

eliminate macroslag inclusions in the alloys will be discussed. Different methods to neutralise the negative effects of pores and slag inclusions will be suggested for each group of alloys.

## 9.2 Units and Laws

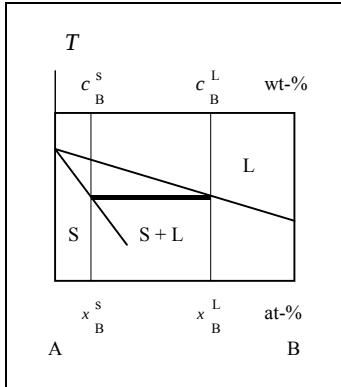
In order to facilitate the discussions of solubilities and the risk of precipitation of various gases in various alloys we will need some special concepts and units. They have been listed in table 1 below. In table 2 there is a review of the most important physical and chemical laws, which will be applied further on. Example 1 illustrates some common types of unit transformations.

Table 1.

| Quantity                                 | Symbol        | Unit                              | Comments                                                                              |
|------------------------------------------|---------------|-----------------------------------|---------------------------------------------------------------------------------------|
| pressure                                 | $p$           | N/m <sup>2</sup> , atm<br>mm Hg   |                                                                                       |
| volume                                   | $V$           | m <sup>3</sup>                    |                                                                                       |
| mole                                     | $n$           | kmole                             | mass (kg) of molar weight                                                             |
| absolute temperature                     | $T$           | K                                 |                                                                                       |
| concentration                            | [ ]           | general designation               |                                                                                       |
|                                          |               | ppm                               | (weight) parts per million                                                            |
|                                          | $c$           | weight %                          | subscript o = initial value                                                           |
|                                          |               | (w/o) or                          | subscript L = liquid phase                                                            |
|                                          |               | kmole/litre                       | subscript s = solid phase                                                             |
|                                          | $x$           | mole fraction                     | number of kmoles of the substance/total number of kmoles. Subscripts as above.        |
|                                          |               | or                                |                                                                                       |
|                                          |               | atomic %                          |                                                                                       |
|                                          |               | (at-%)                            |                                                                                       |
| partition coefficient                    | $k, k_x, k_c$ |                                   | $x^s/x^L$ or $c^s/c^L$                                                                |
| solid phase/liquid phase                 |               |                                   |                                                                                       |
| solubility of a gas in a melt or a solid | $S$           | ppm<br>or<br>cc/100 g<br>weight % | (weight)parts per million<br><br>cm <sup>3</sup> (NTP)/ 100 g<br>subscripts as above. |

Table 2.

|   |                                                                                                                                                                          |                             |
|---|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------|
| • | $pV = nRT$                                                                                                                                                               | <i>General Gas Law</i>      |
| • | The saturation value of the concentration of a gas solved in a melt is proportional to the square root of the pressure of the gas                                        |                             |
|   | $c = \text{const} \cdot \sqrt{p}$                                                                                                                                        | <i>Sievert's Law</i>        |
|   | where $p$ = partial pressure of the gas                                                                                                                                  |                             |
| • | <i>Condition for Precipitation of a Gas in a Melt</i>                                                                                                                    |                             |
|   | $p_{\text{gas}} = p_a + p_h + 2\sigma / r$                                                                                                                               |                             |
|   | where                                                                                                                                                                    |                             |
|   | $p_{\text{gas}}$ = total pressure inside the gas pore                                                                                                                    |                             |
|   | $p_a$ = atmospheric pressure ( <i>not</i> the partial pressure of the gas)                                                                                               |                             |
|   | $p_h = \rho gh$ = hydrostatic pressure                                                                                                                                   |                             |
|   | $\rho$ = density of the melt                                                                                                                                             |                             |
|   | $h$ = distance of the gas pore to the free surface of the melt                                                                                                           |                             |
|   | $\sigma$ = surface energy per unit area of the melt                                                                                                                      |                             |
|   | $r$ = radius of the gas pore.                                                                                                                                            |                             |
| • | $p + \rho gh + \frac{\rho v^2}{2} = \text{const}$                                                                                                                        | <i>Bernoulli's Equation</i> |
|   | where                                                                                                                                                                    |                             |
|   | $p$ = pressure in a liquid or a gas                                                                                                                                      |                             |
|   | $h$ = height over an arbitrary chosen zero level                                                                                                                         |                             |
|   | $v$ = velocity of the particles in the streaming fluid.                                                                                                                  |                             |
| • | For the reaction $a A + b B \leftrightarrow c C + d D$ we have                                                                                                           |                             |
|   | $\frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} = \text{Const}$                                                                                                             | <i>Guldberg-Waage's Law</i> |
|   | Endothermic reaction                                                                                                                                                     | Energy has to be supplied.  |
|   | Exothermic reaction                                                                                                                                                      | Energy is emitted.          |
|   | The value of the constant depends on the concentration units and on the temperature. The equilibrium is altered when the temperature is changed.                         |                             |
| • | $\frac{dm}{dt} = -DA \frac{dc}{dy}$                                                                                                                                      | <i>Fick's First Law</i>     |
|   | When Fick's law is applied one <i>must not</i> simply use dimensionless units for concentration $c$ , for example weight % (w/o), ppm, mole fraction or atomic % (at-%). |                             |
|   | See pages 108-109 for a special analysis of this matter.                                                                                                                 |                             |

**Example 1.**

A binary alloy has a composition which is described by the masses respectively molar weights  $m_A$ ,  $M_A$  respectively  $m_B$ ,  $M_B$ . Express its composition in ppm, weight-% (w/o), mole fraction and atomic % (at-%). In addition transfer  $c$  (w/o) to  $x$  (at-%) and  $x$  to  $c$ .

**Answer:**

$$c_B = \frac{m_B}{m_A + m_B} \cdot 10^6 \text{ ppm} = \frac{m_B}{m_A + m_B} \cdot 100 \text{ w/o}$$

$$c_B = \frac{x_B M_B}{x_A M_A + x_B M_B} \cdot 100 \text{ w/o}$$

The following relations are also valid for a binary system:

Weight per cent:

$$c_A + c_B = 100$$

Mole fractions:

$$x_A + x_B = 1$$

$$x_B = \frac{\frac{m_B}{M_B}}{\frac{m_A}{M_A} + \frac{m_B}{M_B}} (\text{mole fraction}) = \frac{\frac{m_B}{M_B}}{\frac{m_A}{M_A} + \frac{m_B}{M_B}} \cdot 100 \text{ at - \%}$$

$$x_B = \frac{\frac{c_B}{M_B}}{\frac{c_A}{M_A} + \frac{c_B}{M_B}} \cdot 100 \text{ at - \%}$$

**9.3 Precipitation of Gases in Metal Melts****9.3.1 Gas Reactions and Gas Precipitation in Metal Melts**

Precipitation of gas is one of the most severe problems, which appear at casting of iron and steel, aluminium- and copper

alloys. Thus it is urgent to analyse the mechanisms, which control the pore formation at casting.

### **The Most Common Gases in Metal Melts**

During melting the metal is for a long time in contact with the surrounding atmosphere, which normally is air. *Oxygen* and *nitrogen* are therefore always present and may in some cases dissolve in the melt. Because air always contains water vapour one must also take *hydrogen* into account.

All steel and iron alloys contain carbon. The possibility exists in these cases that carbon and oxygen, both solved in the melt, may generate *carbon monoxide*.

During casting, which lasts for a relatively short time, the melt may carry away air mechanically. By a suitable design of the casting process and the mould this complication can be prevented.

Other sources of gases in contact with the melt are chemical reactions between the melt and the material of the mould. Some reaction products may be gaseous, among others *hydrogen*, *oxygen*, *carbon monoxide*, *carbon dioxide* and *sulphur dioxide*. An important example is moist in sand moulds, which give water vapour in contact with the melt. The gas dissociates and generates *hydrogen*. This hydrogen source is hard to eliminate.

### **Reason and Conditions for Gas Precipitation**

The solubility of gases is much greater in the melt than in the solid phase for all common metals. Pressure, temperature and composition of the melt influence the solubility of a gas, i. g. its concentration in the melt, Examples of this in concrete cases will be given later.

When the melt starts to solidify the gas concentrates gradually in the melt. When the solubility reaches its saturation value one of two alternatives will occur.

In the absence of suitable condensation nuclei and/or if the solidification process is faster than the time necessary for reaching equilibrium between the dissolved phase and the gas

phase, a *supersaturated solution* is formed and gas precipitation fails to appear. Under opposite conditions *gas pores* are formed in the melt. The pressure inside the pores is controlled by the equilibrium equation:

$$p_{\text{gas}} = p_a + p_h + 2\sigma / r \quad (1)$$

where

$p_{\text{gas}}$  = total pressure inside the gas pore

$p_a$  = atmospheric pressure (*not* the partial pressure of the gas)

$p_h = \rho gh$  = hydrostatic pressure

$\rho$  = density of the melt

$h$  = distance of the gas pore to the free surface of the melt

$\sigma$  = surface energy per unit area of the melt

$r$  = radius of the gas pore.

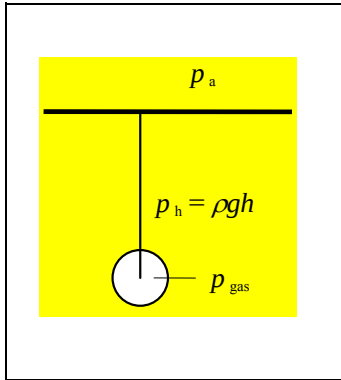


Figure 2.

The larger the surface tension is, the easier pores will form.

Depending on the actual circumstances the bubbles may have various shapes, sizes and distribution after solidification. We will discuss this later in this chapter.

Equation (1) is a necessary but not sufficient condition for gas precipitation. Gas precipitation is a particularly complicated process, which depends on many factors, among others

- concentration of the dissolved gas in the melt
- saturation concentration of the gas in the present alloy
- composition of the alloy
- rates of the chemical reactions
- diffusion rates of the gas in the melt and the solid phase
- access to suitable condensation nuclei
- surface tension of the melt.

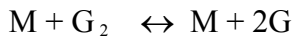
We will consider these factors more closely.

### 9.3.2 Solubility of Gases in Metals. Sievert's Law

#### Sievert's Law

The difference between the solubility of gases in a metal melt and the solid phase after solidification is the basic reason for gas precipitation in metals at casting.

The solubility of a gas in a metal melt depends on its partial pressure in the surrounding atmosphere. Most common gases are diatomic at room temperature. At high temperature (temperature of the metal melt) a dissociation of the gas  $G_2$  occurs at the metal surface in presence of metal atoms M



A chemical equilibrium between the dissolved gas atoms  $\underline{G}$  and the surrounding gas is established. Guldberg-Waage's law controls the equilibrium:

$$\frac{[\underline{G}]^2}{p_{G_2}} = \text{Const} \quad (2)$$

where the value of the constant depends on the temperature. The gas atoms then diffuse into the melt and/or the solid phase and stay there in the shape of a solution. We denote the concentration in the solution with  $[\underline{G}]$  where the underlined letter symbol means that the gas is dissolved in the metal as G-atoms and not  $G_2$ -molecules.

At equilibrium the concentration of the dissolved gas atoms in the melt or in the solid phase is proportional to the square root of the partial pressure of the gas in the surrounding atmosphere. This statement can be written

$$[\underline{G}] = \text{const} \cdot \sqrt{p_{G_2}} \quad \text{Sievert's law} \quad (3)$$

Sievert's law follows directly from equation (2).

The solubility of a gas in metals is often given in the scientific literature at the standard pressure 1 atm. Sievert's law is extraordinary useful for calculation of the solubility  $[\underline{G}]$  in equilibrium with a known partial pressure in the surrounding atmosphere.

$[\underline{G}]$  is normally expressed as  $c_{\underline{G}}$  (w/o) or  $x_{\underline{G}}$  (mole fraction).

### Partition Constant

The concentration of dissolved gas is in equilibrium with the surrounding atmosphere. Analogously there exists an equili-

brium between the concentrations of dissolved gas in the melt and in the solid phase. At equilibrium their ratio is constant.

$$\frac{x^s}{x^L} = k_x \quad \text{alternatively} \quad \frac{c^s}{c^L} = k_c \quad (4)$$

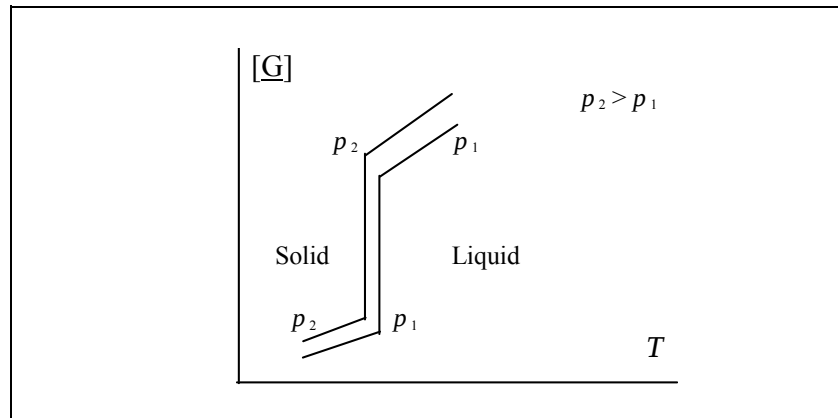
The constant is called *partition constant* or *partition coefficient*. This important concept will often be used throughout this book.

The k-value depends on which concentration unit we use.

### Solubility Diagram

Figure 3 shows a typical case of the solubility of a gas in a metal as a function of temperature.

Figure 3.  
Solubility of a gas in a metal as a function of temperature for the case that the solubility process is endothermic. The solubility of the gas also depends on its pressure.



It can be seen that

- The solubility of the gas is much greater in the melt than in the solid phase.
- The solubility of the gas increases with temperature both in the melt and in the solid phase.

This latter information can be included in equation (3) by replacing it by equation (5) below:

$$[G] = \text{Const} \cdot e^{\frac{-\Delta H_s}{RT}} \cdot \sqrt{p_{G_2}} \quad (5)$$

where

$[G]$  = solubility of the gas  
 $-\Delta H_s$  = heat of solution per kmole of the gas  
 $R$  = gas constant  
 $T$  = absolute temperature.

When hydrogen dissolves in the melt energy must be supplied. The reaction is *endothermic* and  $-\Delta H_s$  is *positive*. If we derive equation (5) with respect to  $T$  we get

$$\frac{d[G]}{dT} = \text{Const} \cdot e^{-\frac{-\Delta H_s}{RT}} \cdot \frac{-(-\Delta H_s)}{R} \cdot \frac{-1}{T^2} \cdot \sqrt{p_{G_2}}$$

or

$$\frac{d[G]}{dT} = \text{Const} \cdot e^{-\frac{-\Delta H_s}{RT}} \cdot \frac{-\Delta H_s}{RT^2} \cdot \sqrt{p_{G_2}} \quad (6)$$

The derivatives, i. e. the slopes of the curves, are positive if  $(-\Delta H_s)$  is positive. This is in agreement with figure 3 on page 10 and is valid for hydrogen in most common metals like Fe, Al, Mg and Cu.

When hydrogen dissolves for example in Ti or Zr, energy is released, i. e. the reaction is *exothermic*. The solubility curves have *negative* slopes in this case (figure 4).

The melt generally contains less gas than the saturation value. It means that there is no risk for gas precipitation during the solidification process in this case.

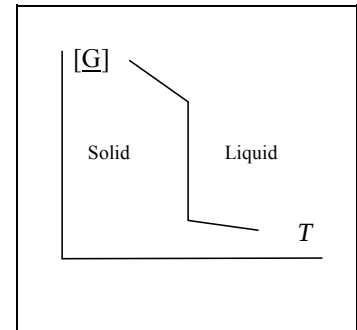


Figure 4.

The solubility of a gas in a metal as a function of temperature when the solution process is exothermic.

### 9.3.3 Reaction Mechanisms and Reaction Kinetics

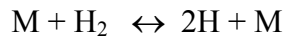
Absorption of a gas in a metal melt occurs in three steps

- 1 diffusion of the surrounding gas to the surface
- 2 chemical reaction at the surface
- 3 atomic diffusion of one or more of the reaction products into the melt.

The slowest of these steps controls the rate of the gas absorption.

Step 1 is normally fast and there is no need to discuss it further. Most gases in question are diatomic, for example  $H_2$ ,  $N_2$  and  $O_2$ .

Step 2 is often a dissociation, which occurs at the metal surface, for example



where M is the chemical symbol for the molten metal, which is not consumed at the reaction. This step is in many cases the slowest one and thus it determines the reaction rate.

Step 3 implies that the atoms diffuse into the melt and stay there as a solution. As mentioned above an underlined atom symbol indicates a monoatomic gas atom dissolved in a melt or a solid phase, for example H or N. Often the diffusion process is supported by the convection in the melt, which increases the rate of this step considerably.

Step 2 or 3 determines how rapidly a gas dissolves in the metal melt. The same is true in reversed order at gas precipitation. Step 3 controls the pore growth during the solidification process. In case of no convection in the melt diffusion occurs in the solid-liquid two-phase region during the solidification process.

### Gas Absorption

During casting from ladle to mould or chill-mould the temperature of the melt decreases due to emission of heat from the metal jet stream to the surroundings. Simultaneously a strong absorption of oxygen, hydrogen and nitrogen occurs because a large area is exposed to the atmosphere. It contains water vapour, which reacts with the metal and results in metal oxide or dissolved oxygen and monoatomic hydrogen.

If the stream is split up its reaction area is doubled many times. Experience shows that the length and shape of the stream are very important.

Example 2 shows that hydrogen concentration in steel increases during the casting process. The hydrogen concentration in steel is very important for the pore formation during the solidification process.

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#### Example 2.

An ingot of 10 tons will be cast. The casting time is 2 minutes. During the casting from ladle to mould it is to be expected by experience that the temperature of the steel melt will decrease 20 °C. A chemical analysis shows that the steel contains 4 ppm hydrogen before the casting. In the present case the third step (page 11), diffusion of H-atoms through a boundary layer into the melt, is the slowest one and determines the absorption rate. This boundary layer is supposed to have an average thickness of 10 µm.

Make a rough calculation to find the increase of hydrogen concentration in the steel during the casting operation.

From the scientific literature the following information has been extracted:

Diffusion rate of hydrogen in a steel melt =  $1.0 \cdot 10^{-4} \text{ cm}^2/\text{s}$ .

Maximum solubility of hydrogen in steel  
at the present temperature and moist concentration in the air

= 20 ppm.

Heat capacitvity of steel

= 0.76 kJ/kgK

The constant in Stefan-Boltzmann's law is  $5.67 \cdot 10^{-8} \text{ J/sm}^2\text{K}^4$ . The steel melt is no ideal black body and a reduction factor, the emissitivity  $\varepsilon$ , has to be introduced. Its value can in this case be estimated to 0.6.

### Solution:

Step 1:

From the information that the melt cools 20 °C we can calculate the effective area  $A$  of the jet stream. The heat loss is equal to the emitted energy of the jet stream.

$$c_p \cdot M \cdot \Delta T = \varepsilon \sigma \cdot (T^4 - T_o^4) \cdot A \cdot t \quad (1')$$

where

$M$  = mass of the ingot

$\Delta T$  = temperature decrease of the melt

$T$  = temperature of the steel melt = 1520 °C = 1793 K

$T_o$  = temperature of the surroundings = 20 °C = 293 K

$t$  = casting time = 2·60 = 120 s.

$T_o^4$  can be neglected compared to  $T^4$  and we get

$$0.76 \cdot 10^3 \cdot 10 \cdot 10^3 \cdot 20 = 0.6 \cdot 5.67 \cdot 10^{-8} \cdot 1793^4 \cdot A \cdot 120$$

which gives  $A = 3.58 \text{ m}^2$ .

Step 2:

The monoatomic hydrogen diffuses into the steel melt. By aid of Fick's diffusion law we can calculate the hydrogen concentration of the ingot at the end of the casting time.

Fick's first law can be written

$$\frac{dm}{dt} = -DA \frac{dc}{dy} \quad (2')$$

where

$m$  = mass of the diffused hydrogen

$D$  = diffusion coefficient of hydrogen in steel

$A$  = total effective area of the stream

$c$  = concentration (w/o) multiplied by the density of steel

(se pages 108 and 109)

$y$  = diffusion distance perpendicular to the surface.

At stationary flow equation (2') can be written

$$\frac{dm}{dt} = -D A \frac{\rho_{\text{Fe}} \cdot \Delta c}{\Delta y} = -D A \frac{\rho_{\text{Fe}} \cdot (c - c_{\text{eq}})}{\delta} \quad (3')$$

where  $\delta$  is the thickness of the boundary layer and  $c_{\text{eq}}$  is the solubility limit for hydrogen in steel at the given temperature.

The mass  $dm$  of the amount of hydrogen, which is transported into the steel melt during the time  $dt$ , increases the hydrogen concentration in the steel melt with the amount  $dc$  and we get the equality  $dm = dc \cdot M$  and equation (3') can be written

$$\frac{M \cdot dc}{dt} = -D A \cdot \rho_{\text{Fe}} \frac{(c - c_{\text{eq}})}{\delta} \quad (4')$$

If we integrate equation (4') we get the hydrogen concentration in the ingot as a function of time. From this relation we can get the desired concentration of hydrogen by inserting  $t = 120 \text{ s}$ .  
 $1 \text{ ppm} = 10^{-4} \text{ w/o}$ .

$$\int_{4 \cdot 10^{-4}}^c \frac{M \cdot dc}{(c - c_{eq})} = - \frac{D A \cdot \rho_{Fe}}{M \delta} \int_0^t dt \quad (5')$$

or

$$\left[ \ln(c - c_{eq}) \right]_{4 \cdot 10^{-4}}^c = - \frac{D A \cdot \rho_{Fe}}{M \delta} \cdot t$$

which can be transformed into

$$\frac{c - 20 \cdot 10^{-4}}{4 \cdot 10^{-4} - 20 \cdot 10^{-4}} = e^{- \frac{D A \cdot \rho_{Fe}}{M \delta} \cdot t}$$

where  $c$  is given in w/o.  $c$  is solved:

$$c = 20 \cdot 10^{-4} - 16 \cdot 10^{-4} \cdot e^{- \frac{D A \cdot \rho_{Fe}}{M \delta} \cdot t} \quad (6')$$

$c$  can be calculated by inserting known values in equation (6').

In addition to earlier given values we have

$$\rho_{Fe} = 7.8 \cdot 10^3 \text{ kg/m}^3 \quad \text{and} \quad \delta = 1.0 \cdot 10^{-5} \text{ m}$$

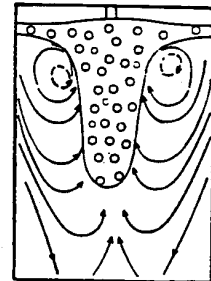
which gives

$$c = 20 \cdot 10^{-4} - 16 \cdot 10^{-4} \cdot e^{-0.33} = 8.5 \cdot 10^{-4} \text{ w/o} = 8.5 \text{ ppm}$$

**Answer:** The hydrogen concentration will be doubled during casting operation.

From the ladle the stream falls into the mould. The stream causes motion and flow in the metal melt in the mould. When the stream hits the surface of the melt in the mould air bubbles are carried down into the steel bath.

If the flow is laminar air is carried into the space between the jet stream and the melt and accompanies the melt into the mould. If the flow is turbulent air bubbles, trapped in the jet stream, follows the melt into the mould. When the air bubbles in the mould rise and leave the surface they cause a strong motion in the steel melt. The rising bubbles also decrease the penetration depth of the jet stream.



The trapped gas in the bubbles reacts chemically with the melt. If the gas is air it causes slag inclusions. For this reason it is important that the atmosphere is as inert as possible.

At downhill casting in a mould this can be achieved by covering the inside of the mould with tar, which is evaporated during the casting. At continuous casting without a casting pipe (chapter 10) rape oil can be added to protect the surface of the melt in the mould from reacting with air.

Figure 5.  
Flow in a steel me  
stream from the la  
mould.

### 9.3.4 Formation of Pores

At casting two main types of cavities or pores in castings and ingots may appear: *shrinkage pores* and *gas pores*. The classification is made with respect to the completely different origins and appearances of the pores.

It is well known that the solid phase generally has a greater density than the melt. The solidification shrinkage is normally compensated by the fact that new melt is sucked into the two-phase area during the solidification process. In many cases, especially when the solidification process is rapid, it is very difficult to compensate the whole solidification shrinkage. Instead pores are formed.

Shrinkage pores arise by formation of cavities in the remaining melt in the interdendritic areas, due to the resistance the melt offers to the transport through the narrow channels. The resistance is caused partly by the viscosity of the melt and partly by the dendrites around the channels. For this reason the transport channels of the melt are normally curved. In this case the surface of the pore becomes thorny and uneven. Shrinkage pores will be treated further in chapter 10.

Gas pores are characterised by the fact that their surface is smooth and even. Absorbed gas in a molten metal is in most cases more soluble in the melt than in the solid phase. Solidification of the metal results in gas precipitation in the interdendritic regions. The released gas has a large volume, compared to the melt, which in most cases causes formation of large pores because the melt is squeezed out of the two-phase areas. The sizes of these pores are determined by the con-

centration of the dissolved gas and by the difference in solubility of the gas in the melt and in the solid phase.

The gas pores can be divided into two subgroups: spherical pores and elongated pores. They will be discussed separately below.

When precipitation of eutectic structure at the end of the solidification process was discussed in chapter 7 we used a phase diagram in order to facilitate the understanding of the process. This method can also be used when precipitation of gas pores is concerned.

### Precipitation of Gas Pores

Consider a gas with a solubility curve similar to the one in figure 3 on page 10. In this case we exchange the axes and get a figure like the one in figure 6. It is the phase diagram of the metal-gas system.

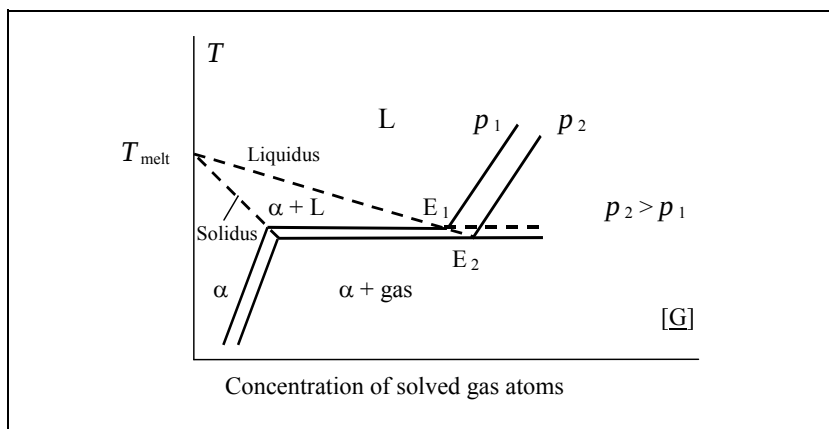


Figure 6.  
Phase diagram of a metal-gas system.

When solidus and liquidus lines have been added, the diagram will be even more like a eutectic phase diagram. As is seen from the figure the position of the eutectic point  $E$  is very sensitive to the pressure  $p$ .

### Spherical Pores

Spherical pores in the melt are formed when the gas concentra-

tion exceeds the solubility of the gas at the current temperature. This occurs when the gas concentration is higher than the eutectic concentration of the gas in the melt as is illustrated in figure 6.

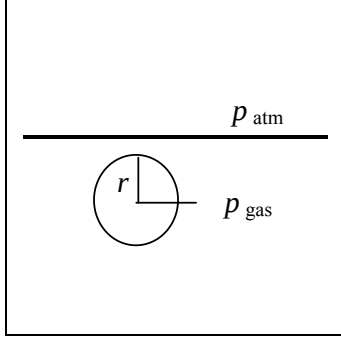


Figure 7.

Pores are formed preferably at the upper parts of an ingot. In this case the surface tension forces and the pressure forces in the melt determine the pressure inside the pores according to equation (1) on page 8.

In order to analyse the pore growth, i. e. the pore radius as a function of time, we consider a pore close to the surface of the melt and the term  $\rho gh$  in equation (1) on page 8 can be neglected.

$$p_{\text{gas}} = p_{\text{a}} + \frac{2\sigma}{r} \quad (7)$$

where

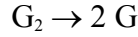
$p_{\text{gas}}$  = total pressure inside the pore

$p_{\text{atm}}$  = atmospheric pressure (*not* the partial pressure of the gas)

$\sigma$  = surface energy per unit area of the melt

$r$  = radius of the gas pore.

In addition we assume that the gas is diatomic and dissociates at the surface of the melt.



Inside the pore gas has been precipitated in the shape of diatomic molecules. By aid of the general gas law the number of kmoles of the gas can be calculated:

$$n_{\text{G}_2} = \frac{p_{\text{gas}} \cdot V_{\text{pore}}}{RT} \quad (8)$$

where

$p_{\text{gas}}$  = pressure inside the pore

$V_{\text{pore}}$  = volume of the pore

$T$  = temperature of the melt.

Equation (7) is combined with equation (8), which gives the number of kmoles in the pore as a function of the radius of the pore.

$$n_G = 2n_{G_2} = \frac{2 \left( p_a + \frac{2\sigma}{r} \right) \cdot \frac{4\pi r^3}{3}}{RT} \quad (9)$$

If we derive equation (9) with respect to time we get a relation between the increase of the number of kmoles per unit time in the pore and the increase of the pore radius per unit time:

$$\frac{dn_G}{dt} = \frac{8\pi}{3R} \cdot \frac{(3p_a r^2 + 4\sigma r)}{T} \cdot \frac{\partial r}{\partial t} \quad (10)$$

We can get another expression of the increase of the number of gas atoms (kmole) per unit time by considering the diffusion of gas atoms from the melt into the pore. Fick's first law will be applied. The increase of mass per unit time is proportional to the area and the concentration gradient.

Fick's first law:

$$\frac{dm}{dt} = -DA \frac{dc}{dy}$$

The growth rate of the pore is proportional to the concentration gradient:

$$\frac{dn_G}{dt} = -D_G \cdot 4\pi r^2 \cdot -\frac{x_G^L - x_G^p}{V_m r} \quad (11)$$

where

- $n_G$  = number of kmoles of gas in the pore
- $V_m$  = molar volume (has to be added because the concentrations are measured in mole fractions and the mass in kmoles)
- $D_G$  = diffusion constant of the solved gas atoms in the melt
- $x_G^L$  = original mole fraction (kmoles) of the gas in the melt
- $x_G^p$  = mole fraction (kmoles) of gas in the pore.

We combine equations (10) and (11) and solve  $\frac{\partial r}{\partial t}$

$$\frac{\partial r}{\partial t} = \frac{3RD_G T}{2V_m} \cdot \frac{x_G^L - x_G^p}{3p_a r + 4\sigma} \quad (12)$$

This is the desired expression of the growth rate of spherical pores as a function of time. It is necessary to know the concen-

tration of the gas in the melt and in the pore if the formula is to be useful.

$x_G^L$  is the original mole fraction of the gas in the melt.  $x_G^p$  is strongly temperature dependent (compare equation (5) on page 10) and can be calculated from the expression

$$x_G^p = \sqrt{\frac{p_a + \frac{2\sigma}{r}}{p_o}} \cdot A \cdot e^{-\frac{B}{T}} \quad (13)$$

where  $A$  and  $B$  are constants and  $p_o$  is the standard pressure of the gas, normally 1 atm. The root expression originates from application of Sievert's rule because the pressure is not 1 atm but has the value given in the numerator within the root expression.

### **Elongated Pores**

Elongated pores are formed when the original gas concentration in the melt is smaller than the solubility of the gas, i. e. smaller than the eutectic concentration of the solved gas atoms (figure 6 on page 17). This type of pores is nucleated at the solidification front and grows successively during the solidification process.

As a concrete example of pore growth we choose a steel melt, which can solve 8 ppm hydrogen in the solid phase and 27 ppm hydrogen at 1 atm (figure 8 on page 21) in the liquid phase.

Figure 8b shows the concentration of  $\underline{H}$  in the melt ( $c_{\underline{H}}^L$ ) respectively in the solid phase ( $c_{\underline{H}}^s$ ) as a function of the distance from the solidification front (100 % solid phase at  $y = y_{\text{end}}$ ).

The initial concentration of  $\underline{H}$  in the melt equals 10 ppm (point A in figure 8 b). It increases then slightly in the area ahead of the tips of the dendrites. At point B ( $y_{\text{front}}$ ) solid phase with a low concentration of  $\underline{H}$  starts to precipitate ( $c_{\underline{H}}^s = 3$  ppm). The more solid phase is precipitated, the higher will the hydrogen concentration in the remaining melt be.

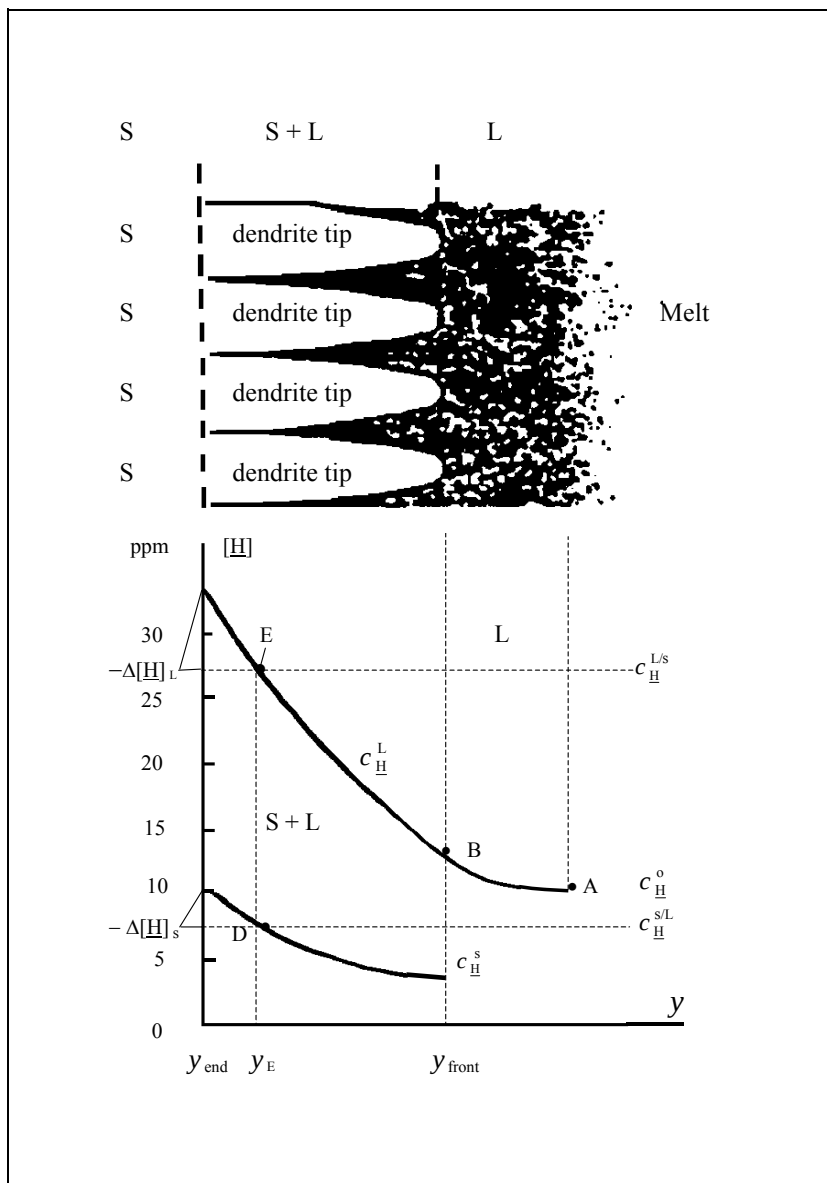


Figure 8.

a) Upper figure.

Sketch of the melt and the two-phase region between the two solidification fronts.

b) Lower figure.

Principal sketch of the solubility of  $\underline{H}$  of the melt and of the solid phase within the two-phase region close to the solidification front.

The concentration difference  $\Delta[\underline{H}]$  between the supersaturated melt respectively the supersaturated solid phase and the  $\underline{H}$ -concentration in the melt respectively in the solid phase, close to the pores, are the driving forces of the diffusion of  $\underline{H}$ -atoms from the melt respectively the solid phase to the pores (figure 9).

The underlined  $\underline{H}$  is the symbol for hydrogen atoms, which are solved in the melt.

S = solid phase

S + L = solid + liquid phase

L = liquid phase.

The ratio of the concentrations  $c_{\underline{H}}^s / c_{\underline{H}}^L$  is constant, which means that the hydrogen concentration in the solid phase also increases with decreasing distance to the solid front  $y_{\text{end}}$ . The lower dotted line corresponds to the saturation value of the hydrogen concentration in the solid phase (6 ppm).

At distances closer to the end of the two-phase region than  $y_E$  the solid phase is supersaturated. At  $y = y_{\text{end}}$  the hydrogen concentration is 10 ppm and equal to the original hydrogen concentration in the melt as no hydrogen has disappeared.

The upper dotted line corresponds to the saturation value 27 ppm of the  $\underline{H}$  concentration in the melt. At distances closer to  $y = y_{\text{end}}$  than point E ( $y_E$ ) the melt is supersaturated. At the end of the solidification front ( $y = y_{\text{end}}$ ) the hydrogen concentration in the last solidified melt has increased to 33 ppm.

It is evident from the analysis above that there are theoretical possibilities for precipitation of hydrogen in the steel melt. Often higher concentrations are required than the theoretical super-saturation limits for spontaneous pore formation. In the present case this condition is fulfilled. The nucleation of pores is very difficult and may occur by heterogeneous nucleation. When a pore is nucleated  $\underline{H}$ -atoms from the supersaturated solid or liquid will diffuse into the pore. A common situation is that the pore grows with the same rate as the solidification front.

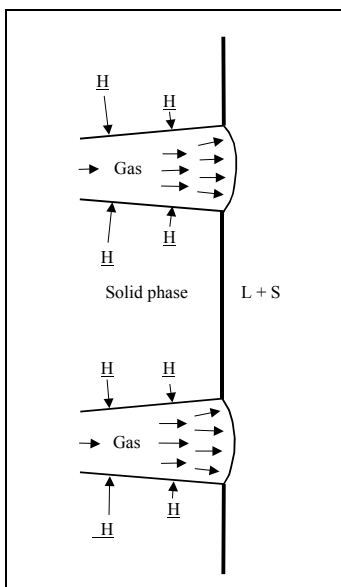
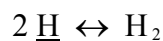


Figure 9 shows a principle sketch of pores, which grow with the same rate as the solidification front. If the pressure of the hydrogen pore corresponds to 1 atm outer pressure it will grow by influx of  $\underline{H}$  from the supersaturated melt and likewise from the solid phase (figure 9). The influx occurs by diffusion in both cases. At the interface there is equilibrium between the solved  $\underline{H}$ -atoms and gaseous hydrogen.



The growth rate, i. e. the velocity of the solidification front, and the hydrogen concentrations control the pore growth. If the solidification front moves slowly the pore volume increases more rapidly than in the case when its velocity is large. The higher the hydrogen concentration is the more rapidly will the volume of the pore grow.

ch of the growth  
pores in the solid  
olidification front  
o  $y_{\text{end}}$  in figure  
sion of  $\underline{\text{H}}$ -atoms  
is not indicated

At low growth rate of the solidification front and/or at high supersaturations the growth of the pore may be so fast that it loses the contact with the solidification front and flows away into the melt ahead of the solidification front.

The sizes, shapes and distributions of the pores in various cases depend strongly on the conditions in each special case. Figure 10 gives some examples of different alternatives.

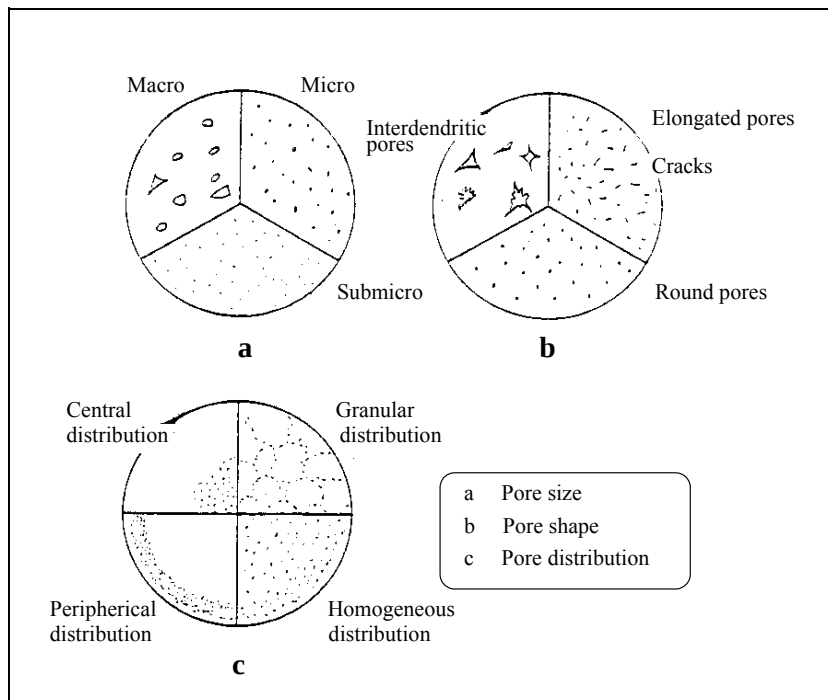


Figure 10.  
Examples of different types of  
pore structure.

## 9.4 Precipitation of Inclusions in Metal Melts

Slag inclusions are chemical compounds of a metal and non-metal components or only non-metal components. Examples are metal oxides, nitrides and sulphides, which are hard to dissolve in metal melts.

Before casting metals are molten and melt-treated in a furnace or a ladle. The metal may react with the fireproof covering of the ladle, which results in a change of the composition of the melt. Fireproof materials often consist of oxides. During the

casting and solidification processes fireproof components may precipitate.

Chemical reactions can be analysed in terms of thermodynamics, i. e. in terms of chemical potentials or by aid of free energy functions. We will choose the latter method and shortly discuss metallurgical reactions in terms of free energy of the reacting system.

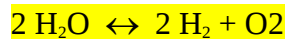
The carbon content in the steel is reduced in the basic oxygen furnace by oxidising carbon by aid of pure  $O_2$ -gas and an iron oxide,  $Fe_2O_3$ . The remaining oxygen is removed by aid of deoxidation agents (page 61) like Si and Al or removed as  $CO_2$  in a subsequent vacuum degassing process. The molten steel is then ready for casting.

During the casting operation gases might precipitate as pores. *Hydrogen, nitrogen, oxygen and carbon monoxide* are the gases, which give a risk of gas precipitation in steel and iron alloys.

During the deoxidising operations slag inclusions are formed and float around in the melt and follow it during the casting process. Below we will discuss different types of slag inclusions during the casting and solidification processes. The slag particles consist of either sulphides or oxides.

### 9.7.1 Hydrogen in Steel and Iron Alloys

Hydrogen is generated by dissociation of water vapour and by a chemical reaction between water vapour in the mould and dissolved carbon in the steel melt



At the surface of the melt dissociation of hydrogen occurs



After the reaction the monoatomic hydrogen diffuses into the steel melt and stays there as a solution. The hydrogen concentration can be calculated by aid of Sievert's law.

$$[H] = const \cdot \sqrt{p_{H_2}} \quad (29)$$

### Sources of Hydrogen in Iron Melts

Liquid steel absorbs hydrogen very easily. The major source of hydrogen in steel is water vapour and the major source of water vapour is the water vapour in the atmosphere in contact with the steel bath. Other sources are water included in slag making and lining materials.

The concentration of  $H$  in a steel melt depends on the external partial hydrogen pressure of the surrounding atmosphere, but also of the concentration of  $O$  in the melt. The solubility product limits the hydrogen concentration and relates it to the oxygen concentration:

$$[H]^2 \cdot [O] = \text{Const} \quad (30)$$

The value of the constant varies with temperature.

Figure 22 on page 51 illustrates the magnitude of the pressure of water vapour in various environments and at different circumstances and the resulting hydrogen concentrations in the steel melt.

At low temperatures the partial pressure of water vapour is very low. The air is dry during the winter. The opposite is true during the summer near the sea with the exception of deserts. Humid air has a much higher partial pressure than dry winter air. Burning oil furnaces give a higher water vapour pressure than the partial pressure during an average summer day as organic compounds often contain much hydrogen.

Figure 22 demonstrates the strong influence of the oxygen concentration. It is urgent to keep the oxygen concentration as low as possible in steel (see figure 1 on page 3) and deoxidation agents are added to the melt (page 61). The decrease of the oxygen concentration leads to an increased hydrogen concentration as a consequence of the solubility product of water. The slopes of all the curves are negative. The curves are straight lines because the scales on both co-ordinate axes are logarithmic.

### Hydrogen Solubility in Steel

Figure 23 shows the solubility of hydrogen in iron as a function of temperature. It can be seen that

- the solubility of hydrogen is much larger in the melt than in the solid phase
- the solubility of hydrogen depends on the type of iron phase. The solubility is larger for austenite ( $\gamma$ ) than for ferrite ( $\delta$ )
- the solubility of hydrogen increases with temperature.

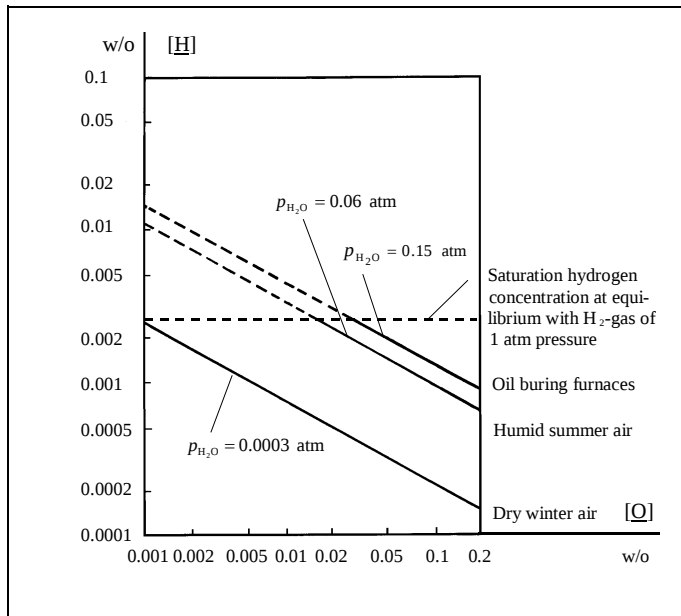


Figure 22.

Hydrogen concentration in a steel melt as a function of the oxygen concentration in the melt with the partial pressure of water vapour of the surroundings as a parameter.

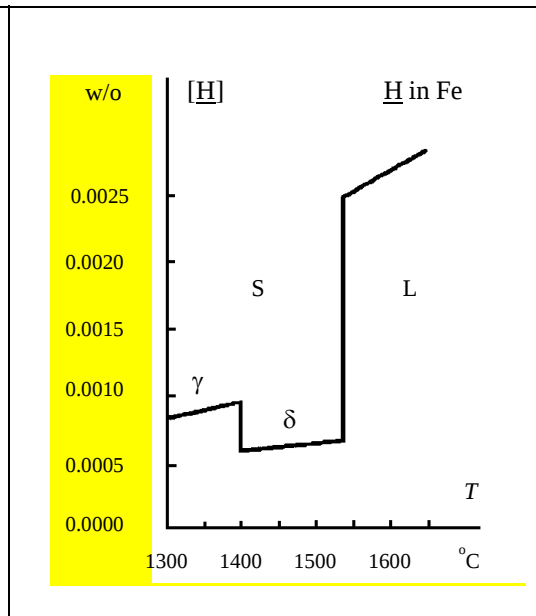


Figure 23.

The solubility of hydrogen in iron at equilibrium with 1 atm  $H_2$  as a function of temperature.

The melt normally contains less hydrogen than the solubility value. It means that a large amount solid phase can form before hydrogen starts to precipitate. We can calculate the fraction of the melt, which can solidify before gas precipitation starts, provided that the supersaturation phenomena can be neglected.

Consider a small volume, which is representative for an alloy with dendritic solidification. We disregard all sorts of macro-segregation and assume that the average composition within the volume is constant and equal to the original hydrogen concentration of the alloy, the mole fraction  $x^0$  or the concentration in weight per cent  $c^0$ . We also assume that the considered volume has a uniform temperature and that each phase has a uniform composition. The last assumption would be unrealistic for alloying metals but is realistic for gases, which have high diffusion rates.

We call the instantaneous hydrogen concentration of the melt  $x^L$  or  $c^L$  and that of the solid phase  $x^S$  or  $c^S$ . At equilibrium between the two phases within the volume in question we have

$$\frac{x^s}{x^L} = k_x \quad \text{or} \quad \frac{c^s}{c^L} = k_c \quad (31)$$

where the partition constant  $k_x$  can be derived from the phase diagram in figure 24.

The assumption we have made allows us to use the lever rule (equation (15) on page 15 in chapter 7) to calculate the instantaneous hydrogen concentration in the melt. The fraction of solidification  $f$ , expressed as the fraction solid phase, will thus be

$$f = \frac{x^L - x^o}{x^L - x^s} = \frac{x^L - x^o}{x^L(1 - k_x)} \quad (32)$$

We solve  $x^L$  in equation (32) and get

$$x^L = \frac{x^o}{1 - f(1 - k_x)} \quad (33)$$

If the concentration is expressed in w/o we get

$$c^L = \frac{c^o}{1 - f(1 - k_c)} \quad (34)$$

It is important to notice that the definition of  $k$  is different, and depends on the unit of concentration, mole fraction or weight per cent.  $c^o$  and  $k_c$  are known quantities. If the solubility limit of hydrogen in the melt is known, it is possible to calculate at what fraction of solid phase the limit will be exceeded and risk of gas precipitation exists. It is convenient to make the calculation graphically.

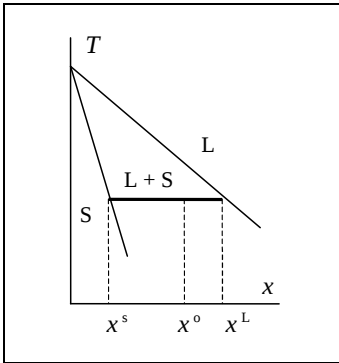


Figure 24.  
Phase diagram of Fe-H.

### Example 5.

A specific sort of steel contains 12 ppm  $\underline{\text{H}}$  and is able to solve 24 ppm in the melt and 10 ppm in the solid phase at the pressure 1 atm.

- Calculate the hydrogen concentration in the melt as a function of the solidification fraction during the solidification process and illustrate the function graphically.
- At what solidification fraction will the solubility limit be exceeded at a pressure of 1 atm?

**Solution:**

- a) From the text we get  $k = 10/24$  and  $x^0 = 12$  ppm. These values are introduced into equation (33):

$$x^L = \frac{x^0}{1 - f_x(1 - k_x)} = \frac{12}{1 - \frac{14 f_x}{24}} \quad (1')$$

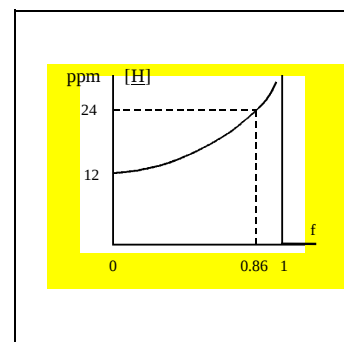
Some  $f$ -values are chosen arbitrarily and the corresponding  $x^L$ -values are calculated. The curve is plotted in a diagram. It shows the concentration of  $\underline{H}$  in a steel melt as a function of the solidification fraction

- b) From the diagram we can read that the solubility limit is reached at the solidification fraction 0.86.

**Answer:**

- a) See equation (1') above and the corresponding diagram in the margin.
- b) The solidification fraction is 0.86 at the solubility limit of hydrogen.

| $f$ | $c^L$ (ppm) |
|-----|-------------|
| 0   | 12          |
| 0.2 | 13.6        |
| 0.3 | 14.5        |
| 0.4 | 15.6        |
| 0.5 | 16.9        |
| 0.6 | 18.5        |
| 0.7 | 20.3        |
| 0.8 | 22.5        |
| 0.9 | 25.3        |
| 1   | 28.8        |

**Removal of Hydrogen in Steel and Iron Alloys**

In order to reduce the risk of precipitation of hydrogen the partial pressure of hydrogen in contact with the melt should be lowered as much as possible.

The melt must be carefully protected against contact with water vapour. Lining materials have to be preheated before contact with a steel melt. Hygroscopic materials, such as lime and other slag forming materials, must be preheated and then protected from contact with water before they get into contact with a steel melt.

Due to Sievert's law, i. e. the equilibrium between dissolved  $\underline{H}$ -atoms and  $H_2$ -gas in the surrounding atmosphere,  $[\underline{H}]$  decreases

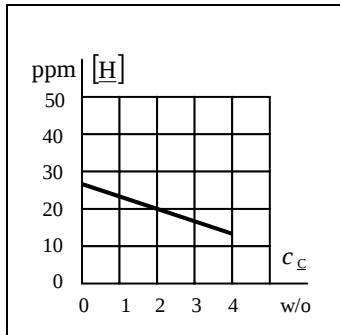


Figure 25.

The solubility of hydrogen in Fe-C alloys at 1550 °C as a function of its  $C$ -concentration.

or disappears when the hydrogen pressure is reduced or becomes practically zero.

High oxygen concentration reduces the dissociation of water vapour and consequently also the possibility of dissolving hydrogen. Deoxidation in a later stage of the production is favourable.

Another suitable method is to let some inert gas, for example Ar, bubble through the melt.  $H$  diffuses into the carrier gas rapidly enough to make the method useful in practice. In 20 minutes the  $H$ -concentration can be lowered from 4 ppm to 1.6 ppm in an Fe + 4.5%C melt of 11 tons if it is treated with bubbling Ar of the speed 0.005 m<sup>3</sup>/s.

The solubility of hydrogen in Fe-C alloys is also lowered by their carbon concentrations as is seen in figure 25.

### 9.7.2 Nitrogen in Steel and Iron Alloys

Nitrogen is in most cases an undesired gas in connection with casting. Precipitation of nitrides deteriorates the elastic properties of the casting. Nitrogen follows Sievert's law

$$[N] = \text{const} \cdot \sqrt{p_{N_2}} \quad (35)$$

and its partial pressure in air is large.

The solubility of nitrogen in iron at 1 atm at various temperatures and structures of the solid phase is seen in figure 26. The figure shows that the solubility of nitrogen in the *melt* at equilibrium with the atmosphere increases with increasing temperature. The solution process is endothermic in this case. This is in agreement with figure 3 and the statements on page 11.

For *austenite* the solution process is exothermic and the solubility of nitrogen in austenite at equilibrium with the atmosphere decreases with increasing temperature (figure 26). This is in agreement with equation (6) and figure 4 on page 11.

In analogy with hydrogen the difference in solubility of nitrogen between the melt and the solid phase at the melting point temperature is very large. The risk of nitrogen precipitation is reduced, like in the case of hydrogen, because the  $C$ -concentration in the steel lowers the solubility of  $N$  considerably

(figure 27). Addition of Si reduces the solubility of nitrogen still further.

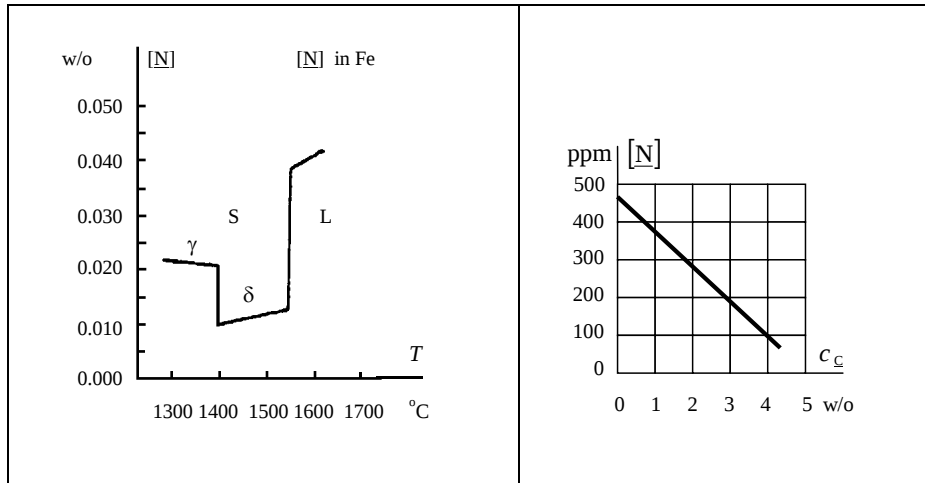


Figure 26.

Solubility of nitrogen in iron at a pressure of 1 atm as a function of temperature.

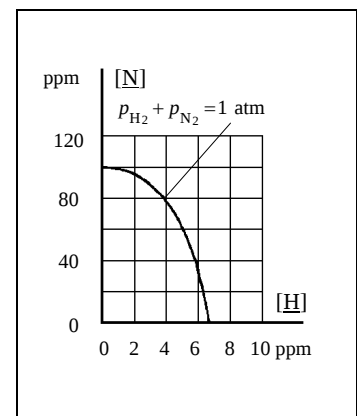
Figure 27.

The solubility of nitrogen in Fe-C alloys at 1550 °C as a function of the C-concentration.

The  $\underline{N}$ -concentration decreases more in the melt than in austenite with increasing  $\underline{C}$ -concentration. At high  $\underline{C}$ -concentrations the solubility of  $\underline{N}$  is higher in austenite than in the melt. This reduces the risk of nitrogen pore formation considerably in high-carbon steel alloys. It is not zero, though, due to micro-segregation in the melt at the end of the solidification process.

The solubilities of  $\underline{H}$  and  $\underline{N}$  in steel melts are not independent of each other. As soon as the added gas pressures equals 1 atm there is a risk of pore precipitation. It can be seen from figure 28 that there is a risk of precipitation of  $\text{N}_2$  and  $\text{H}_2$  already at 80 ppm  $\underline{N}$  + 4 ppm  $\underline{H}$ . In the area above the curve pore precipitation is likely. In the area below the curve the solubility limits are smaller than the maximum values and no pore precipitation occurs.

However, it is not possible to be quite sure because of the effect of high  $\underline{C}$ -concentration described above.



There is a distinction between low nitrogen steel with  $< 0.02\%$   $N_2$  and high nitrogen steel with  $> 0.04\%$   $N_2$ . In certain cases nitrogen is added on purpose to give some special quality of the alloy, for example to stabilise austenite instead of ferrite structure. Another example follows below.

| Alloy | % C  | %Cr | %Ni | %Si | %N  |
|-------|------|-----|-----|-----|-----|
| 1     | 0.15 | 25  | 20  | 2.0 | 0.0 |
| 2     | 0.15 | 22  | 13  | 1.4 | 0.2 |

The properties of the two alloys 1 and 2 described in the table are fairly equal. The lower one is apparently cheaper in terms of raw material costs because the nickel concentration can be lowered at an increased nitrogen concentration.

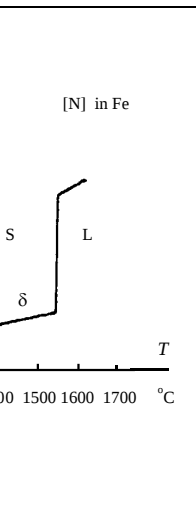
### Removal of Nitrogen in Steel- and Iron Alloys

Flushing with argon cannot eliminate nitrogen to any striking extent in reasonable time. Some other and better ways to reduce the risk of nitrogen precipitation are

- 1 The alloy composition may be changed in such a way that austenite ( $\gamma$ -iron) instead of ferrite ( $\delta$ -iron) is formed during the solidification process. In this case the difference in solubility between melt and solid phase will be smaller.

Figure 28.

Relation between concentrations of  $H$  and  $N$  of the solidification of the alloy Fe+3.8%

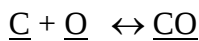


nitrogen in iron  
of 1 atm as a  
temperature.

- 2 The nitrogen solubility in the solid phase may be increased by addition of other metals.
- 3 Addition of surface-active substances like O (0.03 %) and S (0.03 %), which cover most of the surface of the melt, may have the consequence that the dissociation of the nitrogen in the air becomes very slow.
- 4 The reaction rate may be lowered by addition of small amounts of P, Pb, Bi and Te (0.50 ppm of the last mentioned metals give a decrease of  $[N]$  with 80 % respectively 90 %).
- 5 Addition of preferably Ti or Zr, but also Al, may give precipitation of nitride instead of  $N_2$ -pores, which is easier to handle.

### 9.7.3 Oxygen and Carbon Monoxide in Steel and Iron Alloys

Both  $\underline{C}$  and  $\underline{O}$  are present in all steel and iron melts. When the steel solidifies both  $\underline{C}$  and  $\underline{O}$  concentrate in the melt and the saturation limit may be exceeded.



Guldberg-Waage's law is applied on the CO-gas

$$\frac{c_{\underline{C}} \cdot c_{\underline{O}}}{p_{CO}} = \text{const} \quad (36)$$

This equilibrium is of great importance at the production process of steel from iron ore.

The temperature dependence of the constant is rather weak and an average value, valid for the middle of the temperature interval 1500 °C-1550°C can often be used.

$$c_{\underline{C}}^L \cdot c_{\underline{O}}^L = 0.0019 \cdot p_{CO} \quad (\text{w/o and atm}) \quad (37)$$

If the temperature dependence is considered the following empirical relation is often used:

$$c_{\underline{C}}^L \cdot c_{\underline{O}}^L = p_{\text{CO}} \cdot e^{-\frac{2960}{T} - 4.75} \quad (\text{w/o, atm and K}) \quad (38)$$

We will examine the conditions for CO-precipitation in an interdendritic region. The advance of the solidification process is represented by the fraction  $f$  of solid material.

The same reasoning as was applied on hydrogen in a steel melt (pages 51-52) can be used here and the same equations are valid. The following values of the partition coefficients are valid:

$$k_{\underline{O}} = c_{\underline{O}}^s / c_{\underline{O}}^L = 0.054 \quad (39)$$

$$k_{\underline{C}} = c_{\underline{C}}^s / c_{\underline{C}}^L = 0.020 \quad (40)$$

By aid of equation (34) on page 52 we can calculate how the relative concentrations of  $\underline{O}$  and  $\underline{C}$  in the interdendritic melt increase during the solidification process as a function of the solidification fraction  $f$ .

$$y_{\underline{O}} = c_{\underline{O}}^L / c_{\underline{O}}^o = \frac{1}{1-f \cdot (1-0.054)} \quad (41)$$

$$y_{\underline{C}} = c_{\underline{C}}^L / c_{\underline{C}}^o = \frac{1}{1-f \cdot (1-0.020)} \quad (42)$$

In the same way as in example 5 on page 52 arbitrary values of  $f$  can be chosen and the two curves can be drawn. In this case another curve has been drawn, which represent the product of the two curves, i. e.

$$y_{\underline{CO}} = y_{\underline{C}} \cdot y_{\underline{O}} = \frac{c_{\underline{C}}^L \cdot c_{\underline{O}}^L}{c_{\underline{C}}^o \cdot c_{\underline{O}}^o} \quad (43)$$

The curves are plotted in figure 29. The upper curve represents  $\underline{CO}$ .

#### Example 6.

Find the solidification fraction at which gas precipitation of CO can be expected to start in an interdendritic region for a steel melt with 0.050 w/o  $\underline{C}$  and 0.0040 w/o  $\underline{O}$ . The effects of possible nucleation difficulties and the hydrostatic pressure can be neglected.

**Solution:**

The composition of the steel is given in the text.

$$c_{\underline{C}}^o \cdot c_{\underline{O}}^o = 0.050 \cdot 0.0040 = 0.000200 \text{ (w/o)}^2$$

Equation (19) gives the saturation value at  $p_{CO} = 1 \text{ atm}$ :

$$c_{\underline{C}}^L \cdot c_{\underline{O}}^L = 0.0019 \cdot 1 \text{ (w/o)}^2$$

The value of  $f$ , which corresponds to

$$y_{CO} = \frac{c_{\underline{C}}^L \cdot c_{\underline{O}}^L}{c_{\underline{C}}^o \cdot c_{\underline{O}}^o} = \frac{0.0019}{0.00020} \approx 10$$

is read from figure 29. We get  $f = 0.78$ .

**Answer:** There is a risk of gas precipitation if  $f \geq 0.78$ .

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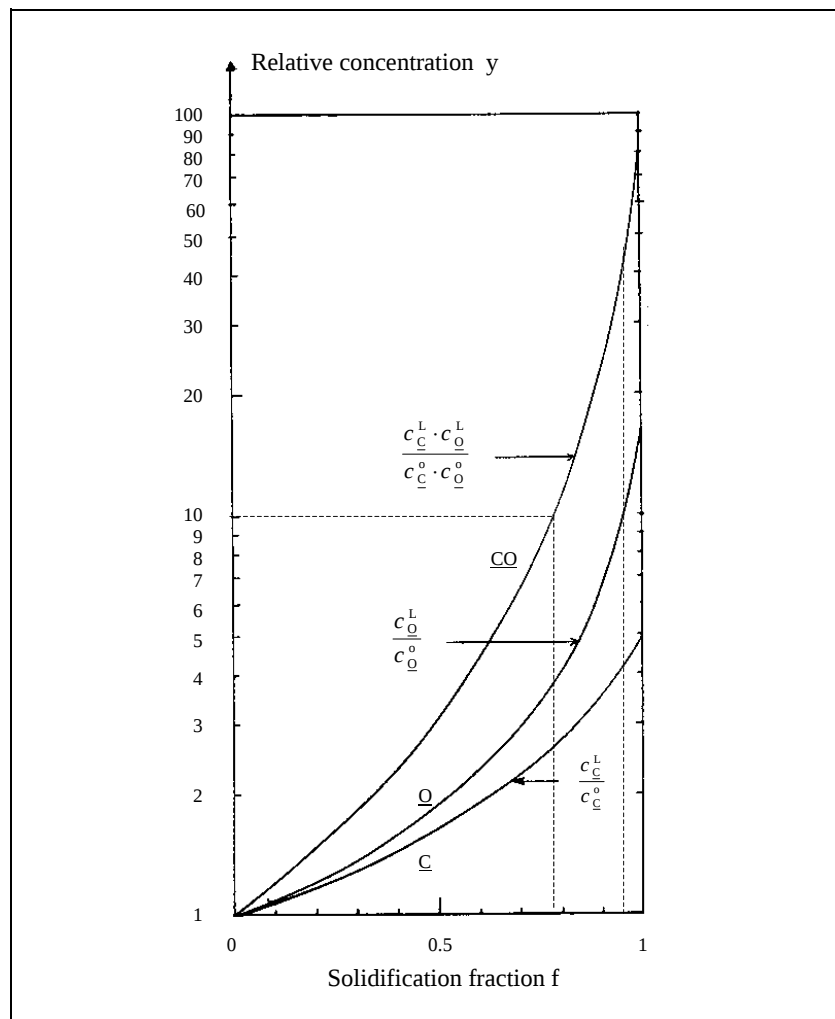
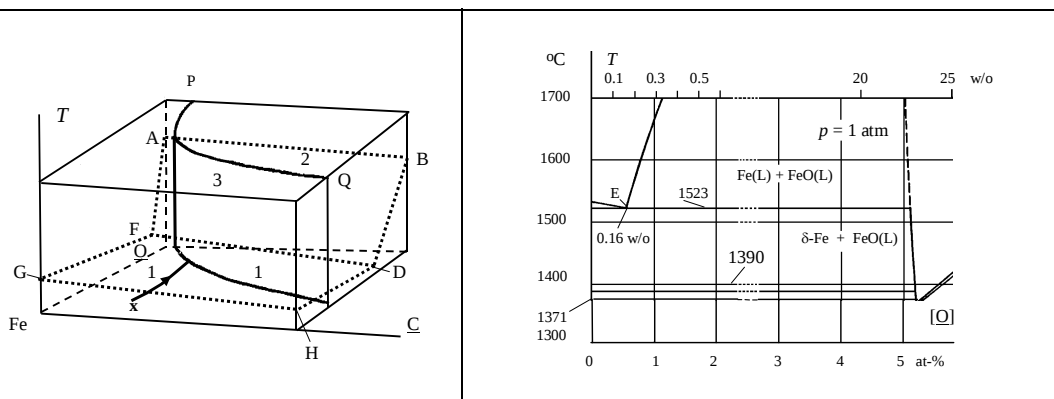


Figure 29.  
Segregation of  $\underline{C}$

For understanding of the interaction between  $\underline{C}$  and  $\underline{O}$  in the melt we have to analyse the ternary system Fe-O-C. The phase diagrams of the binary systems Fe-O and Fe-C are shown on next page respectively page 47 in chapter 7. These two-phase diagrams are included in two vertical planes of the Fe-O-C system in figure 30.

The liquidus line in the Fe-O system is represented by a liquidus surface in the ternary Fe-O-C system, marked by 2 in figure 30, and describes the precipitation of FeO. The precipitation of CO is described by equation (36) on page 57. This equation, applied at a CO pressure of 1 atm, represents the surface marked by 3 in figure 30.



Left figure.  
 e diagram of the  
 em.  
 surface of ferrite  
 GHD.  
 surface of FeO  
 DF  
 surface of CO-gas  
 surface): Vertical  
 surface including  
 PQ.  
 axes: Fe-Q, Fe-C  
 Right figure.  
 n of Fe-O.

Figure 30 a can be used to discuss the possibilities of CO- and FeO-precipitation. The phase diagram shows that formation of FeO may occur if the C-concentration is low enough and the melt reaches point E in figure 30 b. The condition for the FeO precipitation will be analysed in example 7.

### Example 7.

What demand has to be made on the carbon concentration in a steel melt with 0.016 w/o oxygen in order to avoid gas precipitation of CO in favour of formation of FeO? FeO is formed at an oxygen concentration of 0.155 w/o at 1500 °C.

### Solution:

FeO is formed at the solidification fraction, which corresponds to

$$y_{\underline{O}} = \frac{c_{\underline{O}}^L}{c_{\underline{O}}^o} = \frac{0.155}{0.016} \approx 10 \quad (1')$$

Using the Q-curve in figure 29 we find that  $y_{\underline{O}} = 10$  is valid for  $f = 0.95$ .

Simultaneously the  $y_{\underline{CO}}$ -value must be lower than the value, which corresponds to CO-saturation. This value can be read from the CO-curve in figure 29 for  $f_c = 0.95$ .

$$y_{\underline{CO}} = \frac{c_{\underline{C}}^L \cdot c_{\underline{O}}^L}{c_{\underline{C}}^o \cdot c_{\underline{O}}^o} = 40 \quad (2')$$

In addition the equilibrium equation of CO (equation (37) on page 57) is valid at  $p_{\text{CO}} = 1 \text{ atm}$

$$c_{\underline{\text{C}}}^{\text{L}} \cdot c_{\underline{\text{O}}}^{\text{L}} = 0.0019 \cdot 1 \text{ (w/o)}^2 \quad (3')$$

Combining equations (2'), (3') and (4') we get

$$c_{\underline{\text{C}}}^{\text{O}} = \frac{c_{\underline{\text{C}}}^{\text{L}} \cdot c_{\underline{\text{O}}}^{\text{L}}}{y_{\underline{\text{CO}}} \cdot c_{\underline{\text{O}}}^{\text{O}}} = \frac{0.0019}{40 \cdot 0.016} = 0.0030 \text{ w/o} \quad (4')$$

**Answer:** The carbon concentration must be  $< 0.003 \text{ w/o}$ .

---

### Removal of Oxygen in Steel and Iron Alloys

Lowering of the  $\underline{\text{O}}$ -concentration in steel is done by so-called *deoxidation*. Small amounts of a substance  $\text{M}_b$  is added to the molten steel  $\text{M}_a$  which contains  $\underline{\text{O}}$ . The metal  $\text{M}_b$  must fulfil the following conditions:

- 1  $\text{M}_b\text{O}$  must be more stable than  $\text{M}_a\text{O}$ .
- 2  $\text{M}_b\text{O}$  must be easy to separate from the melt.
- 3  $\text{M}_a$  must not be influenced negatively by remaining  $\text{M}_b$  in the melt.
- 4 Remaining  $\underline{\text{O}}$  must not deteriorate the properties of the cast metal alloy.

In steel melts Si, Mg, and Al are used as deoxidation agents.

#### 9.7.4 Gas Precipitation in Rimming Iron Ingots

Killed steel is compact while rimming steel contains pores of various extents. The difference is due to gas precipitation during the solidification process. The main component of the gas is *carbon monoxide*. The gas precipitation, which occurs when rimming steel solidifies, thus depends mainly on its concentration of carbon and oxygen.

An ingot of rimming steel is illustrated in figure 31. It solidifies roughly in the following way:

Already at or immediately after casting there is a violent gas precipitation, which initiates movements in the steel bath. The motion occurs upwards at the periphery and downwards at the

centre. The mould cools the steel melt relatively strongly and a certain nucleation occurs at the mould wall. These primarily formed nuclei are carried into the melt due to the strong motion in the steel bath. There they float in the melt, grow, split up and form new nuclei. Due to the great number of new crystals, which are formed and grow in this way, the melt becomes viscous.

During this process a crystal zone, the so-called rimmed zone, is developed at the surface of the ingot. The zone consists of relatively solid material and is formed due to the strong cooling from the mould.



The zone consists of many small crystals, which initially have been free and then have been added to what reminds of a solidification front. The motion in the bath mainly determines the appearance of the rim zone.

At slow or low gas precipitation *rim bubbles* are formed. Their length direction is perpendicular to the mould wall due to the strong cooling from the mould and the solid material. At strong gas precipitation or violent bath movement the rim zone may be practically free from bubbles. At transition from the first to the last case the gas bubbles first disappear from the upper part of the rim zone. With increased gas precipitation the bubbles also disappear in the lower part of the zone.

The reason why no bubbles are formed in the rim zone at violent gas precipitation is probably that floating crystals and gas bubbles efficiently wash the solidification front. The result is that the gas, which has been formed at the very front, is carried away and gets no hold at the front. This happens obviously most easily in the upper part of the ingot, where more numerous and larger bubbles pass the solidification front.

of a rimming

During the formation of the rim zone an edge is formed at the upper surface of the ingot, a so-called rim (figure 32). This edge grows towards the centre. At last a crust of solid material is formed, which covers the whole upper surface of the ingot.

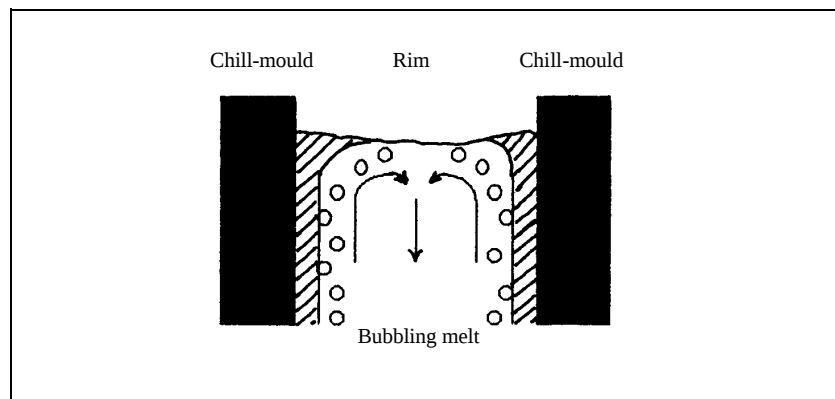


Figure 32.  
Formation of a rim

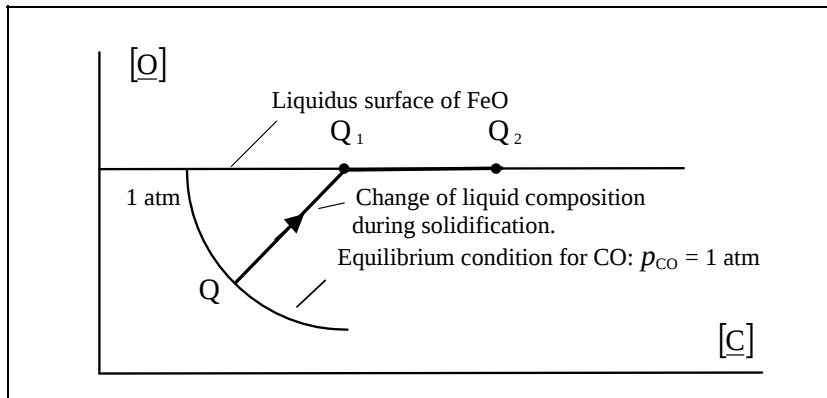
When the crust has been formed the pressure in the centre of the melt increases and the gas precipitation stops. In some cases the pressure can be high enough to break the crust and the gas precipitation may start again. The result will be that a new violent movement in the bath starts at the centre of the ingot.

The more violent this motion is the fewer bubbles are formed inside the ingot. The positions of the so-called *core bubbles* are seen in figure 31. A strong bath motion causes the bubble-free zone between the rim and core bubbles at the moment when the top crust or the rim breaks. Core bubbles are formed when the bath motion or gas precipitation decreases once more. When the rim has been thick enough to resist the pressure from the inner parts of the ingot the rest of it solidifies. The inner parts of the ingot generally consist of a viscous mess of melt and crystals. The melt may contain some gas pores, which may grow somewhat during the solidification process. These pores are the so-called nucleation bubbles.

By aid of the phase diagram of Fe-C-O it is possible to explain what happens when the rims are formed and the pressure increases. Figure 33 shows a projection on the bottom plane of the liquidus surface, marked with 1 in figure 30 a on page 60.

We assume that the pressure is high enough to prevent gas precipitation. In a steel melt with a composition corresponding to point Q  $\delta$ -iron is precipitated. If the pressure is 1 atm precipitation of CO-gas starts simultaneously. During the continued solidification the composition of the solid phase is

process in a rim-  
when gas precipi-  
ent. has been illustra-  
diagram of the  
O. a projection of the  
diagram in figure



changed due to precipitation of  $\delta$ -iron at the same time as the temperature decreases. The change in composition is described by some curve  $QQ_1$ . We know nothing of the shape of this curve and have drawn it as a straight line.

When the composition has been changed so much that the point  $Q_1$  is reached simultaneous precipitation of  $\delta$ -iron and FeO occurs. The composition of the melt will continue to change along the monotectic line  $Q_1Q_2$ . This explains why oxide precipitations are found in the centre of a rimming ingot.

If the steel releases very large quantities of gas at the beginning of the casting process a so-called bootleg is formed (figure 34 a). When the mould is filled the molten steel contains a great amount of gas bubbles. When they have disappeared the upper surface of the melt in the mould sinks and the result is that the upper part of the ingot consists of a thin shell.

If the gas precipitation is somewhat weaker ingots characteristic for rimming steel is obtained (figure 34 b and c). The amount of rim bubbles may be very small and occur for example as a few bubbles close to the bottom if the gas precipitation is extensive enough.

If the gas precipitation is still weaker bubbles are formed in the majority of the rim zone. Due to this bubble formation the level of the steel rises in the mould. The steel is said to *ferment* (figure 34 d).

In many cases an artificial rim is created a certain time after the casting by blowing gas on the surface to cool it or by covering the surface with a steel plate. The bubbles in the rim stops and a central pore is formed.

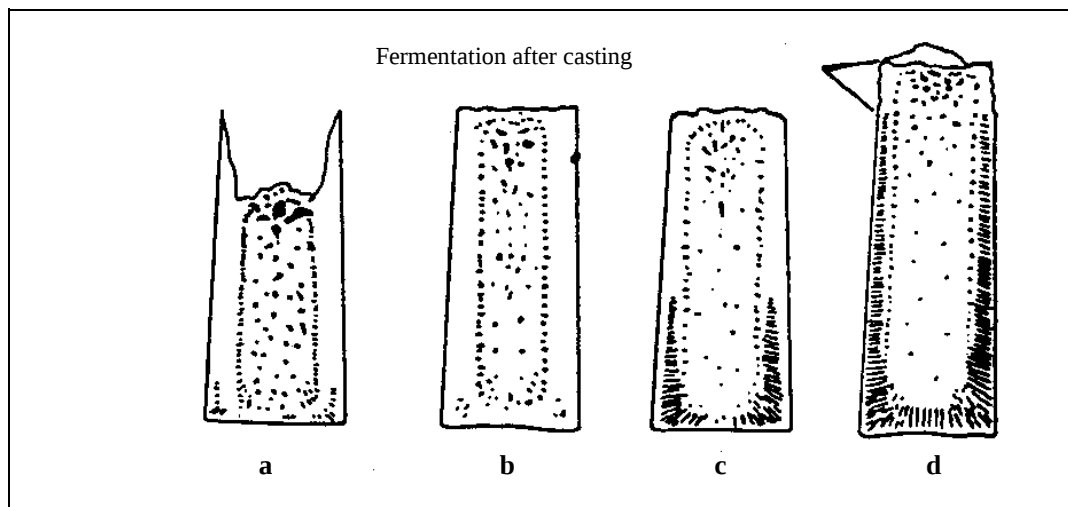


Figure 34 a.  
Very strong gas precipitation. Boot leg ingot. Rim zone nearly free from bubbles.

Figure 34 b.  
Strong gas precipitation. Rim zone nearly free from bubbles.

Figure 34 c.  
No particularly strong gas precipitation. Bubbles in the lower part of the ingot.

Figure 34 d.  
Rather weak gas precipitation. Bubbles in the rim zone. Steel ferments during solidification.

The gas precipitation rate influences not only the vertical position of the rim bubbles but also the thickness of the skin, i. e. the thickness of the part of the ingot, situated between the rim zone and the mould (figure 31). This part is of great importance for the properties of the ingot surface. Bubbles too close to the surface may form during the following heating and cause severe surface errors. It is generally very difficult to predict what oxygen concentration the steel should have to obtain the best possible structure. It is important to consider not only the carbon and oxygen concentrations but also its silicon and aluminium concentrations.

It is also important to adjust the casting rate correctly. If a rimming steel fills the mould rapidly the gas precipitation would start at the top of the ingot where the hydrostatic pressure is zero. Rim bubbles would form close to the surface because there is no motion in the bath.

At a properly adjusted casting rate the increasing ferrostatic pressure, caused by the increasing height of the iron column close to the bottom, will delay the gas precipitation so much that no gas bubbles are formed close to the bottom. When the casting is finished the solidification in the lower part causes a supersatu-

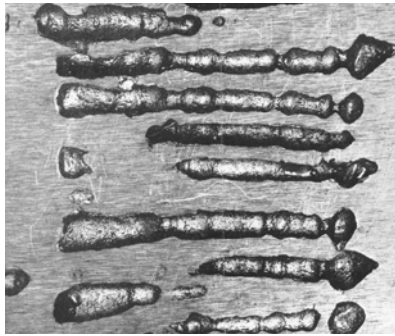


Figure 35.  
Example of rim pores with periodical contractions and expansions. This appearance is seen in the lower part of the ingot.

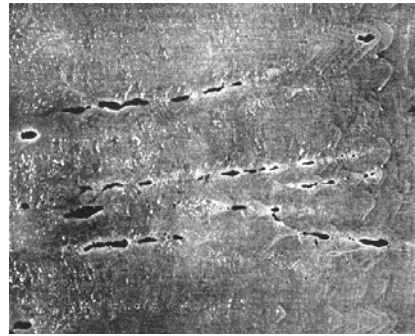


Figure 36.  
Rim pores in the upper part of the ingot. This appearance is common in the upper parts of the ingot. The melt penetrates the pore walls when the rim pores are formed.

ration of  $\underline{\text{CO}}$  in the melt inside the shell, large enough to compensate the higher pressure. For this reason gas precipitation occurs approximately simultaneously from the bottom to the top of the ingot in the ideal case.

The shapes of the rim pores are different in the lower and upper parts of the ingot. In the lower part the pores have the shape of a rotation volume with periodical contractions and expansions formed by release of bubbles as is shown in figures 35. In the upper part the rim pores are less well developed. They look like pearl rows as is seen in figure 36. Each pore is surrounded by a V-shaped segregation pattern.

The formation of these two morphologies is assumed to be as follows. The growth mechanism of rim pores is the same as the growth process of hydrogen pores, described in figure 9 on page 22. In this case it is  $\underline{\text{C}}$  and  $\underline{\text{O}}$ , instead of  $\underline{\text{H}}$ , which diffuse to the pore surfaces. The process is assumed to occur in steps:

- 1 A pore is formed at the solidification front (figure 37 a).
- 2 The solidification front advances and  $\underline{\text{C}}$  and  $\underline{\text{O}}$ , concentrated to the interdendritic regions, diffuse to the pores. The pore grows faster than the solidification front (figure 37 b).
- 3 When the pore has reached a certain critical size, which depends on the flow rate in the melt, some of the gas in the pore is released and forms a rising bubble, which is unlaced (figures 37 b and 37 c<sub>1</sub>). If the flow in the melt is slow or

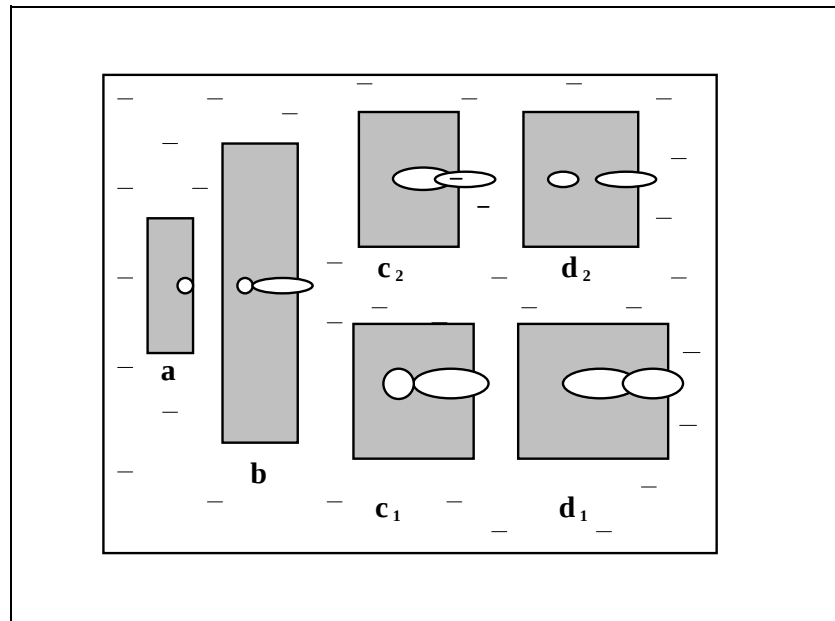


Figure 37.

Formation of rim channels.

Upper part of an ingot:  $a - b - c_2 - d_2$ .

Lower part of an ingot:  $a - b - c_1 - d_1$ .

The solid phase is represented by dark squares.

The schematic diagram in figure 37  $c_2$  means that the solid phase partly penetrates the pore and reduces its size. In figure 37  $d_1$  the solid phase unclases it into two parts.

missing, there will be enough gas left to form a new pore, smaller than the earlier one due to loss of gas. The steel layer, which solidifies next, starts to unclase the pore (figures 37  $c_1$  and 37  $d_1$ ).

- 4 A new expansion replaces the unclase process due to continued gas precipitation (figure 37  $d_1$ ). Figure 35 shows an example of this type of rim bubbles.
- 5 If the melt, which passes a growing pore, has a *high* flow rate, gas may be carried away and the melt may enter the oval pore wall (figure 37  $c_2$ ). When next layer of steel solidifies at the oval wall an indentation is formed or a total separation (figure 37  $d_2$ ) occurs. The outer bubble grows. Next time gas is released from the pore the melt enters the pore again and the process is repeated. Figure 36 shows an example of this type of rim pores.

The process, described in step 5, is common in the upper part of the ingot. The gas precipitation is faster there, due to the lower ferrostatic pressure. Large pores from the lower part of the ingot pass through the melt and bring the small upper pores up to the ingot surface. The amount of gas becomes big enough to cause