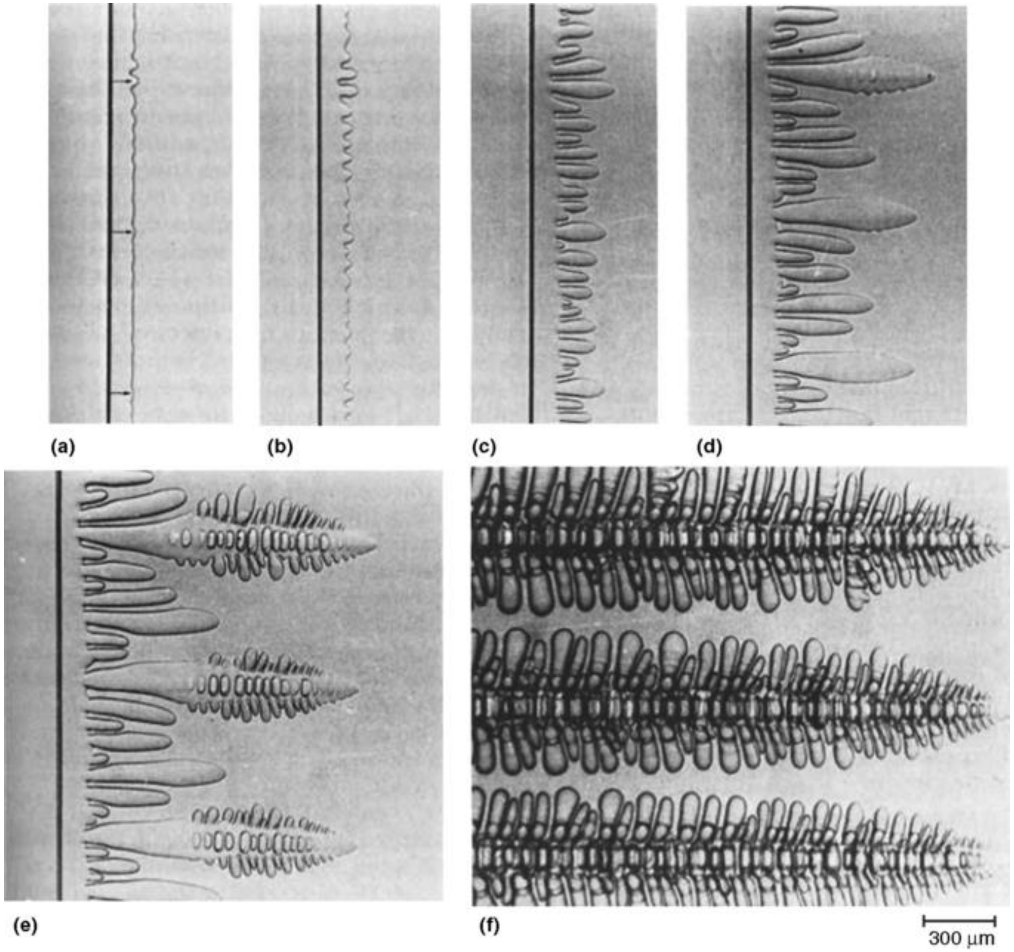
Influence of cooling rate on the secondary dendrite arm spacing of commercial steels containing 0.1 to 0.9%.



Coarse, equiaxed grains produced by dendritic growth

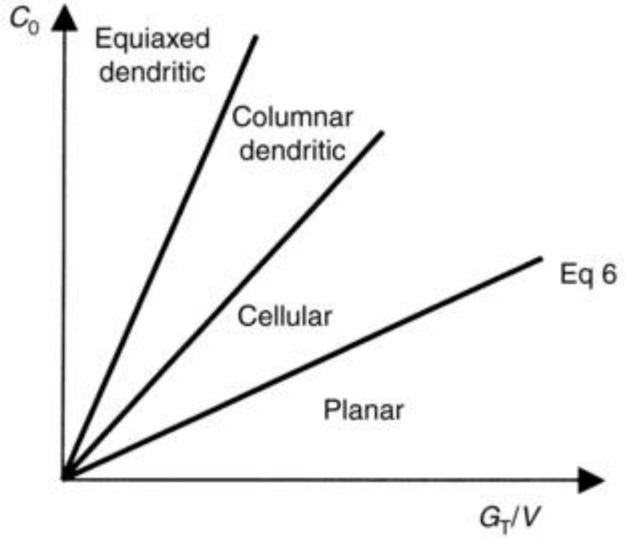


Change in interface morphology of a succinonitrile-4% acetone solution when increasing the solidification velocity from 0 to 3.4 µm/s at a temperature gradient of 6.7 K/mm. (a) 50 s. (b) 55 s. (c) 65 s. (d) 80 s. (e) 135 s. (f) 740 s. Magnification: 30×.

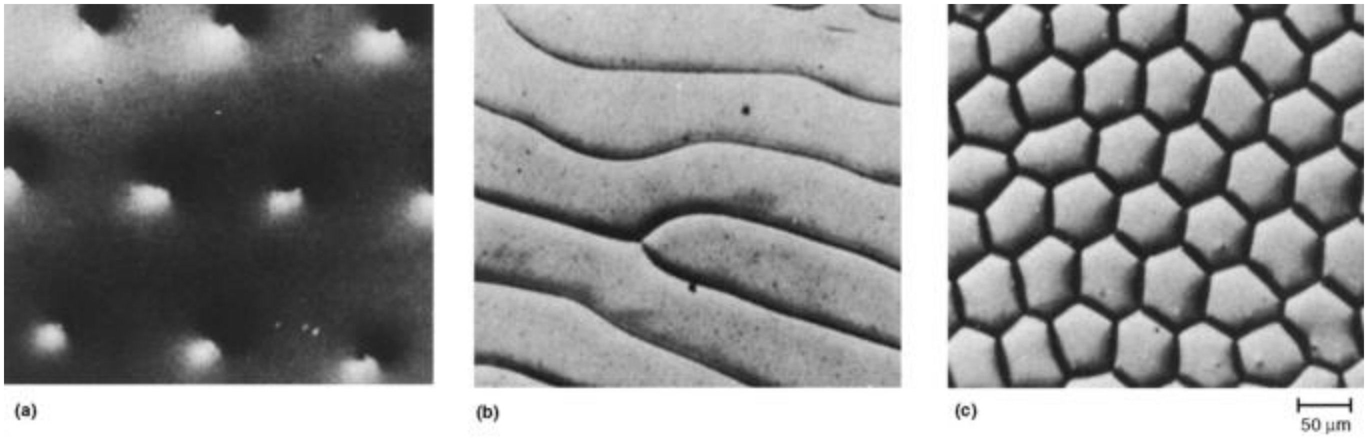


Coarsening of secondary arms
ripening
coalescence

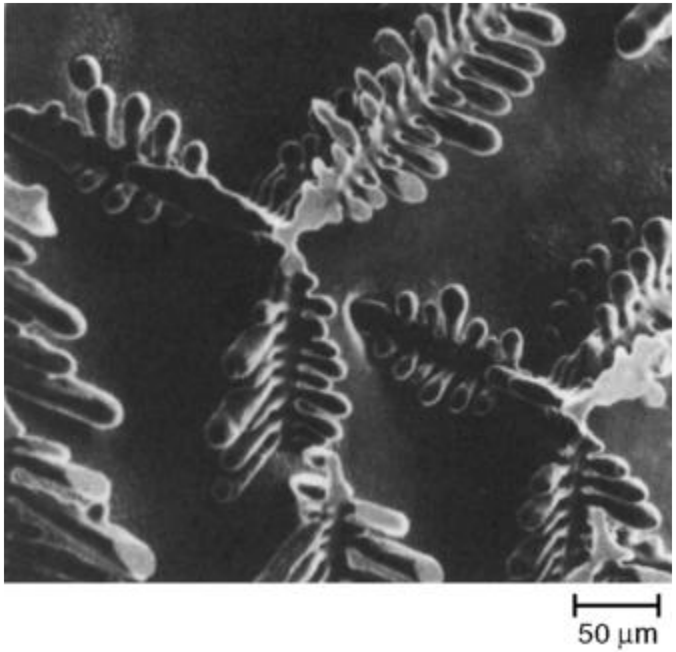
Transition to different interface morphologies as a function of the temperaturegradient/ solidification-velocity ratio (*GT/V) and solute concentration (C0)*



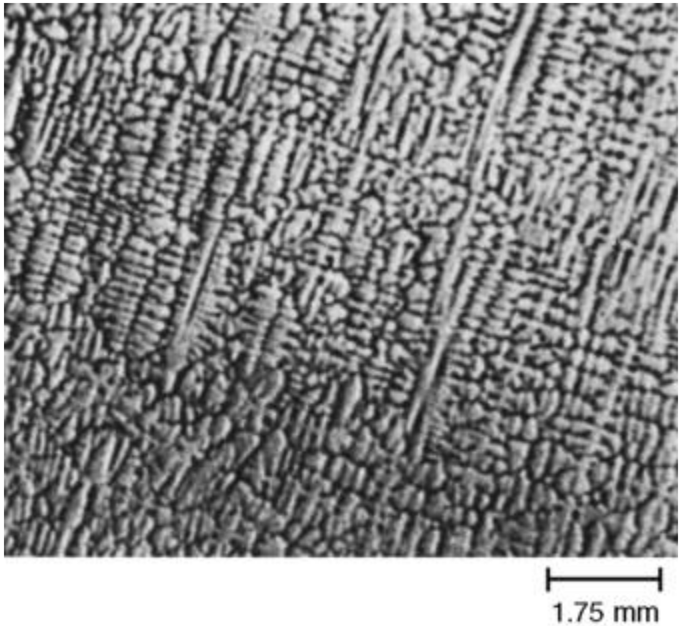
Sn-0.05Pb alloy; liquid decanted to reveal structures of solid/liquid interfaces. (a) Oblique illumination reveals nodes at the solid/liquid interface. (b) Elongated cells at the solid/liquid interface under bright-field illumination. (c) Fully developed hexagonal cells at the solid/liquid interface (brightfield illumination). Unpolished, unetched. Magnification: 150×.



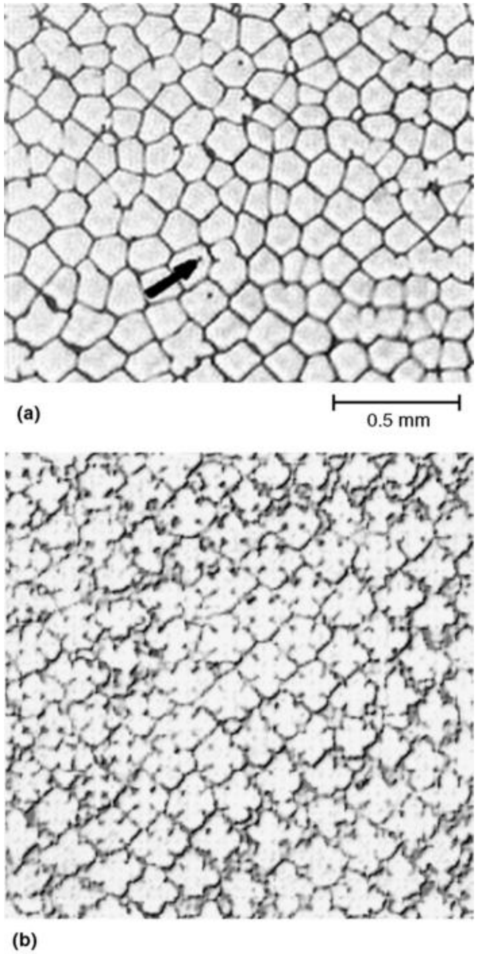
Secondary electron micrograph of Cu-10Co (at.%) alloy casting. Etchant not reported. Magnification: 150×



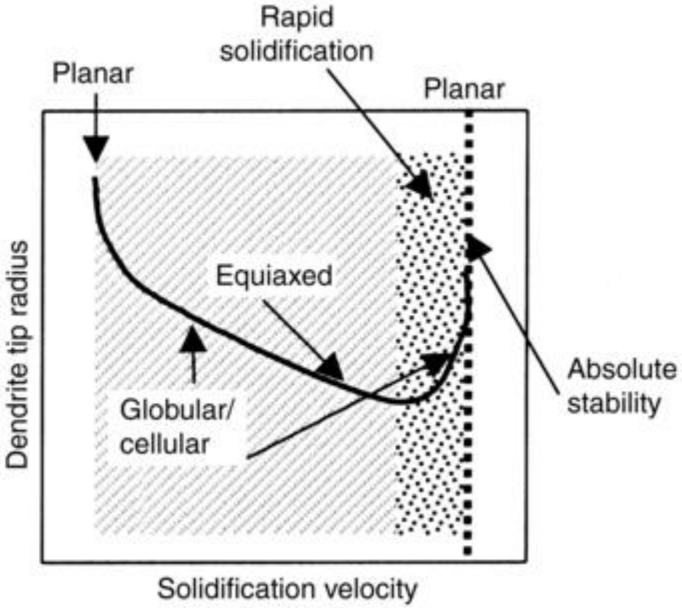
Ni-25Cu (at.%) alloy. Etchant: 70 mL HNO_3 and 30 mL H_2O. Magnification: 10×



Transverse microstructures of Pb-2.2Sb (wt%) alloy single-crystal samples grown along [100] at *GT = 164 K/cm. Etchant: 60 mL acetic acid and 40 mL hydrogen peroxide (30%). (a) Deep cells grown at* 2.5 µm/s. Arrow indicates tip splitting. (b) Completely dendritic structure. Dendrites grown at 10 µm/s



Correlation between solidification velocity and dendrite tip radius



Relationship between Dendrite Arm Distance and Growth Rate

- It has been found that the distance between the secondary dendrite arms is not constant but increases with the distance from the cooled surface at directed solidification and at growth towards the centre in an ingot. It has been shown both experimentally and theoretically that the following relationship between the distance $\text{lamda}_{\text{den}}$ for secondary or primary dendrite arms and the growth rate v_{growth} is valid:

$$v_{\text{growth}}\lambda_{\text{den}}^{2} = \text{const} \tag{6.9}$$

The dendrite arm distance also depends on a number of other factors, among them the composition of the alloy and its phase diagram. The influence of these factors affects the value of the constant in Equation (6.9).

In most experimental investigations, authors have chosen to report relationships between the dendrite arm distance and some other experimental variable, for example, the total solidification time θ. In this case the relationship will be:

$$\lambda_{\text{den}} = K\theta^{n} \tag{6.10}$$

$$\lambda_{\text{den}} = K\theta^{n} \tag{6.10}$$

where K and n are two constants. The constant n has a value between 1/3 and 1/2 for different types of steel alloys. Figure 6.5 shows the result of an investigation of a low-carbon alloy where the primary and secondary dendrite arm distances have been measured as functions of the cooling rate of the melt by microscope studies.

When a network of dendrite arms has been formed there is remaining melt left between the arms. This melt solidifies

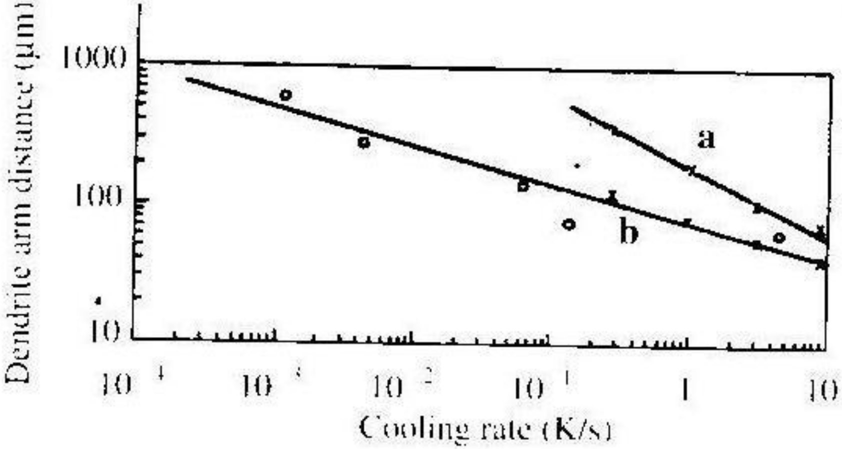
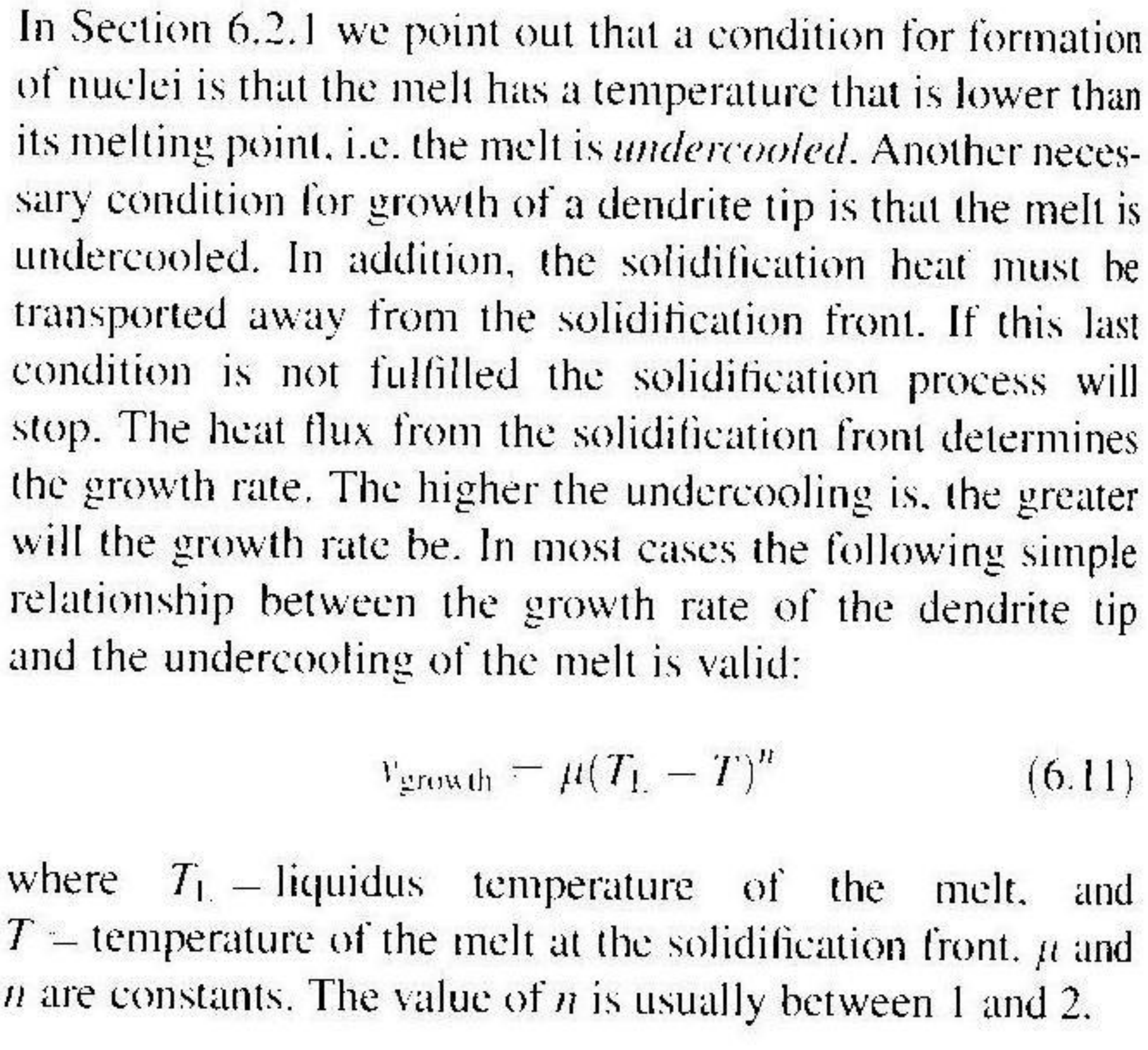


Figure 6.5 The primary and secondary dendrite arm distances as functions of the cooling rate for a steel alloy containing 25 % Ni. (a) Primary dendrite arms; (b) secondary dendrite arms. The growth and the cooling rates are proportional. Reproduced with permission from Merton C. Flemings.

during the continued temperature decrease by precipitation of solid phase on the dendrite arms. The solid phase and the melt of the alloy have different compositions. During the solidification process the melt will successively be enriched by the alloying element and the last solidified melt will therefore have a higher concentration of the alloying element than the one that solidified during an earlier stage. This phenomenon is called *microsegregation* and will be treated in Chapter 7.

Relationship between Growth Rate and Undercooling



In Section 6.2.1 we point out that a condition for formation of nuclei is that the melt has a temperature that is lower than its melting point, i.e. the melt is *undercooled*. Another necessary condition for growth of a dendrite tip is that the melt is undercooled. In addition, the solidification heat must be transported away from the solidification front. If this last condition is not fulfilled the solidification process will stop. The heat flux from the solidification front determines the growth rate. The higher the undercooling is, the greater will the growth rate be. In most cases the following simple relationship between the growth rate of the dendrite tip and the undercooling of the melt is valid:

$$v_{\text{growth}} = \mu(T_L - T)^n \qquad (6.11)$$

where T_L – liquidus temperature of the melt, and T – temperature of the melt at the solidification front. μ and n are constants. The value of n is usually between 1 and 2.

Crystal Multiplication

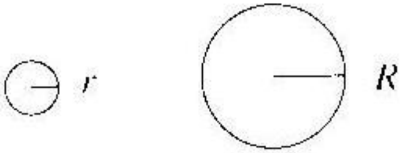
- In Section 6.2.2 we treated inoculation as a method of facilitating ihe formation of crystals.

- A second method is so-called *crystal multiplication. This means that parts of the dendrite skeleton are carried into the melt and serve as nuclei for new crystals. Different mechanisms for spontaneous crystal multiplication have been suggested, one of which is that fragments are torn off purely mechanically from the growing dendrite tips, for example, by influence of the natural convection in the melt. Examples of such a process are the broom structure of cementite in white cast iron (page 151). the corresponding phenomenon for silicon in silumin (pages 147-148), and feather crystal growth in aluminium.*

- This mechanical mechanism of crystal multiplication can be used deliberately in many ways. It has been found that many materials can be forced to fine-grain solidification by ultrasonic treatment. In order to get the full effect, it is necessary to combine the ultrasonic treatment with violent convection to make sure that the torn fragments are carried out into the melt effectively. This method has been successful for both aluminium alloys and stainless steel.

- A rotating magnetic field has also proved to be an effective way to produce a line-grain structure in magnetic metal melts. The electromagnetic field is applied in a circle around the ingot. By choosing a convenient frequency for the alternating current in the magnetic coils it is possible to force the melt to rotate with the magnetic field. To increase the fine-grain structure the direction of the magnetic field is changed regularly. With the forced rotation of the melt, shear forces arise *on the dendrite arms that are great enough to break them and then carry (hem into the melt. This method has been used successfully for both static and continuous casting.*

- The second mechanism for crystal multiplication is based on the principle of *melting off dendrite arms. Papapetrou introduced this method in the 1930s. He found that certain dendrite arms are melted off under the influence of surface tension. The reason for this is that surface tension causes an excess pressure of the melt inside the interface that is inversely proportional to the radius of curvature. This overpressure causes a melting point decrease that is proportional to the pressure. The excess pressure, caused by the surface tension of a small droplet, is larger than the pressure caused by a big droplet (Figure 6.6).*



$$\Delta p_1 = \frac{2\sigma}{r} \qquad \Delta p_2 = \frac{2\sigma}{R}$$

$$\Delta p_1 > \Delta p_2$$

Figure 6.6 Pore pressure related to pore radius.

The secondary dendrite arms are always thinnest at the root, where the radius of curvature is smallest, and the excess pressure at its maximum. Thus the dendrite arms preferably melt off at the roots (Figure 6.7). If this happens the released dendrite fragments may be distributed into the melt by convection and serve as nuclei for new crystals.

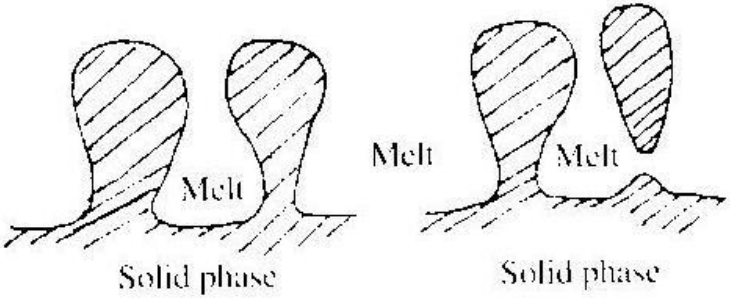


Figure 6.7 Melting off of dendrite arms.

- In practice, the melting off method can be realized in a very direct way by increasing the temperature during the solidification. This can be done by the convection in the melt, which may direct a flow of *hot material to a growing* crystal. The simplest way to cause a desired temperature increase is to add a small amount of hot melt during solidification process.

EUTECTIC STRUCTURE AND EUTECTIC GROWTH

- Twentieth century, eutectic alloys were getting used as composite materials. Two of the most frequently used cast alloys, silumin and cast iron, are eutectic. It is therefore important to understand the eutectic solidification process and its influence on the structure of this type *of alloy too, so that it is possible to give them good material properties.*

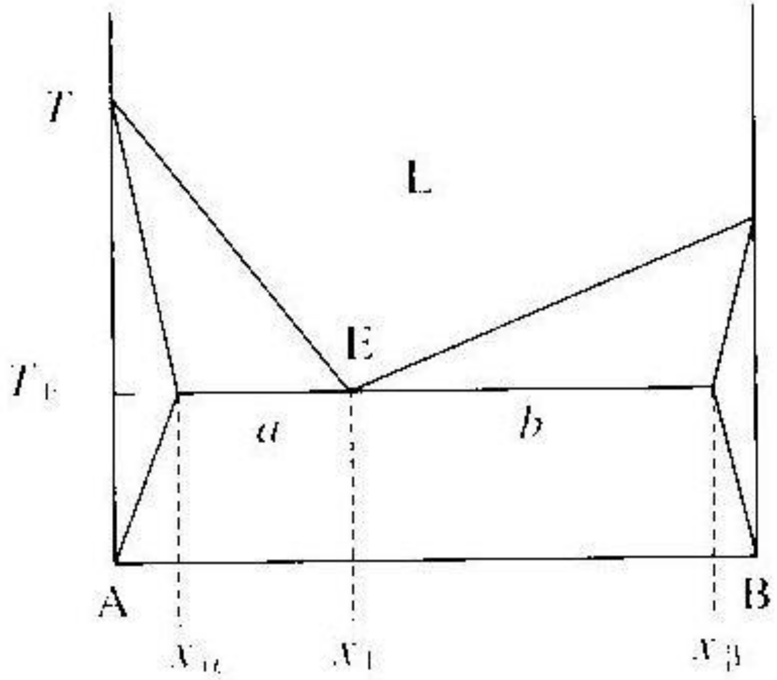
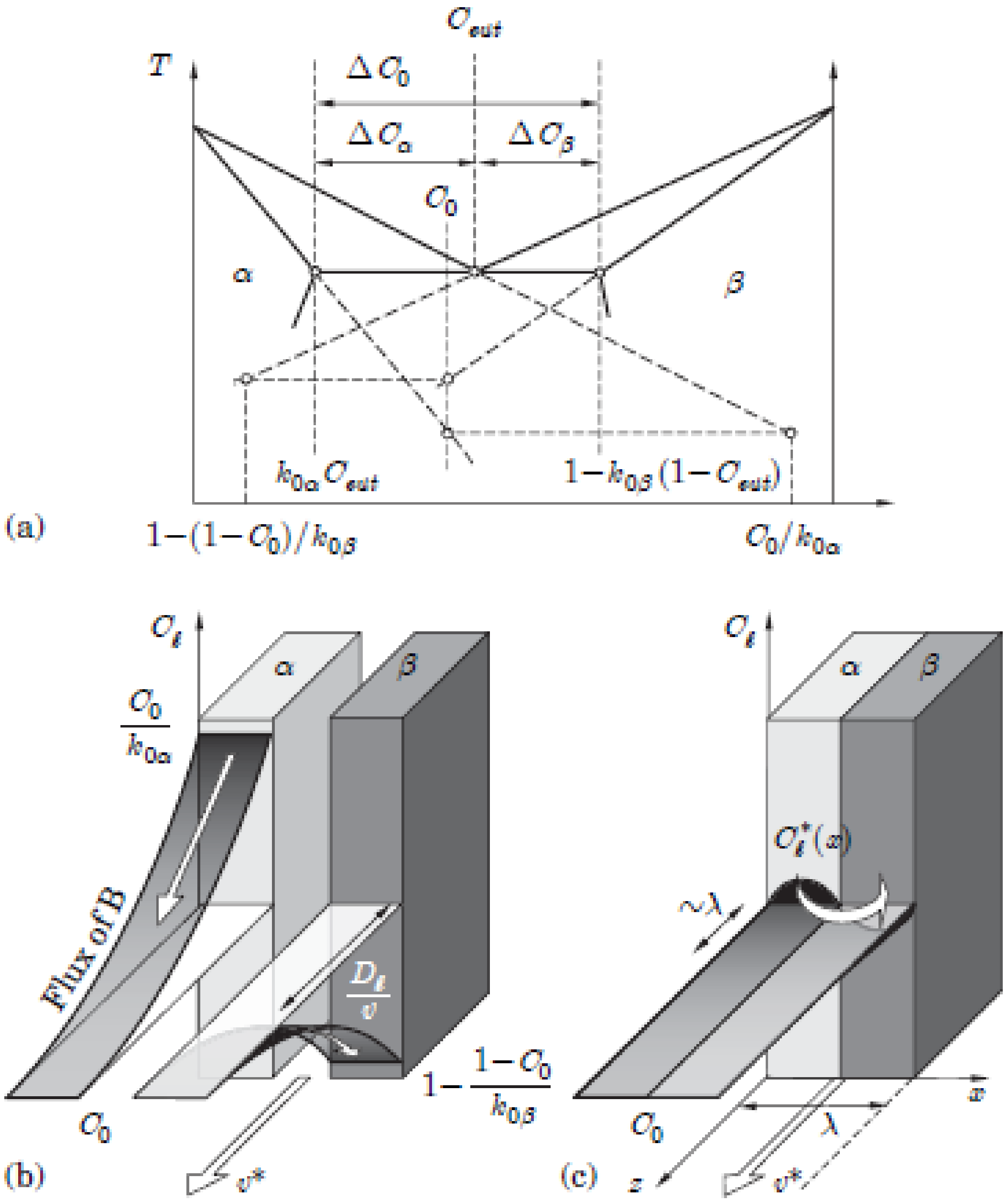


Figure 6.8 Schematic phase diagram of a binary alloy.

If the temperature decreases in a melt having a eutectic composition, no solid phase is precipitated until the temperature has reached the eutectic temperature T_E. The alloy solidifies by precipitation of two solid phases with the compositions x_α and x_β at the constant proportions:

$$\frac{N_A}{N_B} = \frac{b/(a+b)}{a/(a+b)} = \frac{b}{a} \tag{6.12}$$


C_{eut}
T
ΔC_0
ΔC_α
ΔC_β
C_0
α
β
$k_{0\alpha}C_{eut}$
$1-k_{0\beta}(1-C_{eut})$
(a)
$1-(1-C_0)/k_{0\beta}$
$C_0/k_{0\alpha}$
C_ℓ
α
β
$\frac{C_0}{k_{0\alpha}}$
Flux of B
$\frac{D_\ell}{v}$
$1-\frac{1-C_0}{k_{0\beta}}$
C_0
(b)
v^*
C_ℓ
α
β
$C_\ell^*(x)$
$\sim\lambda$
x
C_0
λ
(c)
z
v^*

These constant proportions correspond to a constant chemical composition of the solid and the solidification process is called a *eutectic reaction* for this reason. During the whole solidification process the temperature remains constant and close to T_E. When all melt has solidified the temperature continues to sink.

No microsegregation is present in eutectic alloys. Figure 6.9 shows a typical temperature–time curve at eutectic solidification.

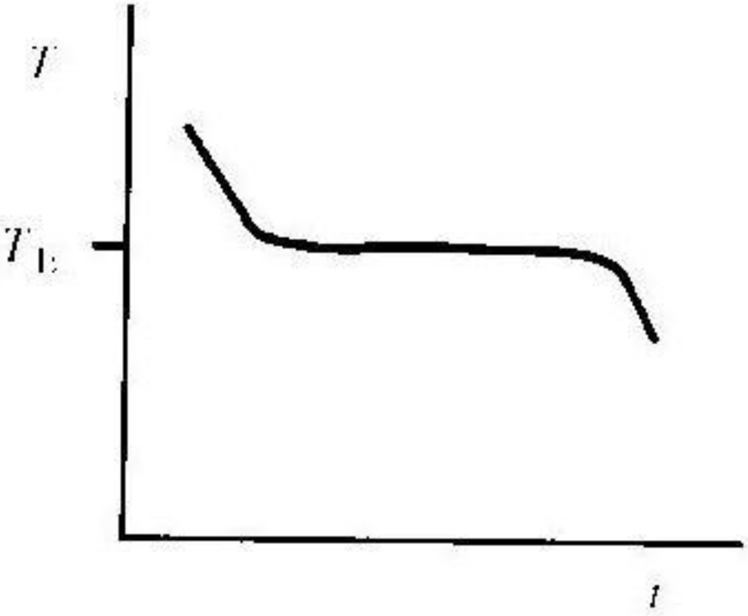


Figure 6.9 Temperature–time curve of a binary eutectic alloy during cooling and solidification.

TABLE 6.1 Eutectic structures.

Designation	Description
Lamella eutectic structure	The two solid phases are tied in separate planar layers.
Rod eutectic structure	One of the phases is precipitated as rods and is surrounded by the other phase.
Spiral eutectic structure	One of the phases is precipitated as spirals and is surrounded by the other phase.
Flake-like eutectic structure	One of the phases is precipitated as plates, separated from each other and surrounded by the other phase.
Nodular eutectic structure	One of the phases is precipitated as spherical particles and is surrounded by the other phase.

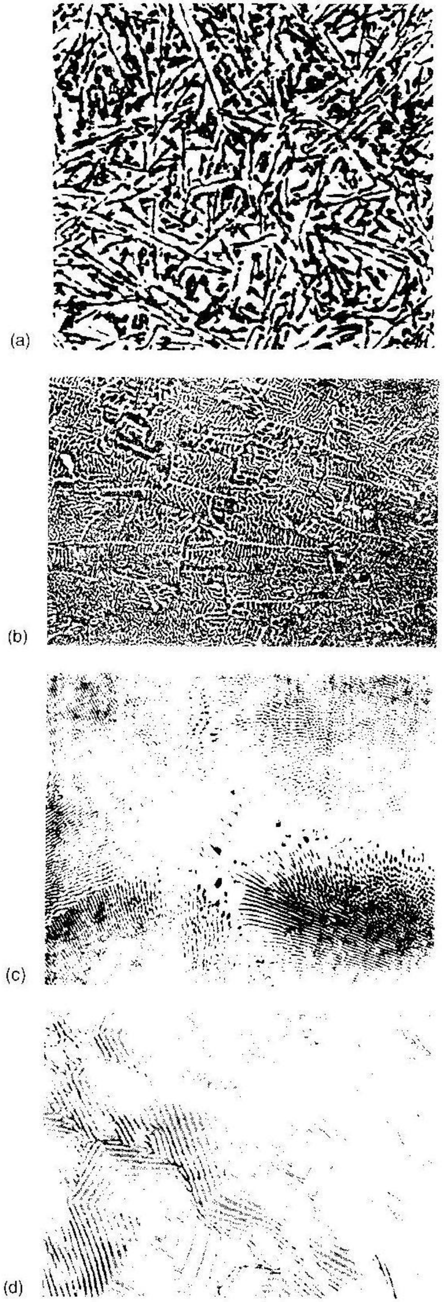


Figure 6.11 (a) Disk-shaped Si plates in a matrix of Al in a eutectic Al–Si alloy. (b) 'Chinese script' structure in a eutectic Bi–Sn alloy. (c) Mixed lamella and rod structure in a eutectic Pb–Cd alloy with 0.1% Sn. (d) Spiral structure in a eutectic Zn–Mg alloy.

- For a *degenerated eutectic reaction* *one of the two phases grows more rapidly than the other phase. For a* *normal eutectic reaction* *both phases grow in close cooperation with each other and with the same growth rate. This is the definition of normal eutectic structure. We will restrict further discussion to this case.*

Lamellar Eutectic Structure

- A lamellar structure is formed when both precipitated phases grow side by side as in Figure 6.12 (a). During the growth of an alpha-lamella, the B atoms will continuously concentrate in the melt in front of the solidification front of the *beta-lamella. In the same way the A atoms concentrate in front of the solidification front of the beta- lamella. This leads to diffusion of A and B atoms as shown in Figure 6.12 (b).*
- It can be shown that that the three-phase equilibrium along the lines where the alpha-phase, beta-phase and melt meet results in curved surfaces instead of planes. The formation *of a lamellar eutectic structure is associated with the surface tension conditions of the alpha- and beta-phases.*

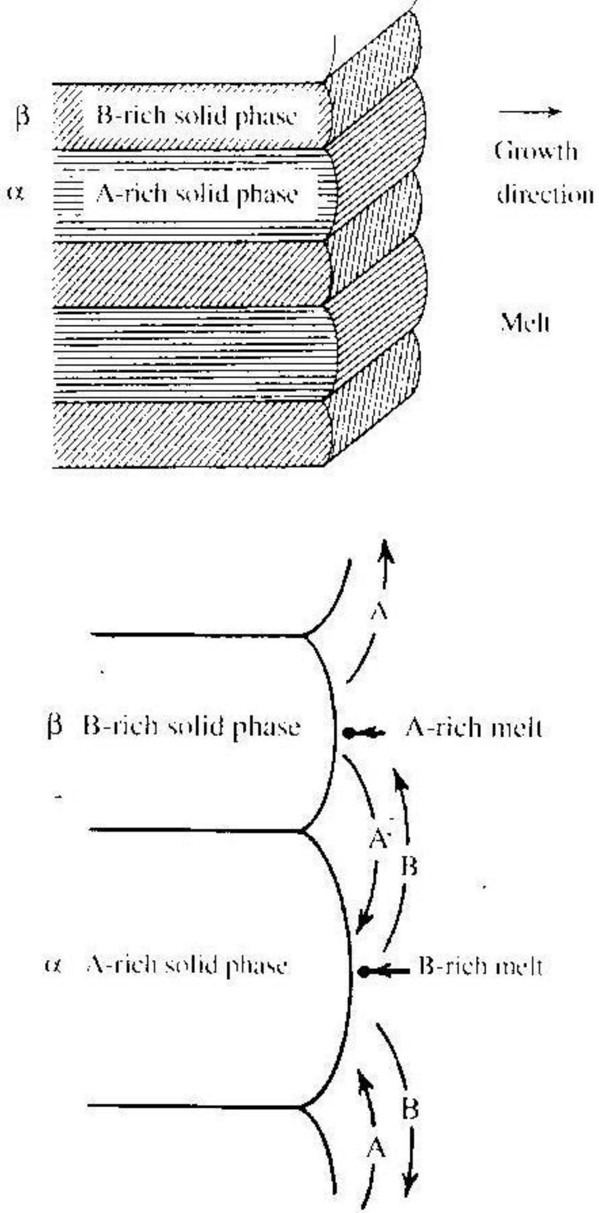
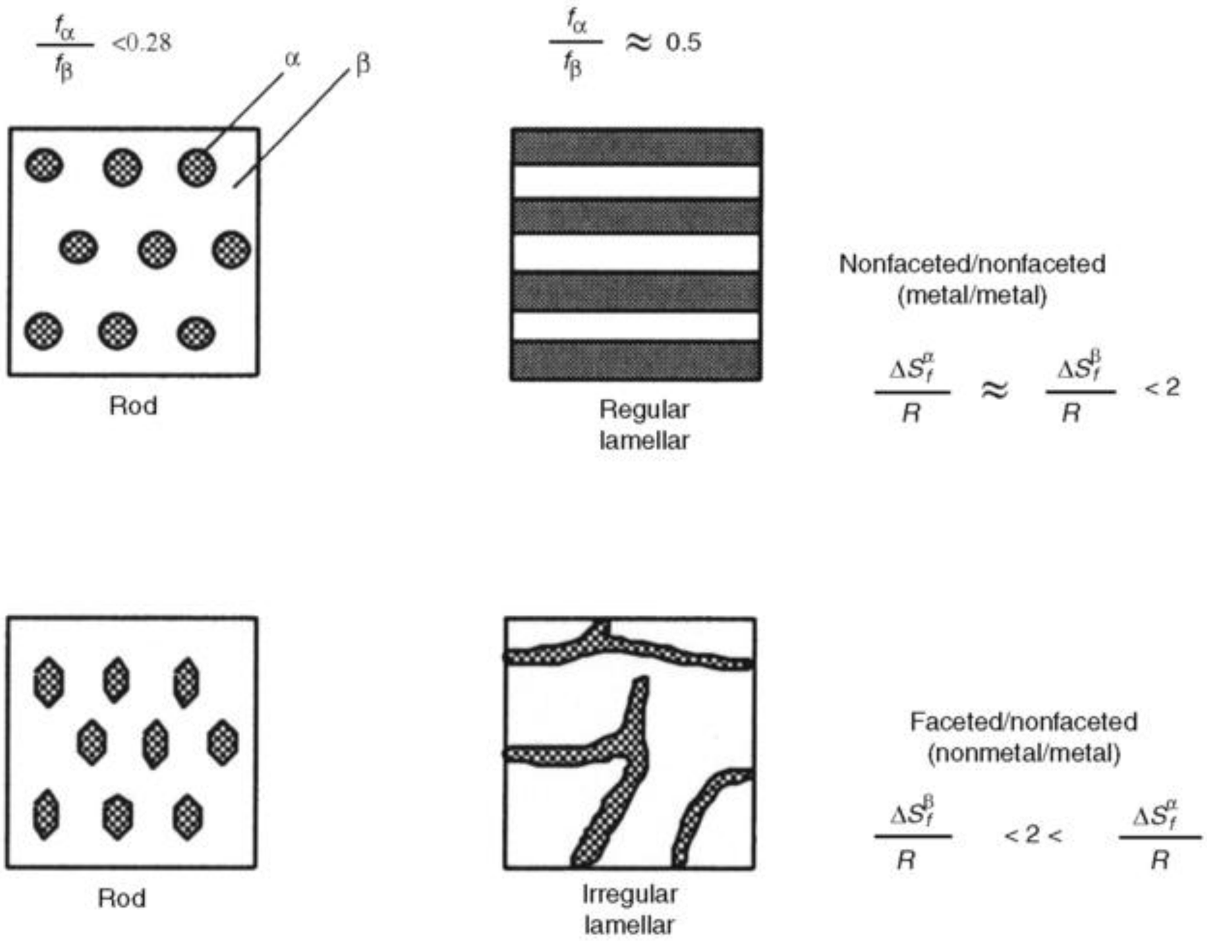


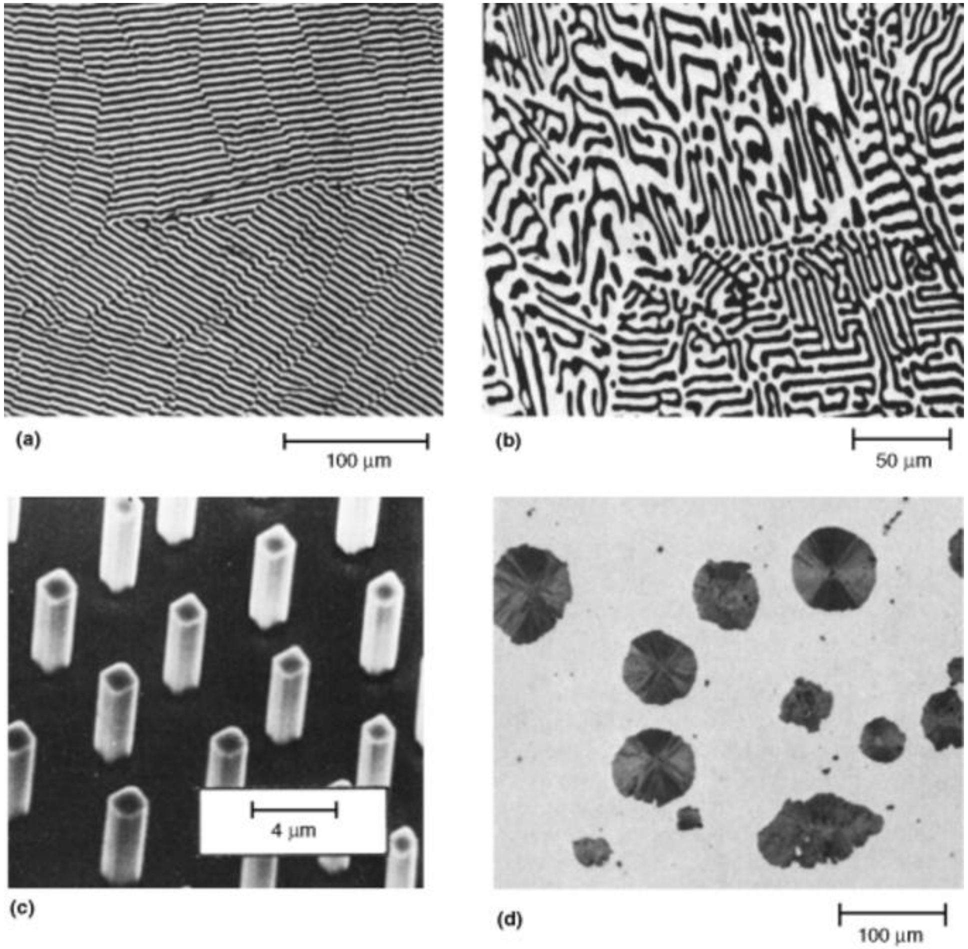
Figure 6.12 (a) and (b) Growth mechanism for a plate-like (lamellar) eutectic alloy. Reproduced with permission from Robert E. Krieger Publishing Co., John Wiley & Sons, Inc.

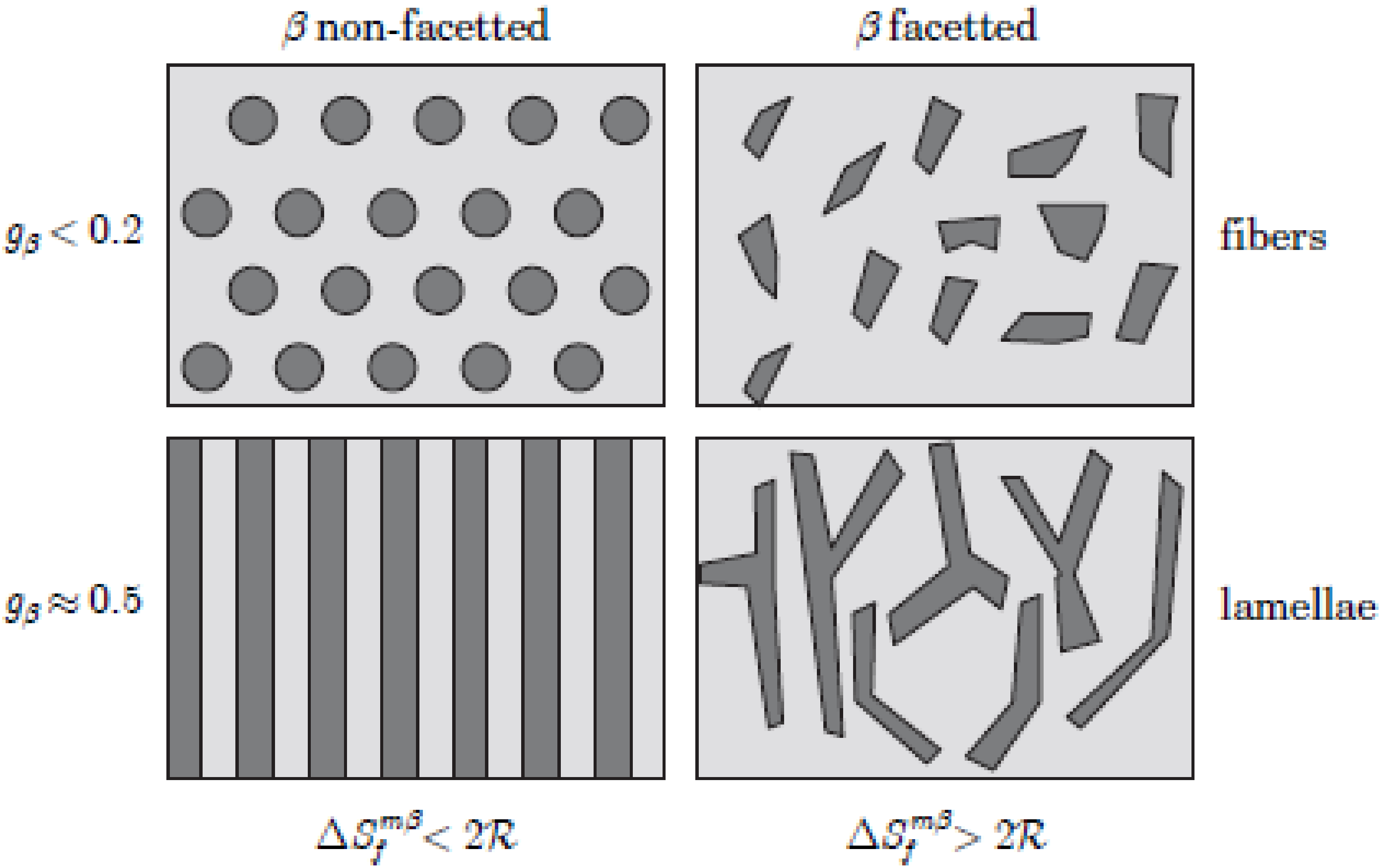
Classification of eutectic morphologies

Types of cooperative eutectics



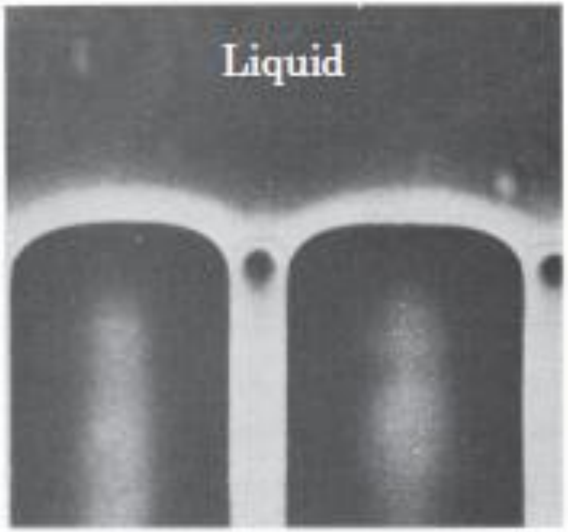
Eutectic microstructures. (a) Regular nonfaceted/nonfaceted eutectic (Al-Al2Cu). (b) Irregular faceted/nonfaceted eutectic (Mg-Mg2Sn). The dark phase is the faceted Mg2Sn. Ref 22. (c) Rod faceted/nonfaceted eutectic (Ni-NbC). Ref 23. (d) Divorced eutectic (Fe-spheroidal graphite)



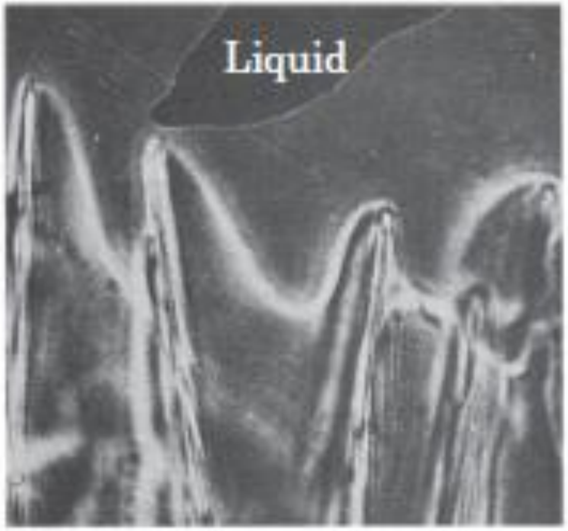

β non-facetted
β facetted
$g_\beta < 0.2$
fibers
$g_\beta \approx 0.5$
lamellae
$\Delta S_f^{m\beta} < 2R$
$\Delta S_f^{m\beta} > 2R$

(a) Al - Au

(b) Al - Si

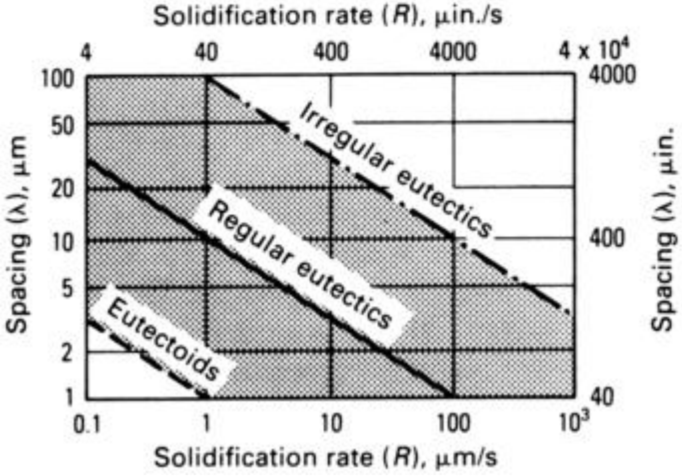


(d) CBr_4 - C_2Cl_6

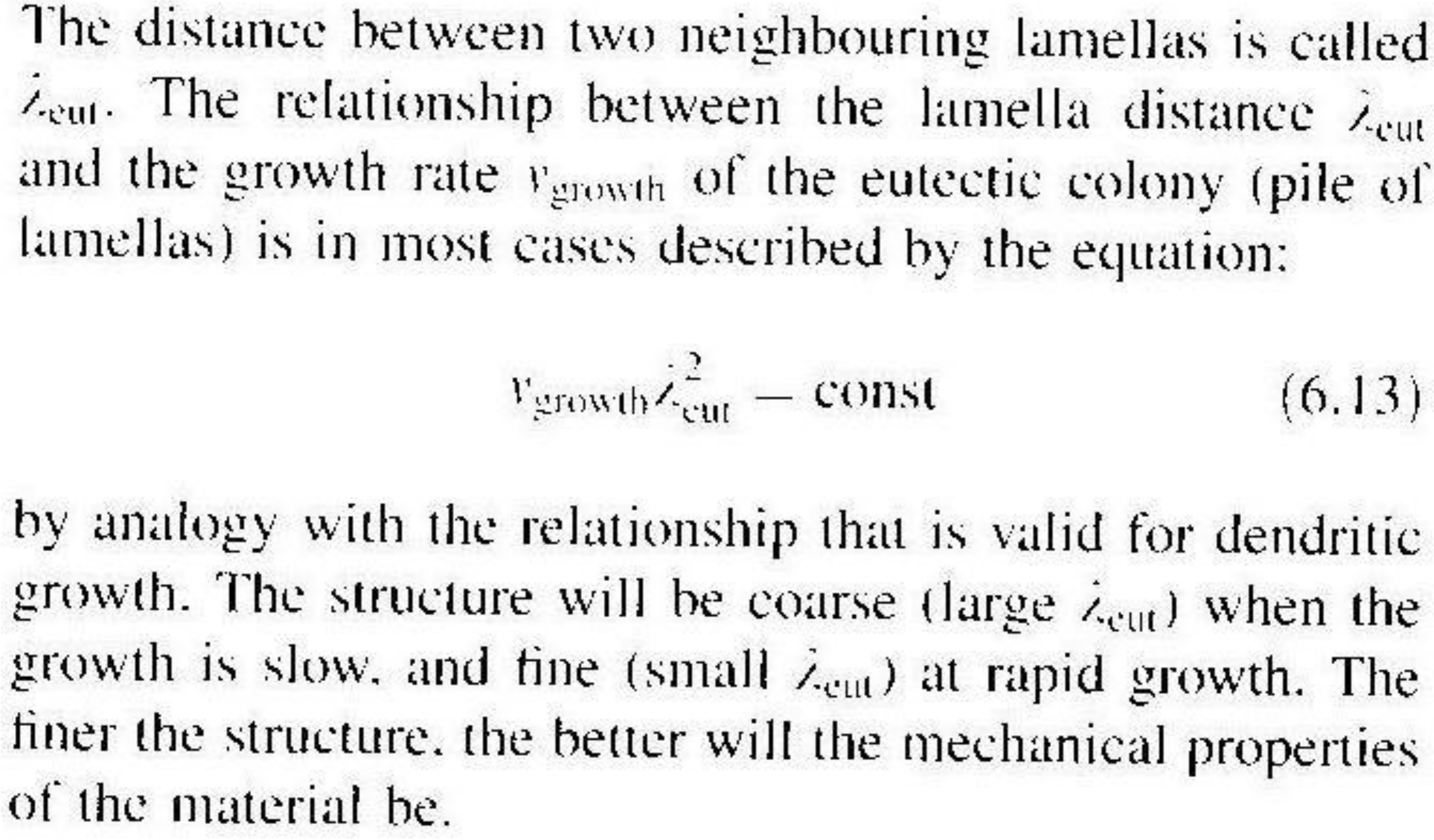


(d) Borneol - SCN

Comparison of the λ - *V correlation for eutectics and eutectoids.*



Relationship between Lamella Distance and Growth Rate



The distance between two neighbouring lamellas is called λ_{eut}. The relationship between the lamella distance λ_{eut} and the growth rate v_{growth} of the eutectic colony (pile of lamellas) is in most cases described by the equation:

$$v_{\mathrm{growth}}\lambda_{\mathrm{eut}}^{2} = \mathrm{const} \qquad (6.13)$$

by analogy with the relationship that is valid for dendritic growth. The structure will be coarse (large λ_{eut}) when the growth is slow, and fine (small λ_{eut}) at rapid growth. The finer the structure, the better will the mechanical properties of the material be.

6.4.2 Relationship between Growth Rate and Undercooling

For eutectic growth there is a relationship between the growth rate v_{growth} and the undercooling corresponding to that which is valid for dendritic growth:

$$v_{\mathrm{growth}} = \mu(T_{\mathrm{E}} - T)^{n} \tag{6.14}$$

where T_{E} – eutectic temperature of the melt, and T = temperature of the melt at the solidification front. μ and n are constants.

As concrete examples of eutectic alloys we will discuss silumin and cast iron. Both have great technical importance and are used to a great extent by the casting industry.

Eutectic Structures of Silumin

- Aluminium-silicon alloys are widely used for producing various commercial products in foundries, for example, engine blocks. In particular the eulectic Al-Si alloy *silumin is of great technical importance.*

Figure 6.13 shows the phase diagram for the Al–Si system. It contains a eutectic point at 12.6 wt-% Si. The eutectic temperature is 577 °C. The Al-phase dissolves a maximum 1.65 wt-% Si while the solubility of aluminium in silicon is very low and can be neglected.

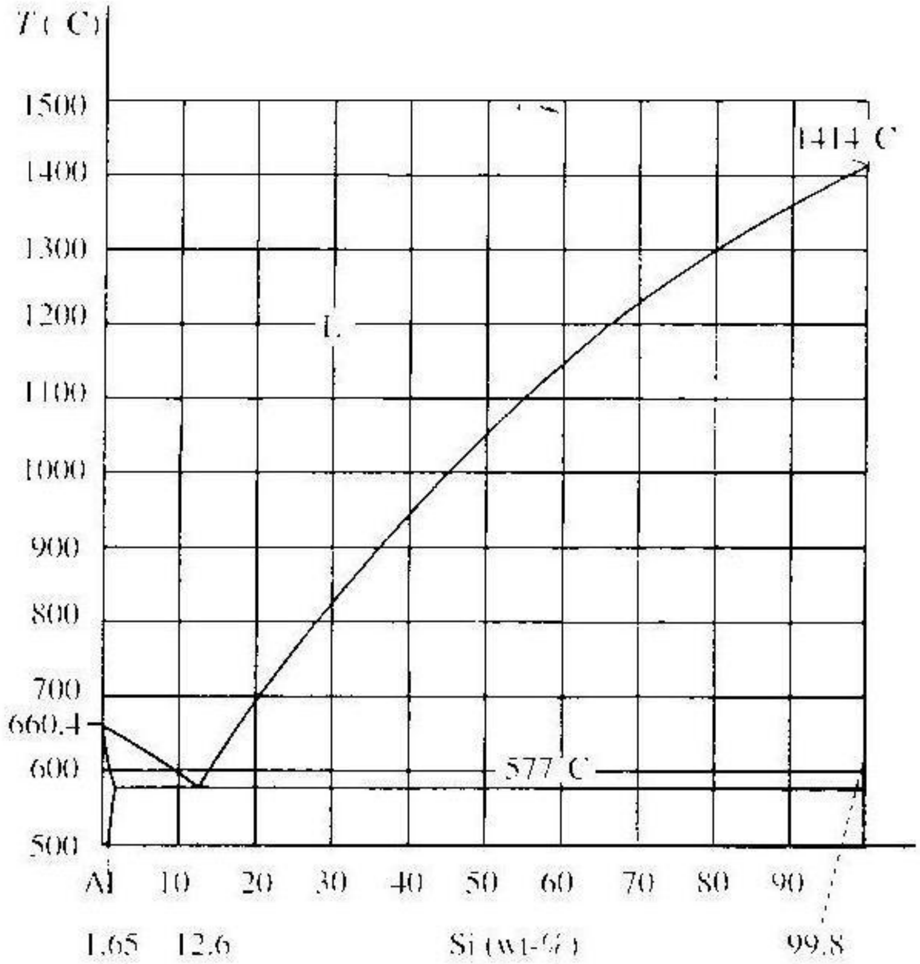
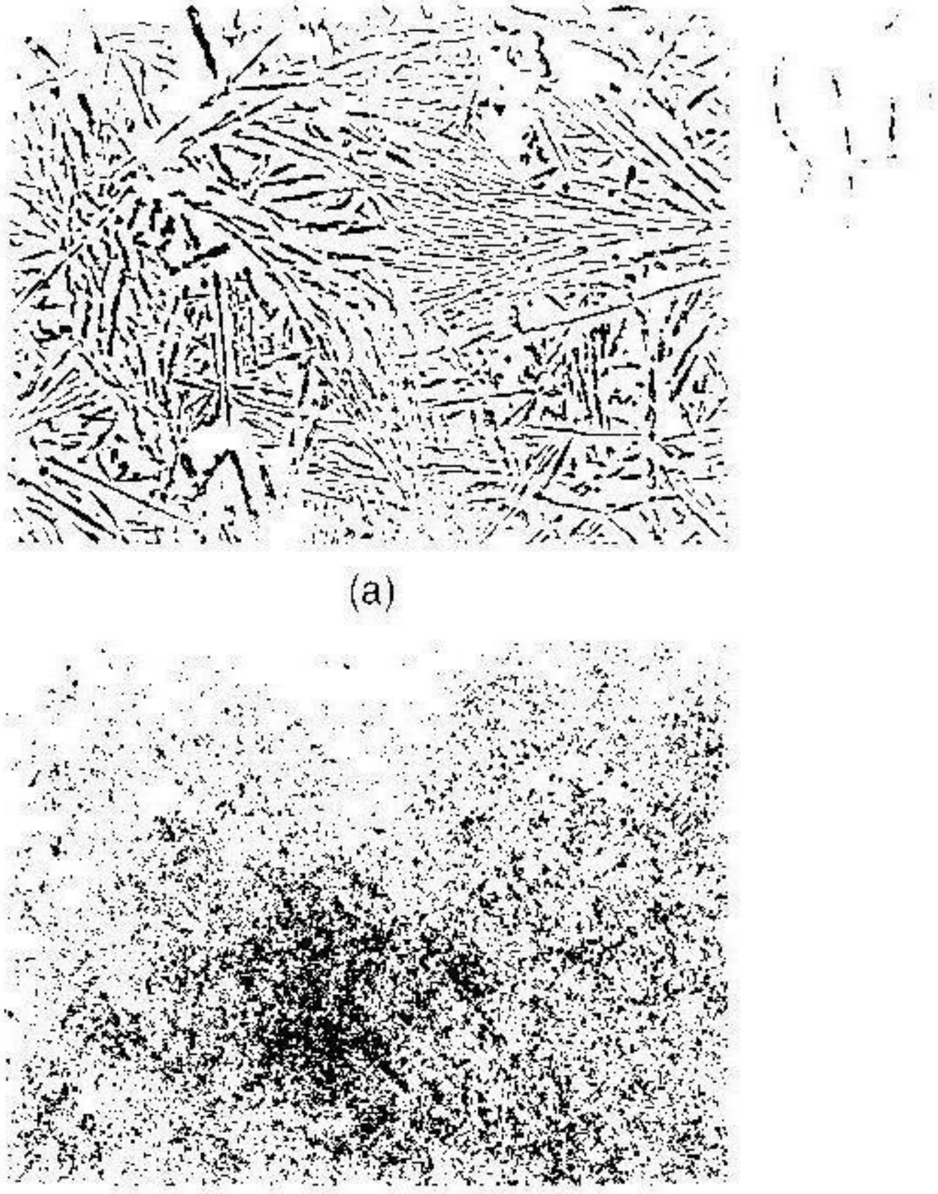


Figure 6.13 Phase diagram for the system Al–Si.

- Figure 6.14 a shows typical microstructure of a euteclic Al-Si alloy that has been formed at a relatively low cooling rate. The structure consists of relatively coarse plates of Si imbedded in a matrix of Al phase.



(a)

(b)

Figure 6.14 (a) Structure of unmodified eutectic silumin. (b) Structure of modified eutectic silumin.

- It can be seen in Figure 6.14 (a) that these plates often have a broom-like shape. The reason for this is that the disc- and flake-shaped Si crystals easily break at the solidification front, which results in crystal multiplication. The broken crystal fragments often turn somewhat before they grow. The result is that the silicon plates have diverging directions and a fan-shaped structure is formed.

- The American metallurgist Pacz discovered in 1920 that addition of small amounts of sodium (a couple of hundredths of a percent) to a silumin melt before solidilicalion changed the flaky, plate-like and branched microstruclure of normal silumin into a much liner, more regular and fibrous microstructure (Figure 6.14 (b)). The product is called *sodium-modified silimin. If the solidification is rapid (quench modification) the structure of the alloy will be even finer, i.e. the lamella distances become smaller than those without inoculation. Modified silumin has better mechanical properties, ductility and hardness than does plain silumin.*

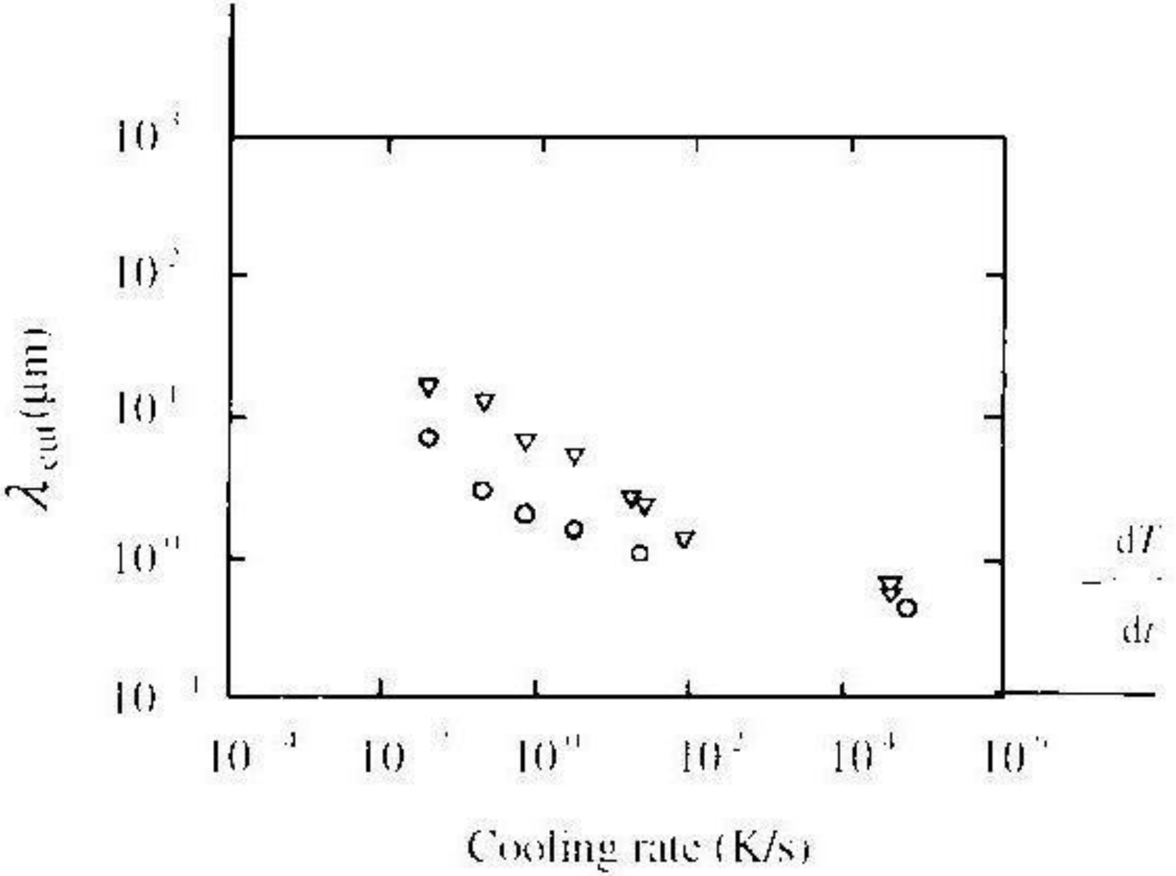


Figure 6.15 The distances between the Si plates as a function of the cooling rate for ∇ unmodified silumin, and ○ silumin, modified with 250 ppm Sr.

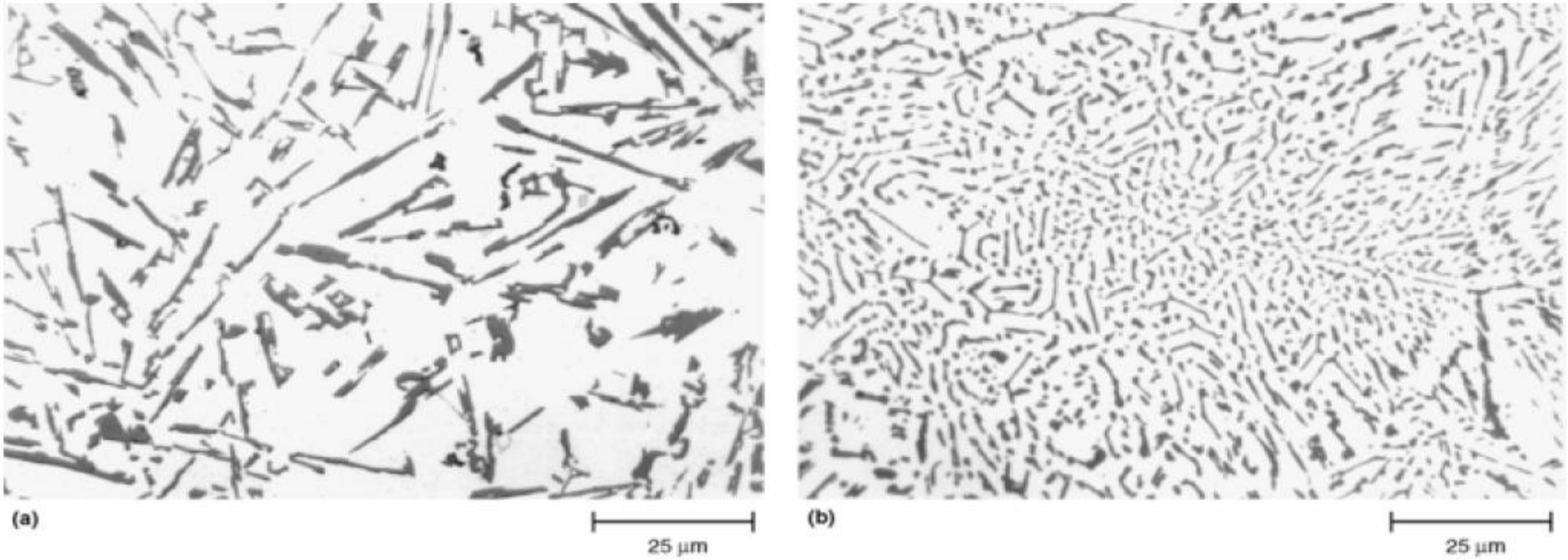


Fig. 10 As-cast morphologies in a eutectic aluminum-silicon alloy. (a) Unmodified alloy with coarse silicon precipitates formed during solidification. (b) Modified alloy with solidification of finer silicon precipitates. Both etched with 0.5% HF (5m in Table 4) and magnified by 750×

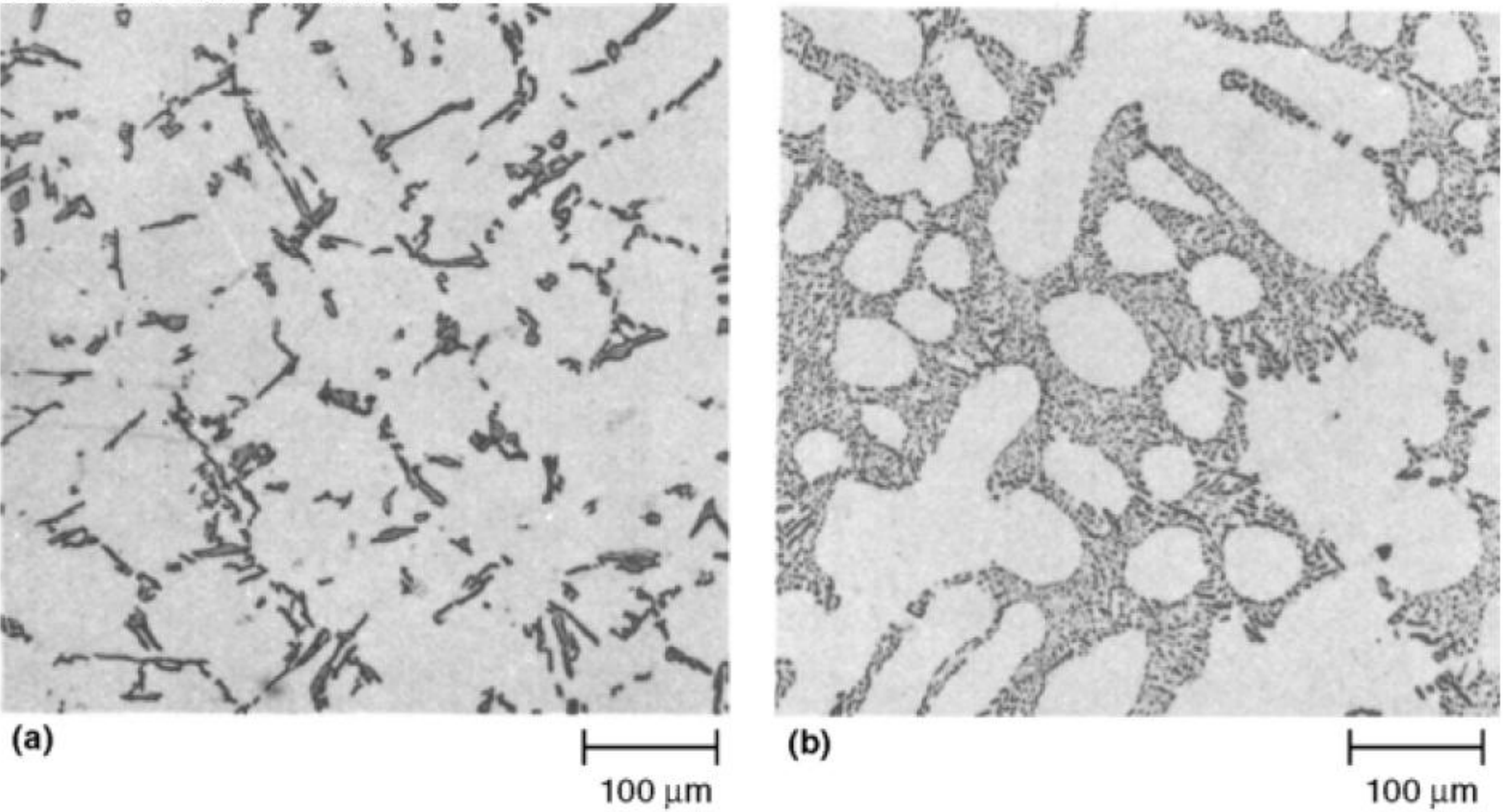


Fig. 16 Effect of sodium modification on microstructure of sand-cast aluminum-silicon hypoeutectic alloy 356-F. Both specimens were etched in 0.5% hydrofluoric acid and are shown at 100×. (a) As-cast structure in unmodified alloy consists of a network of silicon particles (sharp gray), which formed in the interdendritic aluminum-silicon eutectic. (b) Modified alloy by addition of 0.025% Na to the melt. Constituents are the same as in (a), but the particles of silicon are smaller and less angular

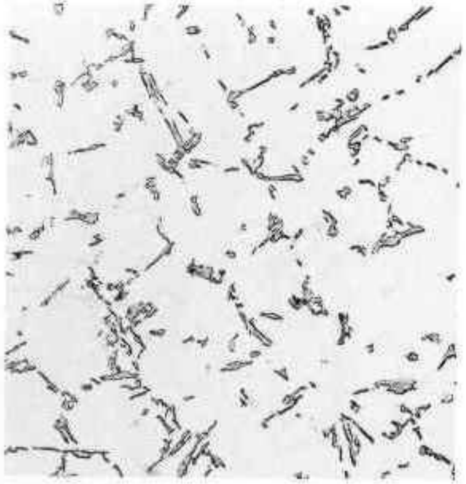


Fig. 121 Alloy 356-F, as sand cast. Structure consists of a network of silicon particles (gray, sharp), which formed in the interdendritic aluminum-silicon eutectic. See also Fig. 122 and 123. 0.5% HF. 100×

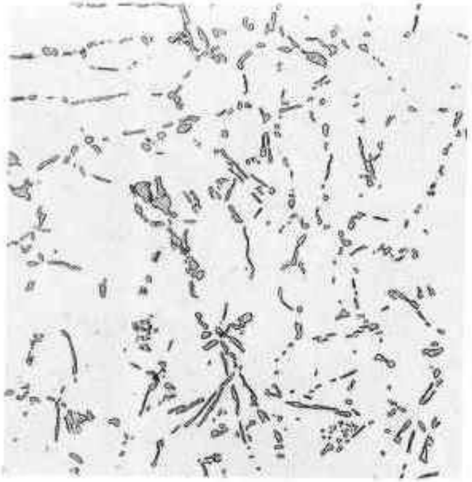


Fig. 122 Alloy 356-T4, sand cast, solution heat treated at 540 °C (1000 °F) for 12 h, quenched in boiling water. Heat treatment caused silicon particles to be rounder than in Fig. 121 (as-cast). 0.5% HF. 100×

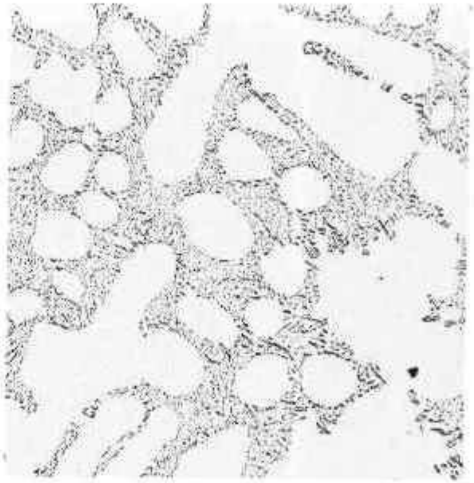


Fig. 123 Alloy 356-F, modified by addition of 0.025% Na to the melt, as sand cast. Constituents same as for Fig. 121, but the particles of silicon in the eutectic are smaller and less angular. 0.5% HF. 100×

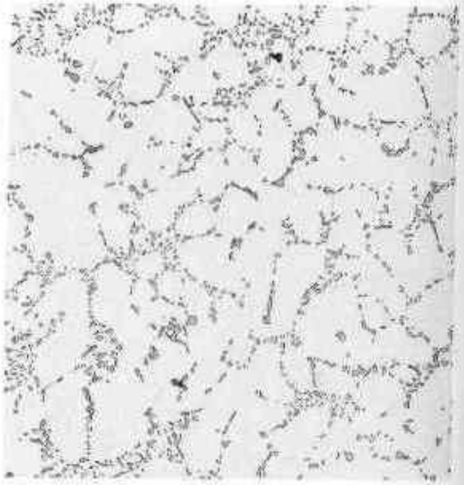


Fig. 124 Alloy 356-T4, modified by addition of 0.025% Na, sand cast and heat treated as described in Fig. 122. Silicon particles are rounded and agglomerated. See also Fig. 121 to 123. 0.5% HF. 100×

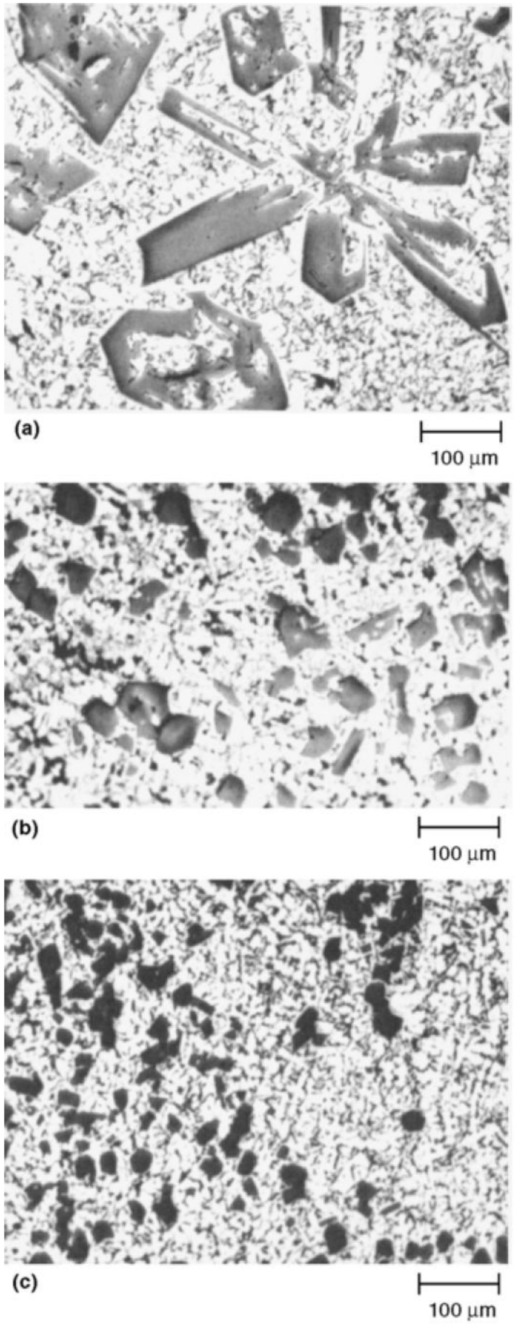


Fig. 17 Effect of phosphorus refinement on the microstructure of Al-22Si-1Ni-1Cu alloy. (a) Unrefined. (b) Phosphorus-refined. (c) Refined and fluxed. All 100×

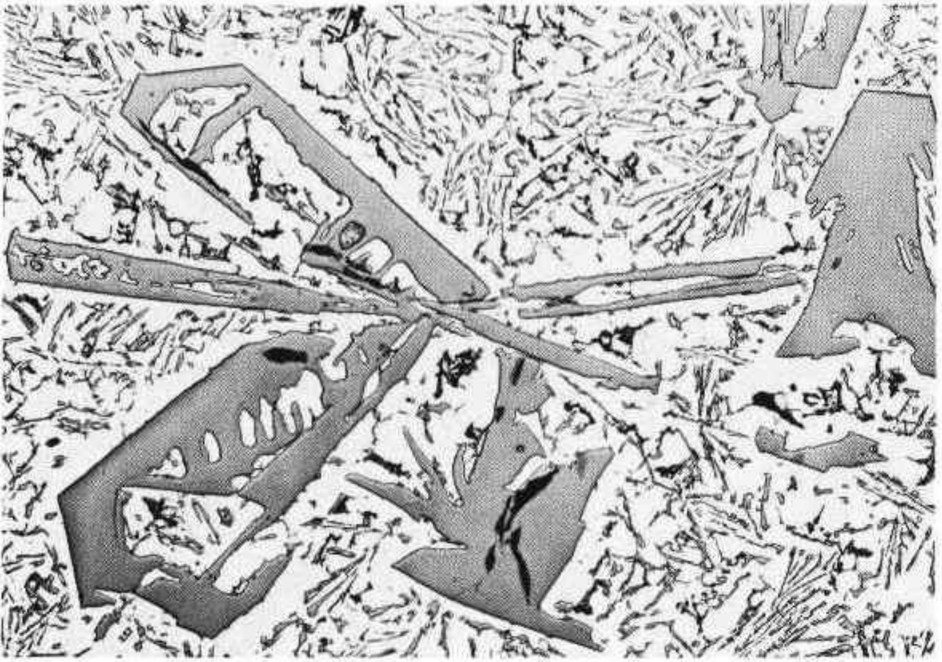


Fig. 134 Alloy 392-F, as permanent mold cast. The structure consists of silicon (small, angular, gray particles in eutectic, and large, unrefined primary particles) and Mg_2Si (black constituent). See also Fig. 135. 0.5% HF. 100×

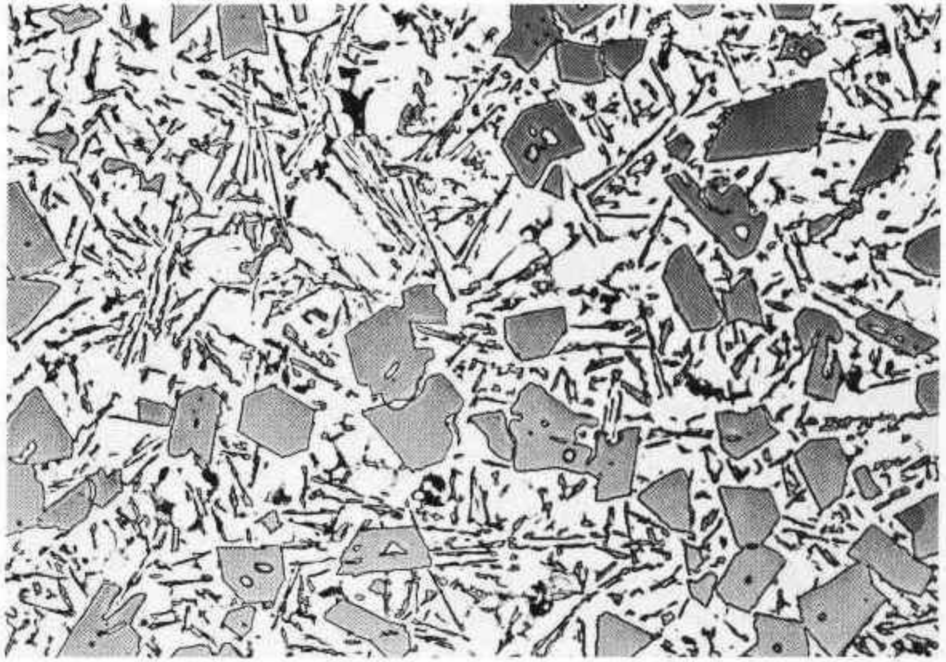
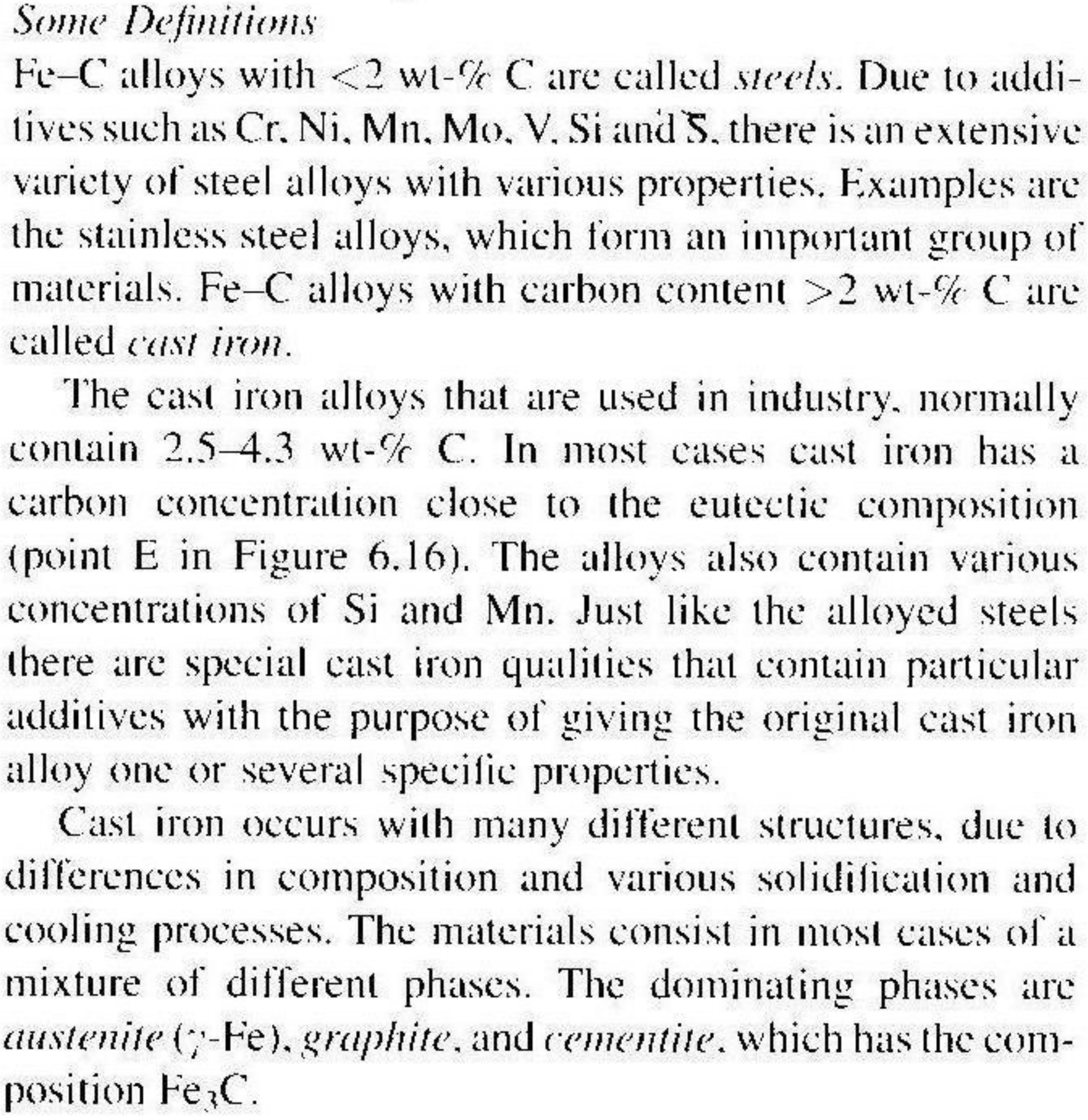


Fig. 135 Alloy 392-F, as permanent mold cast same as for Fig. 134, but phosphorus was added to the melt. This addition refined the size of the particles of primary silicon. 0.5% HF. 100×

Eutectic Structures of Cast Iron



Some Definitions

Fe–C alloys with <2 wt-% C are called *steels*. Due to additives such as Cr, Ni, Mn, Mo, V, Si and S, there is an extensive variety of steel alloys with various properties. Examples are the stainless steel alloys, which form an important group of materials. Fe–C alloys with carbon content >2 wt-% C are called *cast iron*.

The cast iron alloys that are used in industry, normally contain 2.5–4.3 wt-% C. In most cases cast iron has a carbon concentration close to the eutectic composition (point E in Figure 6.16). The alloys also contain various concentrations of Si and Mn. Just like the alloyed steels there are special cast iron qualities that contain particular additives with the purpose of giving the original cast iron alloy one or several specific properties.

Cast iron occurs with many different structures, due to differences in composition and various solidification and cooling processes. The materials consist in most cases of a mixture of different phases. The dominating phases are *austenite* (γ-Fe), *graphite*, and *cementite*, which has the composition Fe_3C.

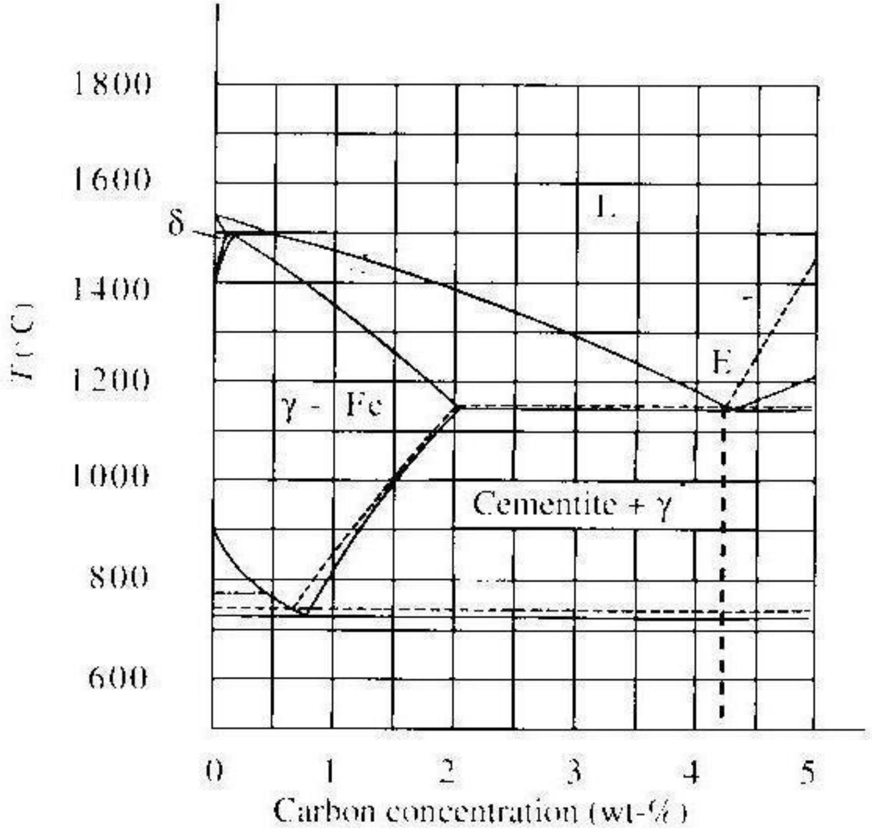


Figure 6.16 Part of the phase diagram for the system Fe-C.

In cast iron the carbon occurs either as free graphite or chemically bound as *cementite*. It is possible to control the solidification processes or composition of cast iron melts in such a way that the carbon either occurs as free carbon with graphite structure (grey iron solidification) or bound as Fe_3C (white iron solidification). Grey and white iron are discussed in detail below.

Grey Cast Iron

Grey cast iron generally shows a variety of different morphologies. Attempts have been made to classify them as different types, called A-, B-, C- and D-graphite. The composition of the melt and the cooling rate – or rather the undercooling of the melt – controls the formation of these different structures.

A-graphite is coarse so-called *flake graphite*, which often has a disc-like appearance. It consists of spherically grown crystal aggregates of graphite and austenite. Figure 6.17 shows an aggregate of austenite and graphite growing from a nucleus in the centre. The growth of the cell occurs mainly radially but with a rather uneven solidification front. The solidification has been interrupted by quenching and the remaining liquid has solidified as white iron (see next section). The cell structure can also be seen in Figures 6.10 (a) and (b) on page 146.

The graphite leads the growth and the austenite is mainly formed behind the tips of the graphite flakes. This growth process can hardly be characterized as a normal eutectic reaction. One can rather say that the graphite is precipitated primarily and that the austenite is formed as a secondary phase.

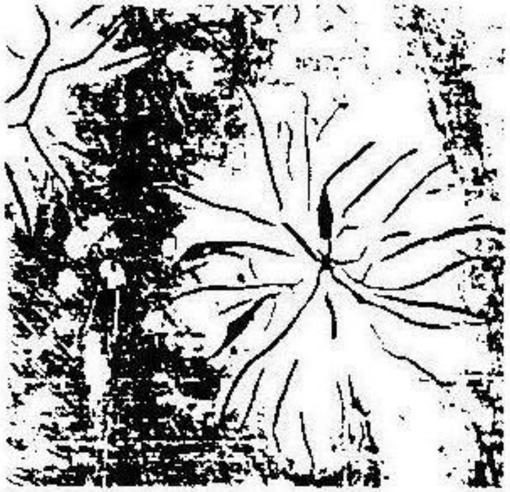


Figure 6.17 Structure of grey cast iron. The background is solidified white iron.

The graphite flakes do not reach their final thickness primarily, but grow successively by diffusion of carbon atoms from the melt across the austenite layer (Figure 6.18).

B-graphite or *nodular graphite* is also called *spheroidal graphite* (SG), which characterizes its structure. The graphite nodules are formed in the melt and are surrounded

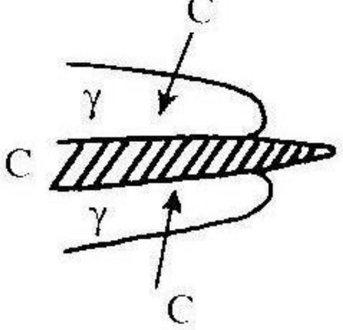


Figure 6.18 Sketch of the growth mechanism in flake graphite. In the centre there is primarily precipitated graphite. It thickens by diffusion of C atoms through the austenite layer.

by an austenite shell. The growth of the graphite mainly occurs by diffusion of carbon through this shell.

Spheroidal graphite in cast iron is obtained by adding *cerium* to the cast iron melt as was first described by Morrogh and Williams in 1948. Later a corresponding magnesium process was suggested. This technique improves the quality of cast iron greatly. Nodular structure in cast iron results in products with measurable degrees of ductility, which has extended its usefulness enormously.

C-graphite or *vermicular graphite* (VG) has a cord-like structure and can be regarded as an intermediate form between flake graphite and spheroidal graphite. The grains are characterized by low l/g ratio (l – length and g – thickness) in comparison with flaky graphite, which has an l/g ratio > 50. Vermicular graphite has generally an l/g ratio between 2 and 10. The l/g ratio of spherical graphite is 1.

D-graphite, which has a very fine graphite structure compared with flake graphite, is also called *undercooled graphite*. In D-graphite the graphite occurs in the shape of rods (Figure 6.19). During the formation of undercooled graphite the solidification front is relatively even. The formation process can be characterized as a normal eutectic reaction with good cooperation between the two phases of graphite and austenite. The formation of undercooled graphite is favoured by high cooling rate but is also promoted by various impurities. Low concentrations of sulfur and oxygen favour the formation of undercooled graphite.

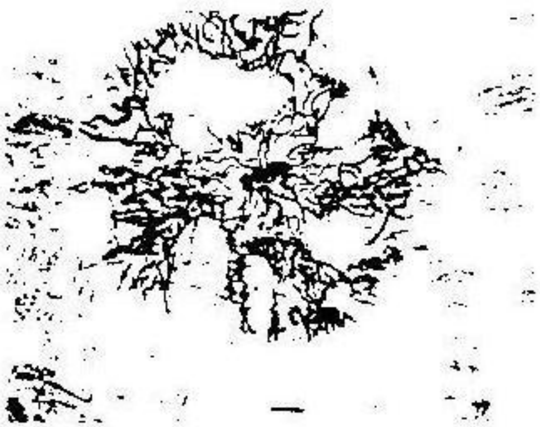


Figure 6.19 Structure of a eutectic colony in undercooled graphite. Reproduced from the Georgi Publishing Company.

White Cast Iron

White cast iron consists of a mixture of cementite and austenite. The eutectic structure can appear in several different morphologies (shapes), mainly depending on whether the cast iron is eutectic or not. An example of the structure of a supereutectic white cast iron is shown in Figure 6.20.

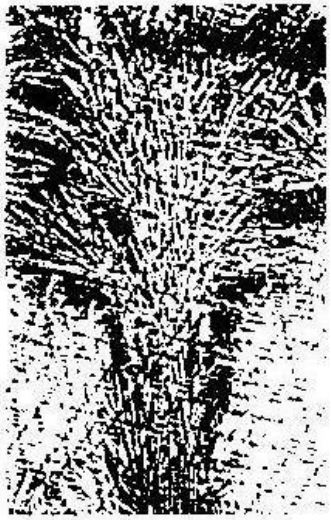


Figure 6.20 Structure of white cast iron. The broom structure is caused by crystal multiplication of fragile cementite discs. Reproduced with permission from Mats Hillert.

White cast iron is hard and fragile. It is difficult to work, for instance, to turn in a lathe and to countersink. For this reason it is in most cases vital to avoid formation of white iron, the exception being applications where materials with high wear resistance are wanted.

Grey cast iron is easier to machine and has much better mechanical properties than white iron. It is therefore desirable that cast iron solidifies as grey cast iron. Measures to control the solidification processes of cast iron melts so that the result is grey and not white iron will be discussed below.

Solidification Control of Cast Iron

- Composition
- Cooling Rate
- Inoculation

Solidification Control of Cast Iron

Three parameters control the formation of white and grey iron of a cast iron melt: (i) composition; (ii) cooling rate, and (iii) inoculation.

Composition There are two types of composition effect: bulk element effects and tracer element effects. *Bulk element effects* imply that alloying elements with concentrations >0.5 wt-% affect the thermodynamic stability of the phases.

The stable eutectic equilibrium corresponds to point E in Figures 6.16 and 6.21, where the horizontal line AE corresponds to the eutectic temperature of the (γ + C) eutectic. The eutectic point E′ corresponds to the eutectic ($\gamma + Fe_3C$). It can be seen from Figure 6.21 that the latter has a eutectic temperature that is normally 6 °C *lower* than the eutectic temperature of the stable (grey) eutectic phase. E′ corresponds to the metastable (white) eutectic phase, which is achieved by *undercooling*. The larger the undercooling is the easier will white iron be formed.

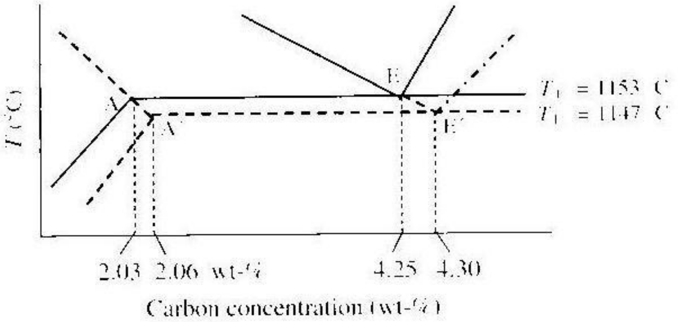


Figure 6.21 Enlargement of the central part of the phase diagram of the system Fe–C in Figure 6.16 (not to scale). Metastable levels have *higher* energy than do stable levels. In a phase diagram the metastable temperature level is consequently *lower* than the stable one.

Alloying elements change the eutectic temperature in different ways. The effects of some alloying elements on the eutectic temperatures E and E′ are shown in Figure 6.22.

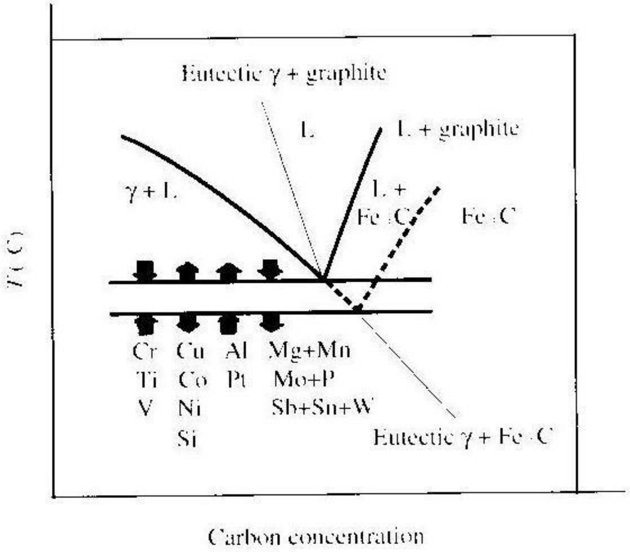


Figure 6.22 The effects of some alloying elements on the stable and metastable Fe–C eutectic temperatures. Reproduced with permission from Plenum Press, Springer.

The most evident effects are found for Cr, Ti and V, which promote formation of white iron. Cu, Co, Si and Ni have a preventive effect. The alloying elements also affect the carbon concentration and carbon distribution during the eutectic reaction. This effect is not shown in the figure.

Tracer element effects means that alloying elements in very small concentrations strongly affect the growth kinetics of graphite in spheroidal cast iron and eutectic cell growth in grey iron. Examples of elements that promote formation of grey iron in this way are S, As, Se, Sb, Te, Pb and Bi. The effects of the individual elements are additive.

Cooling Rate A low cooling rate leads to low growth rate, which corresponds to a low undercooling in accordance with Equation (6.14) on page 147. This favours stable eutectic solidification. i.e. formation of grey iron. On the other hand. a high cooling rate leads to a high growth rate and consequently to high undercooling. which promotes the metastable eutectic reaction. The more rapid the cooling rate is the greater will the undercooling be and the more easily will the lower metastable eutectic temperature be reached. which increases the risk of white solidification.

By analogy with dendritic growth, the eutectic lamella distance is a function of the growth rate and also of the cooling rate. The result, shown in Figure 6.5 on page 144, is valid for eutectic solidification as well. The lower the cooling rate is the coarser will the graphite eutectic structure be.

Inoculation The main purpose of inoculation is to reduce the risk of white solidification. To reduce this risk and promote grey iron formation at solidification of cast iron, it is preferable to increase the number of nuclei in the melt. This is done by *inoculation*, i.e. addition of special alloying elements, immediately before casting. By increasing the number of cells the cooling area increases. At a constant heat flux both the growth rate and the undercooling decrease, which results in a reduced risk of white solidification. This topic is discussed in Exercise 6.5.

By mixing inoculation additives (normally 0.10–0.40 wt-%) into a cast iron melt, many heterogeneities are created, which gives many more growing eutectic cells than in a noninoculated melt. The area of the solidification front becomes larger and the heat of solidification will be released more rapidly. This will reduce the growth rate and the risk of white structure formation decreases. Simultaneously the graphite structure will be coarser, due to the lower undercooling.

Inoculation is particularly important for superheated melts. The majority of the particles that form the heterogeneities for nucleating crystals are dissolved and disappear from the melt at high temperatures. No new heterogeneities are formed during the cooling. Only a few heterogeneities grow to cells during the solidification process with the result that the risk of white structure formation increases. Thus superheating of a melt increases the risk of formation of a metastable solid phase and white solidification. To guarantee the presence of additional heterogeneities that will grow to crystals in the melt, it is important to inoculate a superheated melt *before* the solidification process starts.

There is a relatively large number of possible additives with different compositions. Most of them are based on silicon. Pure graphite is also used as an inoculation agent. In most inoculation additives varying amounts of Ca and Al and small amounts of Ba, Sr, Zr or Ce are included. Some of them have a nucleating effect while others may react with their surroundings and form products that are good nuclei.

The inoculation technique has greatly contributed to improving the reputation of cast iron as a reliable and useful material for engineering construction.

6.4.4 Eutectic Growth of Cast Iron in a Sand Mould

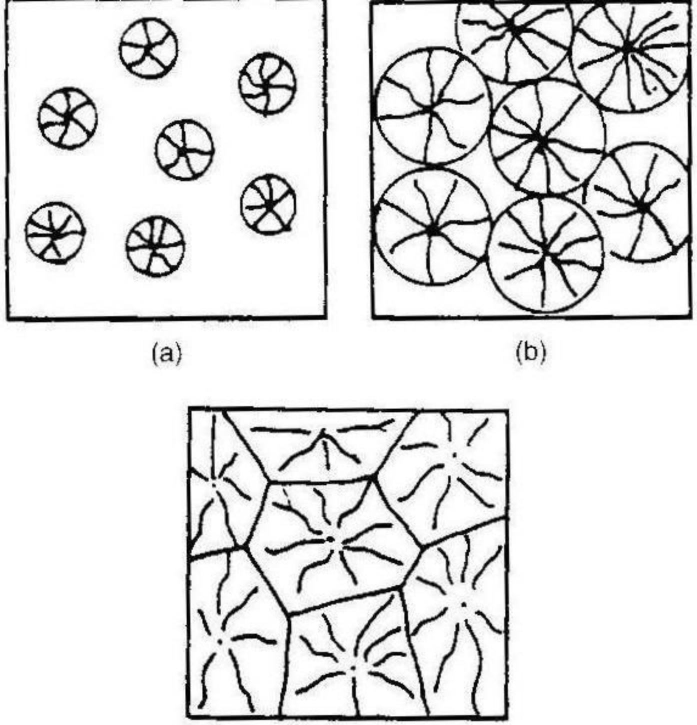
Below we will discuss the crystal growth during casting in a sand mould. As an example we choose to study the growth of a eutectic cast iron alloy. There are two reasons for this choice: First, the theoretical analysis is comparatively simple, and second, cast iron is a very common metal in industrial production.

When cast iron that has been cast in a sand mould solidifies, the solidification occurs by precipitation of graphite flakes as described by Figures 6.23 (a)–(c) where Figure 6.23 (c) is an illustration of the macroetched structure shown in Figure 6.10 (b) on page 146.

The coarseness of the structure is determined by the growth rate v_{growth} of the solidifying shell [Equation (6.13)].

$$v_{\text{growth}} \lambda_{\text{eut}}^2 = \text{const} \tag{6.13}$$

where λ_{eut} is the lamella distance.



(a) (b)

(c)

Figure 6.23 Eutectic growth of grey iron. Reproduced with permission from North-Holland, Elsevier Science.

It is impossible to register the growth rate of each cell but it is possible to calculate the average growth rate. The properties of cast iron depend on the internal structure, the coarseness of each colony. Hence, we want to estimate the average distance between the graphite flakes within the colonies and, in addition, find out how this distance varies from the centre to the periphery of the colonies. It is not possible to do this experimentally because a casting is too big. Instead, theoretical calculations are performed based on some reasonable assumptions. We will illustrate these calculations by a concrete example (Example 6.4).

6.6 UNIDIRECTIONAL SOLIDIFICATION

In Chapters 4 and 5 we discussed solidification processes during unidirectional solidification, which means that the generated solidification heat is conducted away through the solidifying shell. This is the most common case of metal solidification. In this section we discuss the metal structures that arise during such a casting process.

6.6.1 Casting with the Aid of Unidirectional Solidification

During the last two decades of the Twentieth century, production of materials cast using unidirectional solidification started. One example is the casting of turbine blades used in jet engines, which is discussed in Section 6.6.2. The principle of the method used is described in Figure 6.31. A material cast with the aid of unidirectional solidification consists of columnar crystals or of a single crystal.

Casting using Unidirectional Solidification

A mould with melt is placed in an apparatus, the upper part of which consists of a furnace, the temperature of which exceeds the melting point of the metal. The lower part of the apparatus is cooled by air or water. The apparatus is

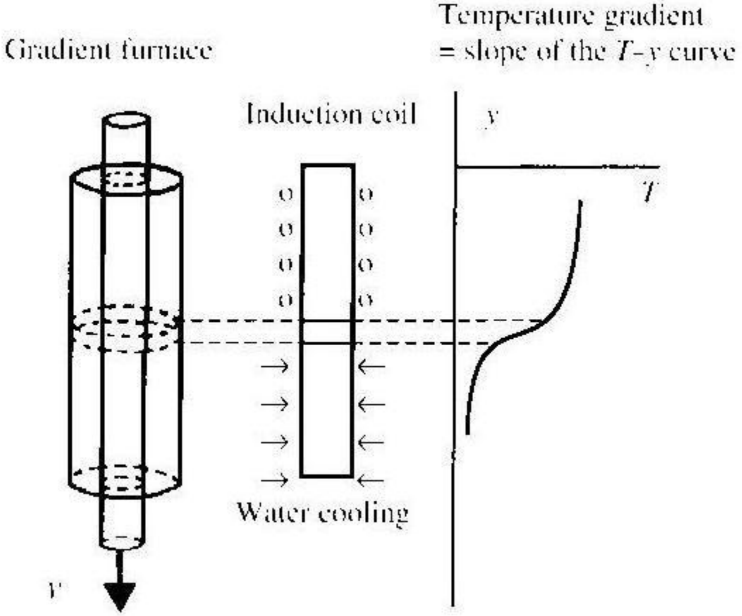


Figure 6.31 Apparatus for production of single crystals by controlled unidirectional solidification.

drawn upwards or, alternatively, the mould is moved downwards at a constant velocity. The rate of solidification of the metal melt will be the same as the relative velocity between the mould and the apparatus.

The advantages of unidirectional solidification, performed under careful temperature control, are (i) uniformity, and (ii) good mechanical properties of the cast materials. The cast structure is carefully controlled to get the same coarseness along the whole casting. The grain structure is also easy to control, due to competition in growth between crystals of different orientations. The advantage of unidirectional growth of single crystal materials is their superior mechanical strength as compared with ordinary casting materials.

Melt and Mould Temperatures during Unidirectional Casting

The melt is normally cast in an inert atmosphere or in vacuum. During conventional casting the mould is kept at a temperature below that of the melt. The casting operation is finished within a short time (of about 1 minute). The temperature as a function of time for an ordinary turbine blade of a super-base alloy (steel, alloyed with Ni or Co) is illustrated in Figure 6.32.

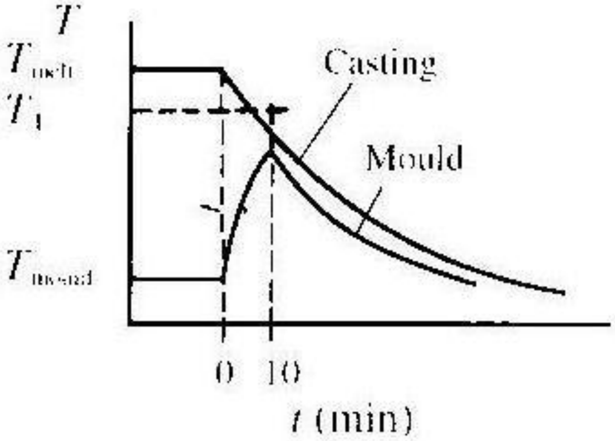


Figure 6.32 Melt and mould temperatures as functions of time during conventional component casting. The total solidification time and cooling time are much shorter for conventional casting than for unidirectional casting. Reproduced with permission from The Metals Society, The Institute of Materials.

In the case of unidirectional solidification, the mould is preheated above the solidus temperature to prevent thermal stresses during casting. The superheated alloy melt is poured into the preheated mould, which is then withdrawn from the furnace in such a way that the melt remains in contact with the chilled plate during the whole directional solidification process. The solidification and cooling time is of the magnitude of 1 to 10 hours (Figure 6.33). It can be seen from Figures 6.32 and 6.33 that the total solidification time from start to finish is much longer for unidirectional casting than for conventional component casting.

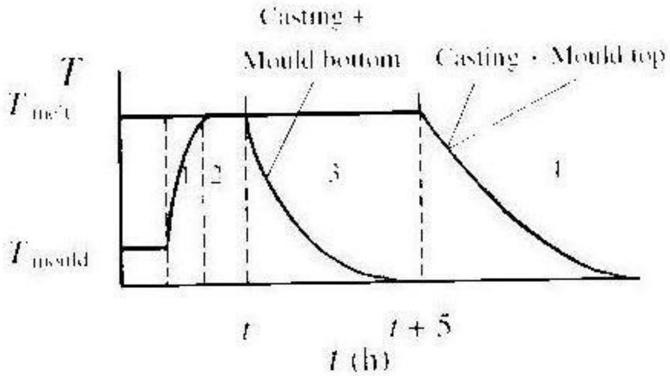


Figure 6.33 Melt and mould temperatures as functions of time for unidirectional solidification. Regions: (1) preheating of the mould; (2) casting time; (3) cooling of the bottom and solidification of the rest of the casting; (4) cooling of the casting and the mould at the top. Reproduced with permission from The Metals Society, The Institute of Materials.

6.6.2 Applications of Unidirectional Casting – Single Crystal Production

The Power-Down Process

By use of modern automatic control devices, the industrial equipment for directional solidification is much more sophisticated than the simple apparatus illustrated in Figure 6.31. One example of this is the so-called power-down process.

The power control of the electrical furnace is external and independent of the casting. The casting temperature can be monitored and the rate of power adjusted to the value required to give a constant solidification rate. The process is operated by use of induction heating, directly coupled to conventional investment moulds (wax-melting method) as illustrated in Figure 6.34. Quite regular and constant cooling rates can be obtained by programming the power input in different sections of the coil with careful design of the winding configuration.

Production of Turbine Blades

Turbine blades in jet engines or water power plants are exposed to very strong forces. Hence the demands on the mechanical strength of the blades are very high. The demands on turbine

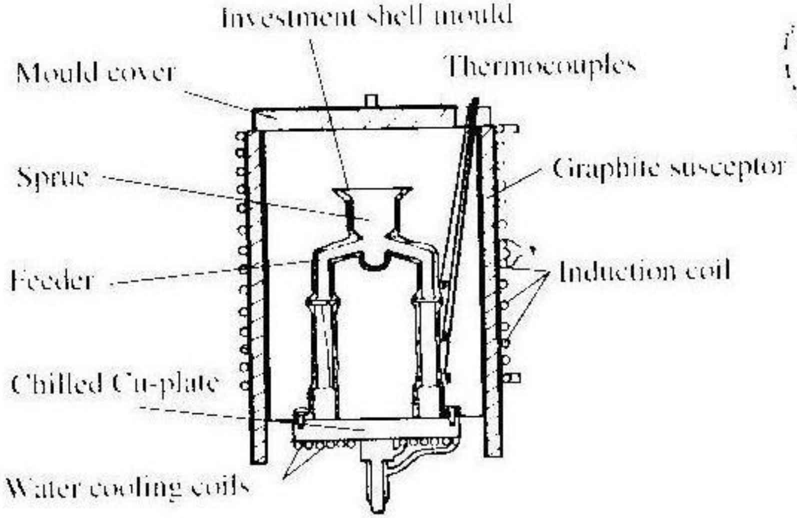


Figure 6.34 Schematic diagram of inductively heated mould apparatus for casting of unidirectionally solidified turbine blades using the power-down process. Reproduced with permission from The Metals Society, The Institute of Materials.

blades in jet engines are high because of the high temperatures (900–1100 C) that arise when the fuel is burnt. Turbine blades in jet engines are cooled with the fuel or air. Below we briefly describe the production of turbine blades.

The first step is to make moulds of sufficient strength and that are resistant to high temperatures. The process is the same as that described on page 1 in Chapter 1. The moulds are produced by coating a wax model with several layers of ceramic powders (fine-grained $ZrSiO_4$, alumina Al_2O_3, or silica SiO_2), held together by a suitable binder, which can be either colloidal silica or ethyl silicate. Then the mould is dried and dewaxed before it is finally fired to increase its mechanical strength and remove the last traces of wax.

A turbine blade is complex, as it must be equipped with cooling channels. A *ceramic core*, which corresponds to the shape of the channels, has to be inserted into the mould. The core materials must be sufficiently stable to exclude interaction with the melt during casting and be capable of being removed from the channels after casting.

Single-Crystal Production

The method used for unidirectional solidification and illustrated in Figure 6.31 on pages 159–160 is also used in single-crystal production for various purposes. In practical cases the design of the equipment resembles that illustrated in Figure 6.34.

Constrictions can be inserted into the mould during the production of single-crystal components in order to select a single crystal for the top part of the casting. Such constrictions in various designs operate successfully. Below we discuss and analyse the formation of macrostructures in unidirectionally cast materials.

6.6.3 Crystal Growth in Unidirectional Solidification

Figure 6.35 shows a partly insulated melt in a mould that is in close contact with a strongly chilled copper plate. Heat is

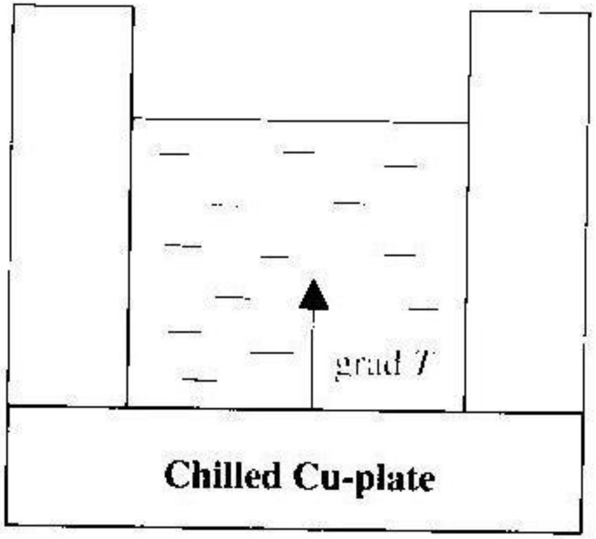


Figure 6.35 The temperature gradient at the bottom is directed from the cold bottom surface into the melt. The envelope surface of the melt is insulated.

removed from the melt and a temperature distribution is rapidly developed in the melt. The temperature gradient in the melt is vertical in this case and can be written:

$$|\text{grad}\ T| = \frac{dT}{dy}$$

The temperature is a scalar quantity. The temperature gradient is a vector that is directed from the lower to the higher temperature (compare page 61 in Chapter 4).

Small crystals having random orientations are nucleated in the melt when the melt at the bottom has reached the critical nucleation temperature. They start to grow in different directions under the influence of the temperature gradient, which has a constant direction. For this reason the process is called unidirectional solidification. During unidirectional solidification, the crystals are mainly oriented in the direction of the temperature gradient. The reason for this is so-called competitive growth.

With dendrite growth, the primary arms grow faster than the secondary and tertiary arms. Initially there is a random orientation of the crystals, which are formed by nucleation at the beginning of the solidification process. The crystals with primary arms in the solidification direction grow faster than all other crystals and conquer them in competition for the available space. When the slower primary arms of crystals with other orientations try to grow, the space in front of them is already filled with the network of primary, secondary and tertiary arms of the faster growing dendrites. After a short time the pattern with parallel crystals growing in the direction of the temperature gradient is distinctly established. We will illustrate competitive growth by a concrete example below.

6.7 MACROSTRUCTURES IN CAST MATERIALS

Eutectic growth and dendrite growth are discussed earlier in this chapter. Eutectic growth is a special case of solidification as it occurs only in alloys with eutectic compositions.

Solidification occurs in the majority of alloys and in pure metals by means of dendrite growth of nucleated crystals in the metal melts. This fact has been known for more than a century and will be applied to solidification processes of metal melts after casting.

Background

At the end of the Nineteenth century the Russian metallurgist Tschernoff published an epoch-making report concerning the solidification of steel ingots. He performed a detailed study of the crystal shapes of both the uncovered crystals that he found in the shrinkage cavities in steel ingots and the crystals tightly grown together, which he could observe in a microscope. He found that the macrostructure of a steel ingot could be divided into three distinct zones (Figure 6.36):

- a surface zone with small crystals of approximately equal size, *the surface crystal zone*;

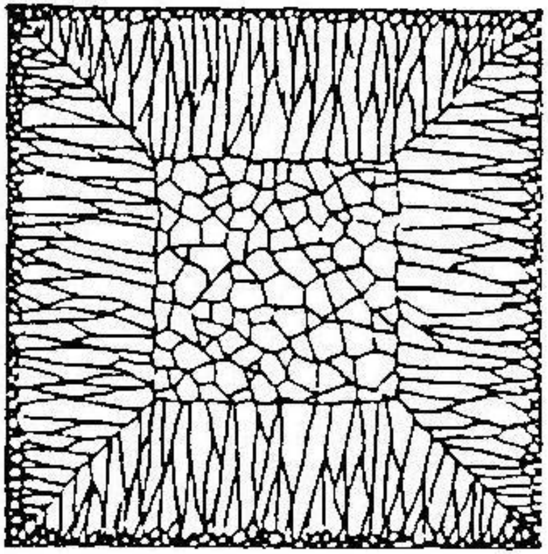


Figure 6.36 Principle sketch of the macrostructure of the surface zone, the columnar zone and the equiaxed zone in the centre of an ingot. Medium casting temperature. Reproduced with permission from The Metals Society, The Institute of Materials.

- a zone with long columnar crystals, *the columnar zone*;
- a zone in the centre with relatively large equiaxed crystals, *the equiaxed crystal zone*.

The production of large steel ingots, which could be forged and rolled, started in the middle of the Nineteenth century, when new steel processes such as the Bessemer and Martin processes were developed. The knowledge of the metal structure was very diffuse, and since then much research on the structure of metals at solidification has resulted in greatly improved casting methods and properties of the final products.

Macrostructures of Unidirectionally Cast Materials

Tschernoff's observations have subsequently been confirmed experimentally in many ways and are the basis for the modern conception of the macrostructure of cast metals. If we look with the naked eye at the crystals in a macroetched sample we can see the macrostructure, i.e. the surface zone, the columnar zone and the central zone. The crystal region in the columnar zone has increased in accordance with the mechanism described in Example 6.5 on page 161 and in Figure 6.37.

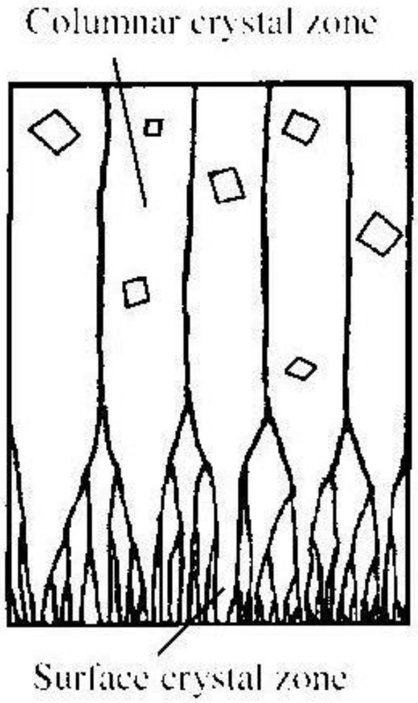


Figure 6.37 Equiaxed crystals in the columnar crystal zone of an ingot.

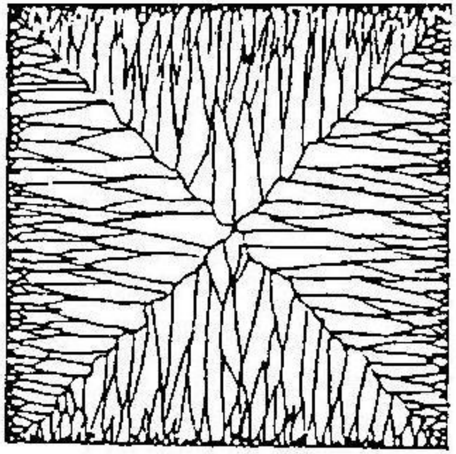
In the columnar zone smaller and larger single crystals of different shapes, sizes and random orientation can be observed (Figure 6.37). They are equiaxed crystals of the same kind as the ones in the central zone, and their origin will be discussed on page 166.

The three basic zones occur in the final products of all types of casting process. Experimental evidence of the influence of various parameters that influence the macrostructure is discussed below. The formation of each of the three zones is then discussed separately in Sections 6.7.1, 6.7.2 and 6.7.3.

Influence of Casting Temperature and other Parameters on the Crystal Structure

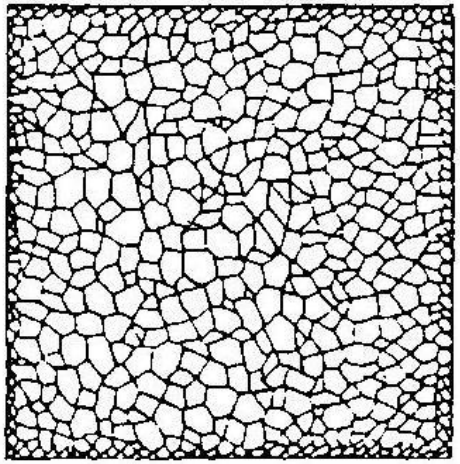
In modern times much work has been done to explain the influence of various factors on the casting structure. The Swedish metallurgist Hultgren's series of publications, starting in the 1920s, constitutes a milestone within this field. The research has since continued for the whole of the Twentieth century and is still going on.

Hultgren showed that it is possible to vary the length of the columnar crystals by varying the casting temperature. An increase of the casting temperature leads to an increase of the columnar zone at the expense of the central zone [Figure 6.38 (a)]. A decrease in the casting temperature



(a)

Figure 6.38 (a) Principle sketch of the macrostructure of the surface zone and the columnar zone in an ingot. High casting temperature.



(b)

Figure 6.38 (b) Principle sketch of the macrostructure of an ingot. The equiaxed zone has grown at the expense of the columnar zone. Low casting temperature.

gives the structure illustrated earlier in Figure 6.36. At low temperature the columnar zone may be completely absent [Figure 6.38 (b)].

Hultgren also found that the structure was influenced by other factors such as stirring the melt during solidification, slow tapping into the mould and refilling during solidification. It has since been found that the structure can be changed similarly due to the properties of the mould, by addition of small amounts of foreign elements and by changing the composition of the alloy.

Experience shows that the surface crystal region is always small, while the shapes and relative sizes of the columnar and central zones vary considerably, depending on factors such as:

- casting temperature of the melt;
- casting method;
- growth rate;
- cooling rate.

Table 6.2 characterizes roughly the most common casting methods and relates the macrostructure of the metal to some of the most important factors listed in the table. The temperature distribution in the melt, solidified metal and mould results in the characteristic features of the different casting methods. Variation is achieved by change of cooling conditions.

TABLE 6.2 Influence of some parameters on the macrostructure of castings.

Casting method	Cooling rate	Growth rate	Columnar zone	Macrostructure
Continuous casting	Very strong	High	Long	Figure 6.38(a)
Ingot casting	Strong	Medium	Short	Figure 6.36
Sand mould	Weak	Low	Absent	Figure 6.38(b)

6.7.1 Formation of the Surface Crystal Zone

During permanent mould casting processes the melt is cast in close contact with a metal/mould surface, which is at room temperature or may be water cooled. The melt is rapidly cooled to the critical temperature T^* required for nucleation. A large number of nucleated, randomly oriented, small crystals is formed. The temperature gradient in the melt favours crystal growth in the direction of grad T (Example 6.5, page 161) at the lower surface. The structure is called the *surface crystal zone*.

We assume that the temperature distribution in the melt is given by the curve 1 in Figure 6.39 when the first nucleus of solid phase is formed. The surface of this growing crystal is initially small, which means that the generated solidification heat per unit time is small even if the growth rate is high. This amount is not enough to balance the amount of heat that is carried away by cooling and the temperature in the melt decreases, as illustrated by curve 2 in Figure 6.39.

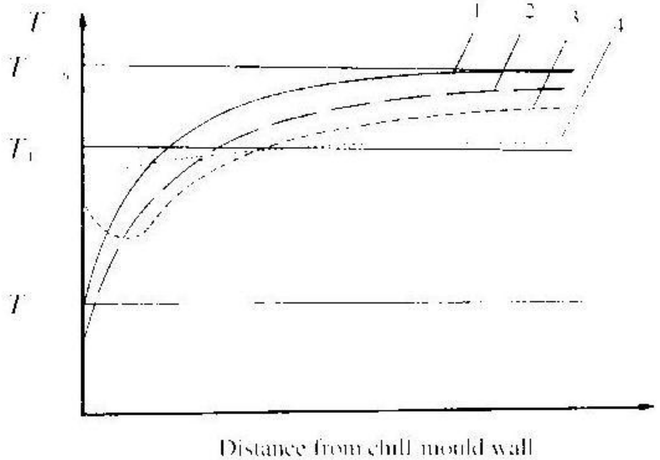


Figure 6.39 Temperature distribution in a metal melt at the initial stage of solidification as a function of time – one curve for each value of time.

Several nuclei may be formed, even within the very farthest layer. When the number of nuclei is large enough and there is a sufficiently large total surface, the generated solidification heat becomes so large that it more than balances the amount of heat carried away by cooling, if this latter is not too great. The temperature of the strongly undercooled zone increases and the temperature conditions are illustrated by curve 3 in Figure 6.39. No new nuclei are formed.

The temperature of the melt increases until the growth rate of the formed nuclei has decreased to the extent that the solidification heat balances the outer cooling and a relatively homogenous temperature of the melt is obtained – curve 4 in Figure 6.39.

6.7.2 Formation of the Columnar Crystal Zone

The whole initial solidification process occurs in connection with the growth of the nuclei of solid phase to crystal skeletons, dendrites. It has been shown that part of these crystal skeletons will be broken by strong convection, which is always present in the melt immediately after the casting. For this reason a large crystal multiplication appears in certain cases, which contributes considerably to the increase in the number of nuclei in the surface zone.

The reasoning above shows that formation of many nuclei is to be expected during the initial stage of solidification. These nuclei constitute the origin of the so-called surface crystal zone, which often is rather fine grained. After this initial stage the formation of nuclei normally ceases, which is caused by an increase of the temperature, as the curves 3 and 4 in Figure 6.39 show.

The continued solidification occurs almost entirely by growth of already nucleated crystals. Due to competitive growth, the crystals grow in the direction of the temperature gradient, i.e. inwards from the surface zone and towards the centre of the melt. Each crystal consists of several parallel primary dendrite arms, all of which have grown equally far into the melt. Dendrites are initially formed by growth of arms and branches in certain crystallographic directions. During a later stage these arms grow together and form distinct planes.

By making a cut through a columnar crystal from the surface and inwards towards the centre, it is possible to follow the extension of the individual dendrite crystals. Figure 6.40 shows a sketch of a columnar crystal.

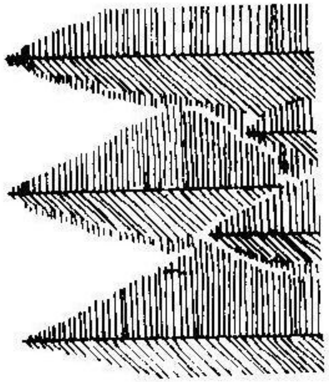


Figure 6.40 Parallel primary dendrite arms, which grow inwards in the melt, together form a columnar crystal. The three dendrite arms in the same horizontal plane.

As a consequence of the decrease in the growth rate at the solidification front with distance from the surface of the casting, the distance between the dendrite tips increases according to the relationship (6.9) on page 144. When the growth rate decreases, the structure becomes coarser, as is evident from Figures 6.43 and 6.45 on pages 168 and 169 respectively.

6.7.3 Formation of the Central Crystal Zone – Equiaxed Crystals of Random Orientation

Tschernoff was the first to discuss the formation of equiaxed crystals and a central zone in the scientific literature. His observations on ingots have been confirmed by microscopical studies and other convincing experimental evidence.

The crystals have a random orientation - all directions are equally frequent. The proper technical term to describe these crystals is *equiaxed crystals of random orientation*. The fact that the crystals have various orientations (Figure 6.41) when they precipitate from the melt shows that they are formed from separate nuclei. Sometimes during the precipitation process these crystals have floated freely in the melt. They are designated as free or freely floating crystals in the melt at this stage.

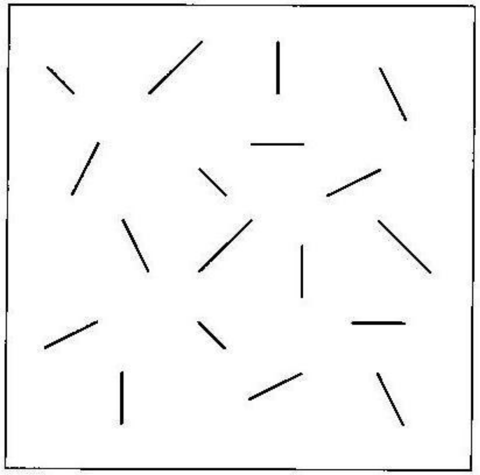


Figure 6.41 Illustration of the crystallographic directions of equiaxed crystals in the central zone, orientated at random.

Studies of the solidification process, based on rapid cooling while the reaction is going on, show that these crystals that float freely in the melt can grow to a considerable size.

Formation of Equiaxed Crystals of Random Orientation

There are several different theories about the nucleation of freely floating crystals. These theories have been applied to ingots in the text below but are valid for other types of castings as well.

One theory is that new nuclei are formed by *crystal multiplication* within the melt. This process is discussed earlier in Section 6.3.3. Both Hultgren and Southin have showed that there are crystals in the central zone that, in part, have the same structure as the crystals at the upper surface of the ingot. The explanation of this may be that dendrite fragments from the solid metal layer at the upper surface can be torn off, due to convection in the melt, and act as heterogeneities for nucleation of equiaxed crystals in the central zone (see Figure 6.37). Of course it is not necessary for crystal fragments to get torn off from the upper surface of the ingot in particular. It may happen all over the ingot wherever the proper conditions for fractures of the crystal arms occur.

Another theory, presented by Howe, is that the concentration of segregated elements ahead of the solidification front may cause *undercooling of the melt* with the consequence that new crystals form at the lower temperature. Hultgren investigated this theory. He claimed that an undercooled zone may appear, due to the diffusion ahead of the solidification front, and that nucleation of new equiaxed crystals ahead of the front may occur there. Figure 6.42 shows how such an undercooled zone may arise. The left side of the figure shows the concentration profile of alloying elements in the melt in front of a growing dendrite tip. The right side of the figure shows how this profile can be transformed into a curve, which describes how the temperature must vary theoretically in order to cause every point in the melt to be at the liquidus temperature, the highest temperature at which solid phase can exist in the melt. If the real temperature profile is shallow enough, an undercooled zone may arise, which is the condition for formation of freely floating crystals.

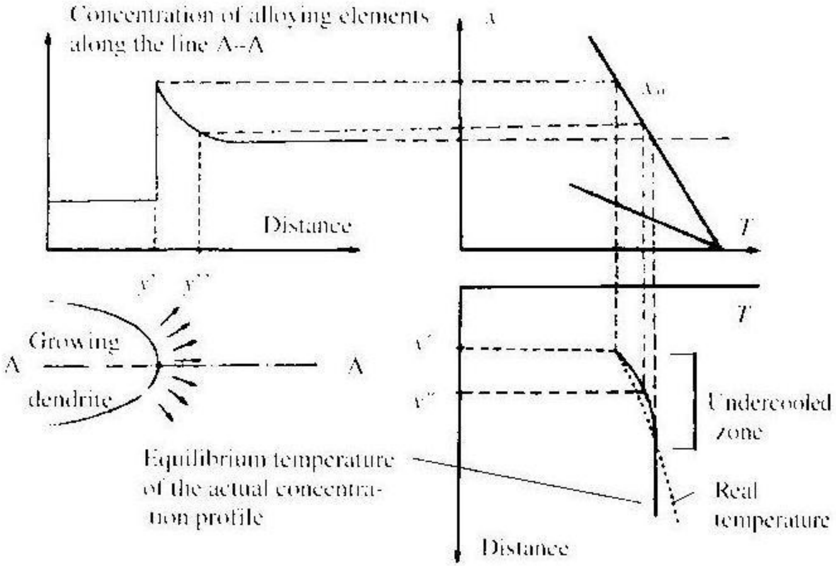


Figure 6.42 Formation of an undercooled zone in front of a growing dendrite tip in a metal.

In many cases a lot of impurities are present in the melt and new equiaxed crystals can easily be formed by nucleation on these heterogeneities. In addition, the number of growing crystals can be increased by crystal multiplication, enhanced by convection in the melt.

Formation of the Central Zone

When the number of freely floating crystals is large enough and the growing crystals have reached a certain critical size, they will effectively block the further growth of the columnar crystals. Then the central zone will replace the columnar zone. However, there will be no growth of the new crystals and no zone change unless the released heat of formation is transported away. As an example this topic is discussed for ingots on page 170.

6.8 MACROSTRUCTURES IN INGOT CAST MATERIALS

In Section 6.7 a general discussion of the macrostructure in castings is given. In this and the following two sections some additional specific properties of the macrostructures of materials, cast using the main cast house processes, are discussed.

6.8.1 Columnar Zone in Ingots

In 1920 the English metallurgist Stead originally suggested the theory of competitive growth (Sections 6.6.3), which later was confirmed by Hultgren. Today it is generally accepted as the explanation of the columnar zone.

The columnar character of the crystal is illustrated in Figure 6.43. It arises by the simultaneous growth of several dendrite crystals side by side. The figure also shows that the cross-section area of the columnar crystal increases with the distance from the cooled surface. The reason for this is that there is an elimination of columnar crystals with less favourable crystal orientation, which results in an increase of the cross-section diameters of the remaining columnar crystals.

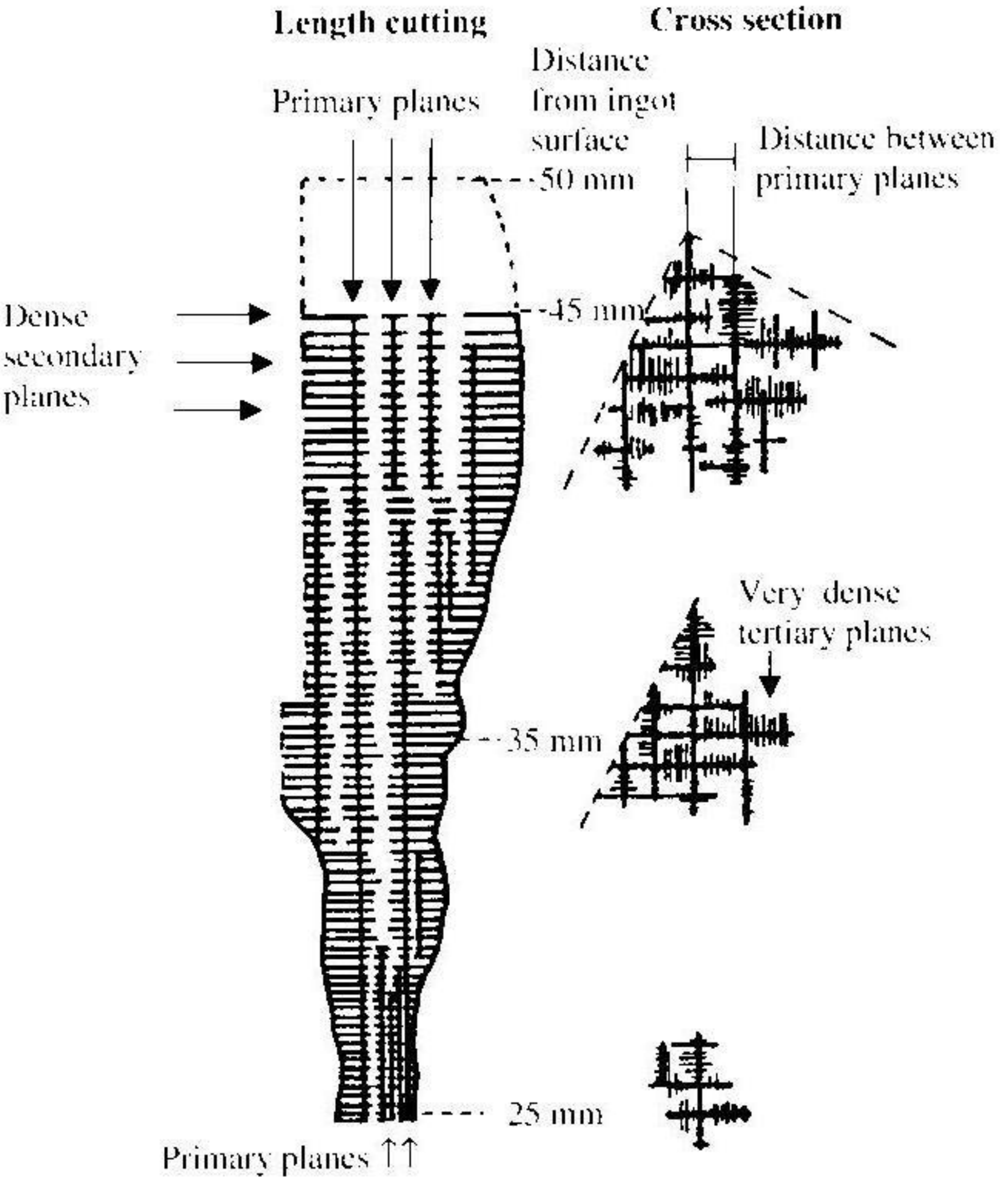


Figure 6.43 Cut through the length axis of a steel crystal. Reproduced with permission from the Scandinavian Journal of , Metallurgy. Blackwell.

The crystal area, perpendicular to the mould surface, will thus increase during the development of the columnar crystal zone. Figure 6.44 shows the crystal area as a function of the distance from the ingot surface for two ingots of ball bearing steel. As a consequence of the fact that the growth rate of the solidification front decreases with the distance from the ingot surface, the distance between the dendrite tips increases. This is illustrated in Figure 6.45.

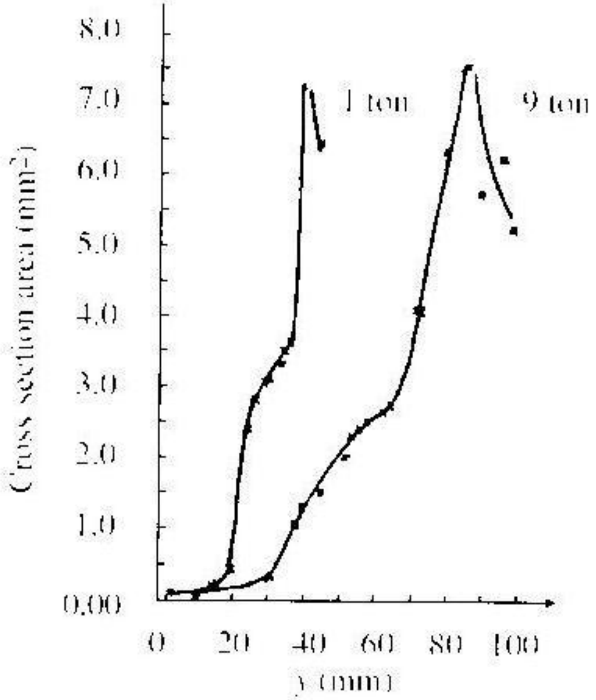


Figure 6.44 Transverse section area of columnar crystals in two ingots as a function of the distance from the ingot surface. Reproduced with permission from the Scandinavian Journal of Metallurgy, Blackwell.

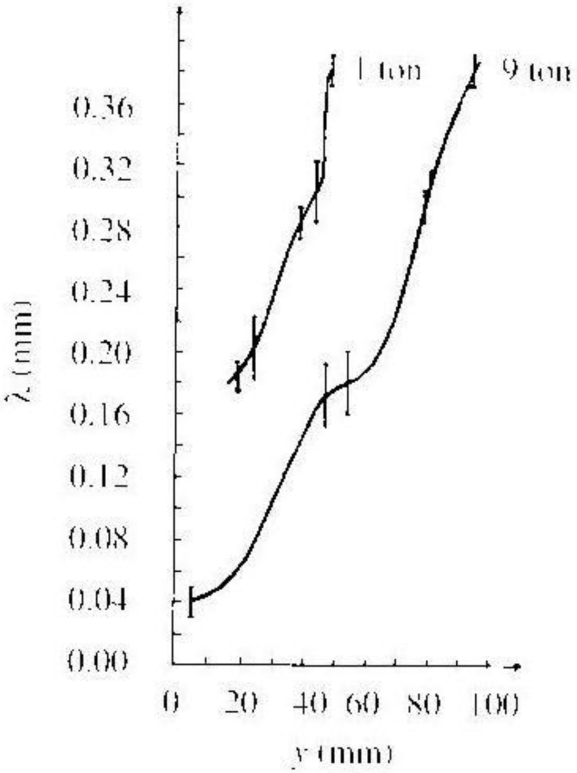


Figure 6.45 The spacing of the secondary plates in the columnar zone of the ingots in Figure 6.44 as a function of the distance from the ingot surface. Reproduced with permission from the Scandinavian Journal of Metallurgy, Blackwell.

Figure 6.45 does not correspond to the simple parabolic relationship, between the dendrite arm distance and the distance from the cooling surface [Equation (7′)] in Example 6.6 on page 16. The reason for this is that the growth conditions and consequently also the structure morphologies are not constant. The dendrite arms and the crystal cross sections seem to grow in two or three different steps. For each step the relationship $v_{\mathrm{growth}} \lambda_{\mathrm{den}}^{2} = \mathrm{const}$ is valid, but with different contants for each step.

Close to the interface there is a subzone with cellular-like dendrite structure with weakly developed secondary arms (cellular crystals being crystals, with no secondary arms, that are formed at high growth rates and large temperature gradients). A second subzone of normal dendrites succeeds this zone. At larger distances from the ingot surface a third subzone of superdendrites can be identified (superdendrites are characterized by very large distances between their primary arms. They were first discussed by Bolling in 1968). The formation of superdendrites seems to be related to the superheating of the melt ahead of the growing dendrites.

6.8.2 Change from Columnar Zone to Central Zone

The question as to whether or not the change from columnar zone to central zone is coupled to equiaxed crystals has been debated for a long time. One of the very first scientists to discuss the formation process was the English metallurgist Stead. He claimed that the free crystals at the centre of an ingot might grow to a considerable size at the same time as there is a certain tendency of sedimentation. In this way he could explain another of his observations, namely that the ingot material is more pure in the lower than in the upper part (Figure 6.46 on page 170). The theory, that the zone of equiaxed crystals is built up from the bottom of the ingot by sedimentation, was further developed by among others Hultgren and is fully accepted today.

Various opinions concerning the ability of floating crystals to stop the growth of columnar crystals at the vertical solidification front of an ingot have been presented. To explain this change it was originally suggested that the columnar zone continues to grow as long as the remaining melt has a temperature that is sufficiently high to prevent the formation of floating crystals. However, Hensel showed that the melt is cooled surprisingly rapidly and often reached approximately the same temperature as the solidification front of the columnar crystals long before their growth ceased. He suggested convection in the melt as the reason for the rapid cooling process.

Nowadays the explanation of the change from columnar to equiaxed crystals in an ingot is the following. The floating crystals in the melt generally have a certain tendency to sedimentation, which increases gradually when the crystals grow. At last the crystals are so big that they can no longer float but sink to the bottom. On the way, some of the free crystals stick to the dendrite tips at the vertical solidification front and stop their growth. In those cases where the number of free crystals in the melt is large, this change will occur early.

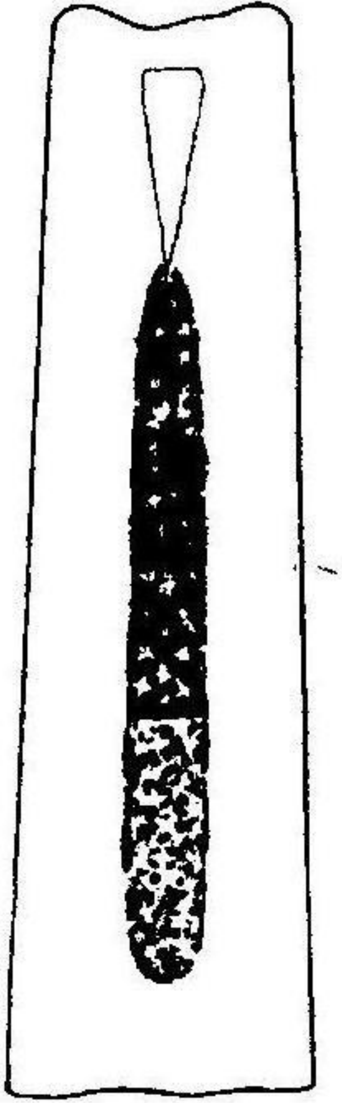


Figure 6.46 Sketch of the equiaxed crystal zone in the centre of an ingot according to Stead. The dark area is remaining melt with bright star-like equiaxed crystals. Reproduced with permission from the Scandanavian Journal of Metallurgy, Blackwell.

because the probability of the crystals sticking to the vertical solidification front increases with their number per unit volume. Numerous free crystals are nucleated in the melt if the casting temperature is low. At temperatures below the liquidus temperature a large number of free crystals are formed in the melt during the casting operation due to convection and crystal multiplication. In this case, the columnar crystal zone will end and the ingot structure will consist of small equiaxed crystals, provided that the heat flux from the ingot is sufficient.

A change from columnar crystals to equiaxed crystals of random orientation can occur only if the heat transfer to the surroundings is so rapid that the temperature gradient remains relatively unchanged by the heat released from the growing crystals.

6.8.3 Structures within the Central Zone

Different formation conditions for equiaxed crystals will result in differences in structure between the equiaxed zone, which is formed with the aid of sedimentation, and that which is formed at the vertical solidification front. This results in differences in material properties between the various parts of the ingot. From a practical point of view it may be important to realize that the zone of randomly oriented crystals in the centre of the ingot in reality consists of two different zones. The distinction between them will be more pronounced the bigger the ingot is.

The crystals that stick to the vertical solidification front and stop its growth often grow somewhat themselves. Then they become larger than the crystals in the sediment zone and get a somewhat longish form. This is the reason why this zone often is designated as the *branched columnar zone* in the scientific literature.

The *globular dendrite zone* consists of sedimented freely growing crystals that grow in the melt and acquire a rounded shape before they settle. Thus the crystals in the sedimented zone often show a globular morphology.

In big ingots with long solidification times, the number of new free floating crystals will decrease during the solidification process and the central zone of branched columnar crystals will be extended over the whole cross section in the upper part of the ingot as shown in Figure 6.47.

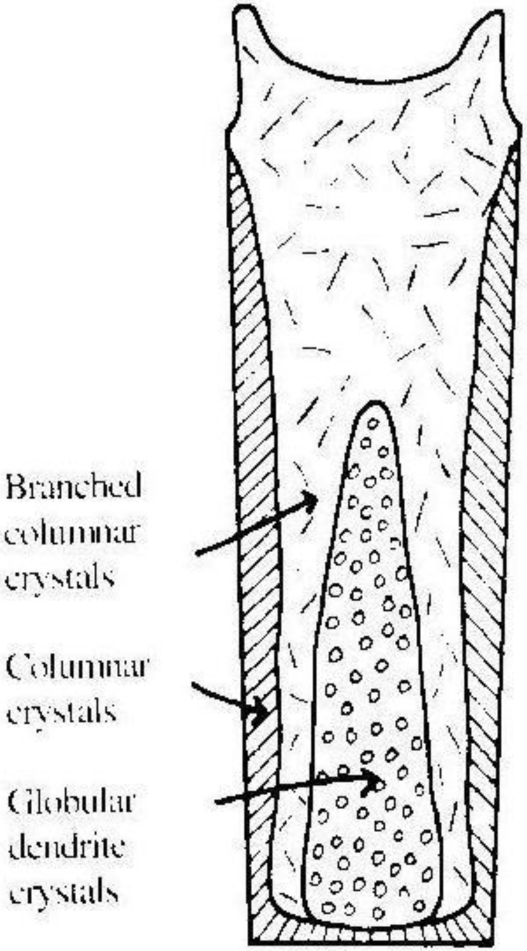


Figure 6.47 Sketch of the extension of the zones in an ingot of 9 tons. Reproduced with permission from the Scandinavian Journal of Metallurgy, Blackwell.

6.8.4 Time for Change from Columnar to Central Zone in an Ingot during Solidification – Length of the Columnar Zone

The time for the change from columnar zone to central zone in an ingot is closely related to the temperature of the melt T_{melt} in the interior of the ingot as a function of time. This function is calculated in Section 5.3.2 in Chapter 5 for the case when the formation of equiaxed crystals or freely floating crystals is neglected. We will use these calculations and modify them by taking account of the influence of the formation of equiaxed crystals.

and with decreasing excess temperature $T_{\text{melt}} \quad T_{\text{L}}$. The reason for this is that an increased number of crystals per unit volume increases the probability of crystals sticking to the solidification front. At lower excess temperatures the temperature minimum is reached in shorter time, which gives a shorter length of the columnar crystal zone.

6.9 MACROSTRUCTURES IN CONTINUOUSLY CAST MATERIALS

The macrostructure of a continuously cast material resembles the macrostructure found in ingots. The formation mechanisms of the crystal types and crystal zones are the same in both cases, and the discrepancies that appear originate from the different casting conditions. Two cases of macrostructures in continuously cast materials are analysed and discussed below.

Figure 6.50 shows the macrostructure of a slab cast in a bent machine for continuous casting. The specimen consists of a small piece of the slab, cut along two parallel cross sections of the strand and then parted into two equal halves. The figure shows one of these halves. The width of the slab is 250 mm.

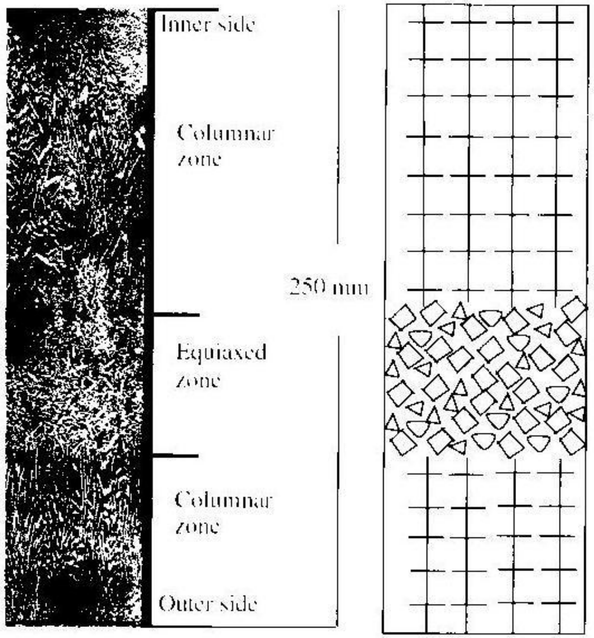


Figure 6.50 Macrostructure in a cross section of a continuously cast slab.

The upper part of the figure shows the structure formed on the inner radius side, and the lower part shows the structure on the opposite, outer side. The central part has a dark line along its length. This corresponds to a crack and segregated material, called centreline segregations. It has nothing to do with the structure. Macrosegregation is discussed in Chapter 11. The structure can be characterized as a very fine surface zone that consists of a fine network of thin dendrite arms and *not*, as in ingots, of a great number of fine-grained crystals.

When a shell is formed in the chill-mould, close to the meniscus, some crystals grow along the surface in the withdrawal direction. However, cooling in the chill-mould is very strong and the dendrites become very thin. Due to the high temperature gradient the thin dendrite crystals grow inwards and form columnar crystals. The growth of columnar crystals is stopped by the formation of equiaxed crystals that have grown freely in the melt. The figure shows that the growth of the columnar crystal zone stopped *earlier* on the *outer* side (lower part of the figure) of the strand than at the inner side of the slab. The reason is sedimentation of the equiaxed crystals during their growth in the same way as was discussed for ingots.

The columnar crystals on the *inner* side grow towards the central part of the strand and sometimes even into the outer side (lower part of Figure 6.50). The reason is that the melt between the two growing zones does not contain enough equiaxed crystals to stop the columnar crystals effectively at the inner side.

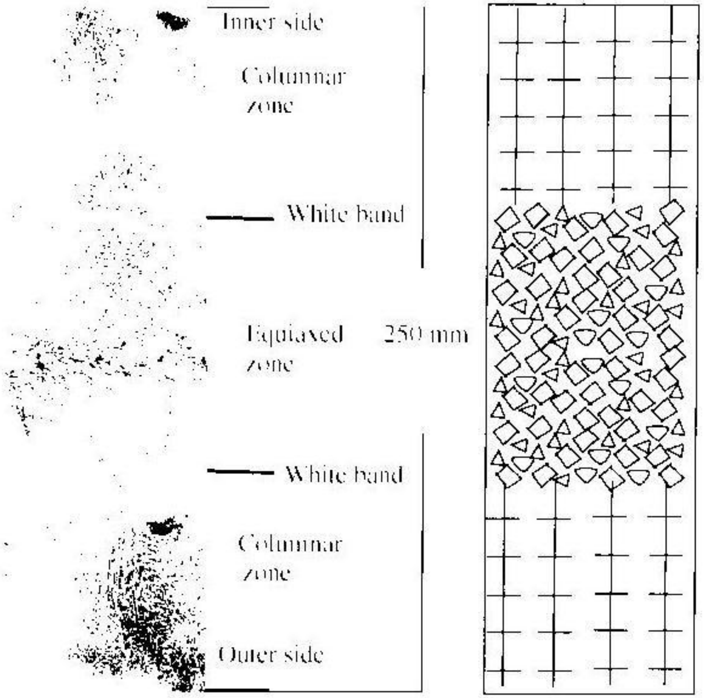


Figure 6.51 Macrostructure in a cross section of a continuously cast slab with electromagnetic stirring.

The pattern will be different if there is a great number of equiaxed crystals in the melt. Figure 6.51 shows the structure of such a continuously cast material in which measures have been taken to increase the number of freely growing equiaxed crystals. Electromagnetic stirring of the melt has increased the convection, and the convection caused formation of white bands (ghost lines), which are seen in Figure 6.51. In this way the number of crystals is enhanced by crystal multiplication at the same time as their opportunities to grow have increased. Again we disregard the appearance of the central part and the white bands. These effects have nothing to do with the macrostructure and are treated in a later chapter.

Figure 6.51 shows that the change from columnar zone to central zone occurs at the same distance from the cold wall for the inner and outer sides of the strand. The stirring eliminates the sedimentation and the asymmetry between the two sides that are present in Figure 6.50.

6.10 MACROSTRUCTURES IN NEAR NET SHAPE CAST MATERIALS

During the 1970's and later, different types of rapid solidification process were developed. Cast steel with better properties than those achieved using conventional casting methods was produced with the new rapid solidification methods. The effects of the higher cooling rates can be summarized as follows:

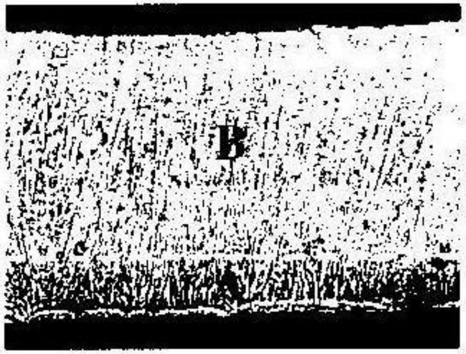
- refinement of grain size and more uniform dispersion of primary carbides;
- more uniform distribution of alloying elements in the matrix and reduction of alloy segregation, particularly in highly alloyed steels, where segregation can not be eliminated even after extensive working;
- increase of solid solubility of carbon and alloying elements;
- a better structure;
- formation of nonequilibrium crystalline phases or amorphous phases.

6.10.1 Structures of Rapidly Solidified Steel Strips

Figure 6.52 shows the structure of a steel alloy that consists of austenite crystals (γ-iron) and Cr–Fe–Mo eutectic carbides. Figure 6.52 (a) shows that the structure consists of two parts: a chill-region A and a cellular or dendrite region B.

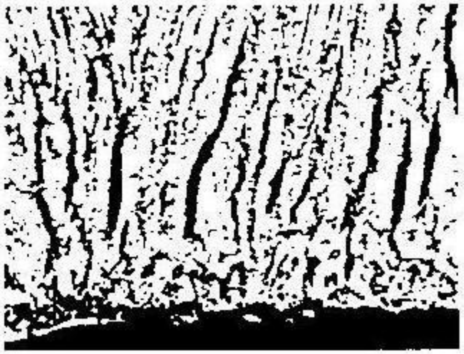
Region A is restricted to the surface of the strip, where the contact between the strip and the wheel of the strip casting machine is good. This region consists of very fine-grained equiaxed crystals that are formed at the beginning of the solidification process. At some distance from the wheel surface the upper crystals in region A start to grow. Metallographic examination shows that these crystals grow with very fine cellular morphology and low microsegregation or even free from microsegregation.

Region B consists of either columnar or equiaxed crystals, depending on the local variation in the cooling rate. The mechanism behind the transition from the columnar to the



(a)

Figure 6.52 (a) Structure of a strip that consists of a mixture of γ-iron and Cr–Fe–Mo carbide. A = lower zone; B = upper zone. Reproduced with permission from Elsevier Science.



(b)

Figure 6.52 (b) Enlargement of the A-region, close to the wheel surface, at the bottom of Figure 6.52 (a). Reproduced with permission from Elsevier Science.

equiaxed zone is the same as that discussed earlier. The high cooling rate will increase the length of the columnar crystals.

6.10.2 Influence of Lattice Defects on Rapid Solidification Processes

In Section 4.3.4 in Chapter 4 we found that lattice defects are formed in the solid during solidification processes. This will be more and more pronounced the higher the cooling rate is. Crack formation is an indication of lattice defects. Such cracks can be seen in Figure 6.52 (b), where the long black, nearly vertical, stripes are elongated cracks.

Formation of lattice defects requires energy. When the defects are formed the energy of the solid increases proportionally to the amount of defects and varies with the defect type. The defects influence the latent heat of the material as was discussed in Section 4.3.4 in Chapter 4. The proportion of defects in the metal also influences the liquidus and solidus temperatures. This will thus affect the whole solidification process.

6.11 AMORPHOUS METALS

The kinetics of solidification can briefly be described by the constant μ in Equation (6.11) on page 144. Difficulties in transforming the system from an unordered structure in the melt to an ordered structure in the solid result in a small value of μ, mainly due to the diffusion process across the interface.

The more difficult the kinetics is, i.e. the slower the solidification process is, and the easier the nucleation of new equiaxed crystals occurs, the shorter will the columnar zone be. If the kinetics (the nucleation and growth processes) is slow enough, the crystallization process stops completely and the liquid becomes supercooled at a temperature where a so-called *glass transition* will occur.

The glass temperature is defined as the temperature at which the diffusion of the atoms is so low that no crystallization can occur. At the glass temperature T_{glass} an *amorphous phase* is formed.

6.11.1 Properties of Amorphous Phases

Amorphous phases have no structure. The atoms are in an unordered state, reminiscent of the liquid state. The lack of a regular or crystalline structure is confirmed by X-ray examination of amorphous materials. No sharp intense lines, characteristic of crystalline materials, are obtained, only diffuse and broad lines or rings that are typical of liquids.

At the glass transition temperature, sudden and drastic changes in specific volume, viscosity, and heat capacity are observed. Figure 6.53 illustrates the change in specific volume as a function of the temperature for an amorphous metal.

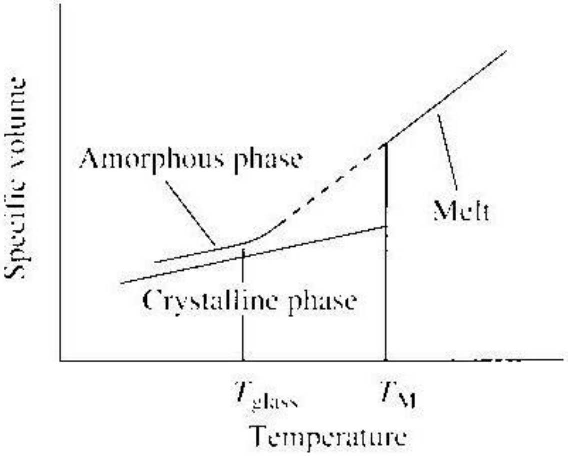


Figure 6.53 Specific volume as a function of the temperature for an amorphous metal. The dashed line indicates that no measurements have been possible at these temperatures.

The glass transition temperature is a material constant and is specific for each alloy. Amorphous metals have excellent mechanical properties. They are hard but very plastic, compared with crystalline metals. Amorphous metals show very good soft magnetic properties. They must not be heated above the glass transition temperature because of the risk of a transition to a crystalline phase.

6.11.2 Formation of Amorphous Phases

A necessary condition for formation of an amorphous phase is that *the metal melt has to be cooled quickly enough to avoid nucleation and crystallization.* The lower the temperature, the slower the solidification rate.

The critical cooling rates for metals are of the order 10^4 K/s or higher. In very special cases one can get amorphous metals at cooling rates of the magnitude 10^2 K/s. Experimental evidence shows that formation of amorphous metals will be enhanced if:

- the melting point of the alloy is *low*, compared with that of the pure metal;
- the glass transition temperature is *high* relative to the melting point of the alloy.

This is illustrated in a so-called temperature–time–transition diagram (TTT diagram) in Figure 6.54, where

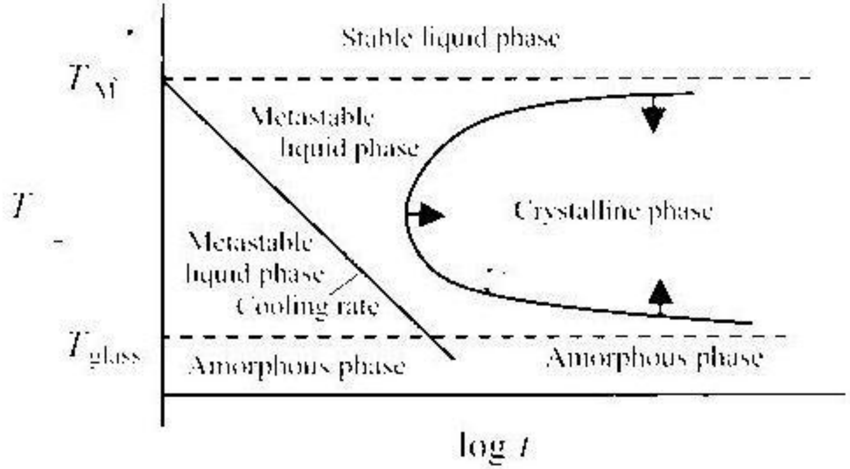


Figure 6.54 TTT diagram of an amorphous metal.

changes that promote formation of amorphous phases are marked with arrows.

The shape of the curve depends on (i) the melting point temperature T_M, (ii) the critical transition temperature T_{glass}, and (iii) the growth kinetics. Formation of amorphous material occurs in materials with a low melting point (↓ in Figure 6.54), high glass transition temperature (↑), and rapid nucleation and crystal growth (→).

6.11.3 Casting Methods for Production of Amorphous Metals

The critical cooling rate, required for formation of an amorphous phase, is a material constant. It is the lowest possible cooling rate that can give an amorphous material and can be drawn in the TTT diagram as a tangent from the T_M point to the curve. This fact restricts the possible casting methods for production of amorphous metals.

Pressure die casting methods can be used at cooling rates of the order 12 K/s. At higher critical cooling rates spray casting methods are optimal. For continuous production of strips, the melt-drag, melt-spinning, and twin-roller technologies are used.