

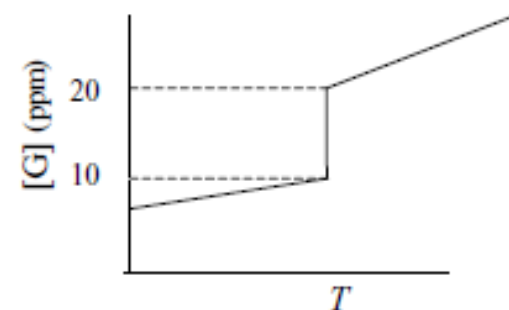
Problem 9.1

9.1 In cast metal alloys one can often find three kinds of pores:

1. Interdendritic pores, often called shrinkage pores.
2. Spherical pores, which are either randomly distributed in the material or more often concentrated close to the upper surface.
3. Elongated pores in the columnar crystal zone.

Explain the mechanism of formation of the three types and mention likely gas concentrations in the melt, required for formation of the three types (see the diagram below).

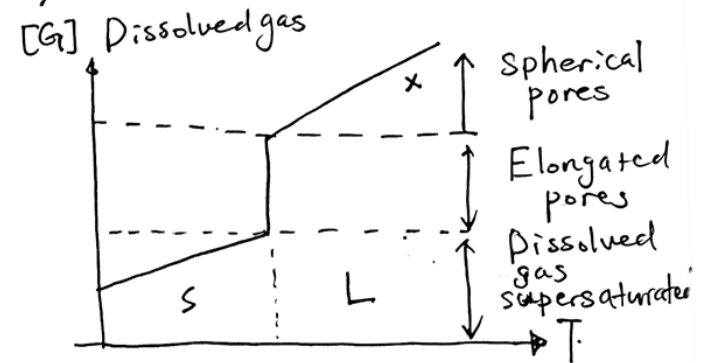
Hint B20



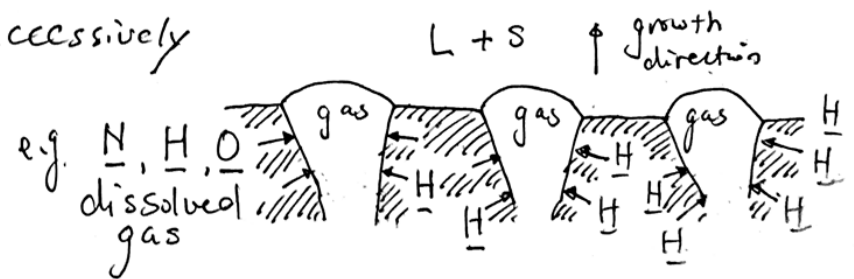
(9.1)

① Interdendritic pores form in the last solidified region between the dendrite arms, since it is difficult for melt to transport through the narrow channels and compensate for solidification shrinkage. These pores are usually thorny and uneven in shape. The pore cavities are usually vacuumed.

② Spherical pores form when the gas concentration exceeds the solubility of the gas in the liquid. The pores usually have smooth surfaces and more rounded shapes.



③ Elongated pores form when the original gas concentration in the melt is lower than the solubility of the gas, (i.e. lower than the "eutectic" concentration). This type of pore nucleate at the solidification front and grows successively during the solidification process.



Problem 9.3

In the production of copper alloys, hydrogen and oxygen are dissolved in the melt. This often results in pore formation when the metal is cast and allowed to solidify. The pores are formed by precipitation of water vapour. Calculate the maximum hydrogen concentration in a Cu melt with 0.01 wt-% $\underline{\text{O}}$, which can be present from the beginning, if formation of water vapour during the solidification process is to be avoided. Cu_2O will precipitate instead of water vapour.

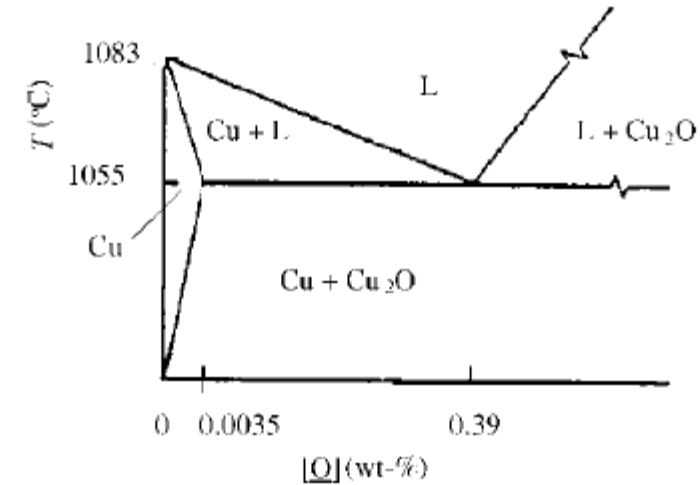
Calculate the maximum hydrogen concentration in a Cu melt with 0.01 wt-% $\underline{\text{O}}$, which can be present from the beginning, if formation of water vapour during the solidification process is to be avoided. Cu_2O will precipitate instead of water vapour.

The solubility product of the reaction $2\underline{\text{H}} + \underline{\text{O}} \rightleftharpoons \text{H}_2\text{O}$ is:

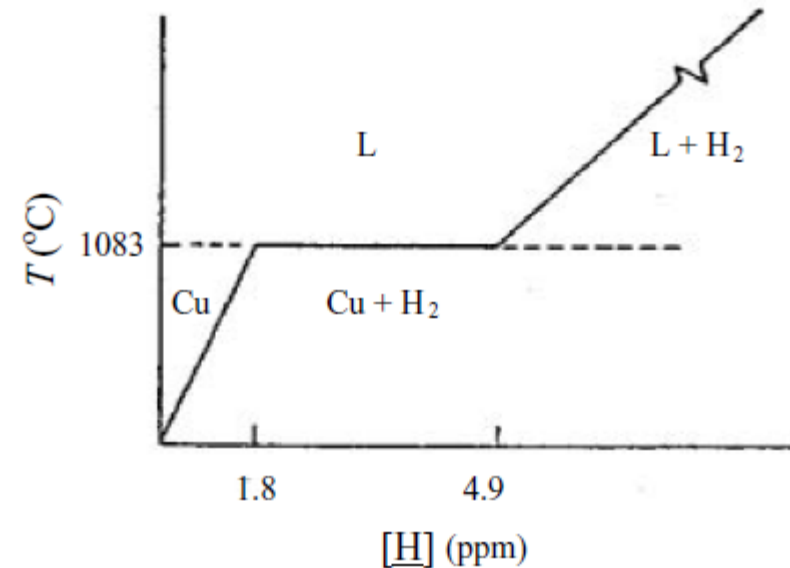
$$c_{\underline{\text{H}}}^2 c_{\underline{\text{O}}} = 2 \times 10^{-11} p_{\text{H}_2\text{O}}$$

where $p_{\text{H}_2\text{O}}$ is measured in atm and $c_{\underline{\text{H}}}$ and $c_{\underline{\text{O}}}$ are expressed in wt-%.

The binary phase diagrams of the systems Cu–O and Cu–H are given above.



Simplified phase diagram of the system Cu–O at 1 atm O_2 .

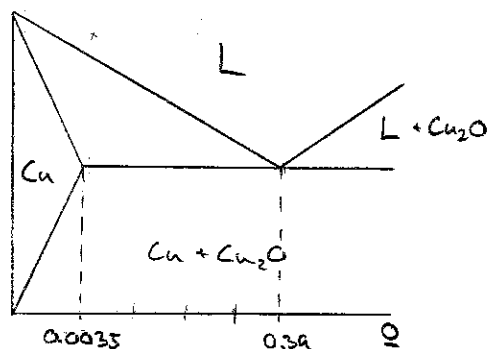


Simplified phase diagram of the system Cu–H at 1 atm H_2 .

9.3) During copper casting, if there is dissolved hydrogen and oxygen in the melt, water vapor can form pores.

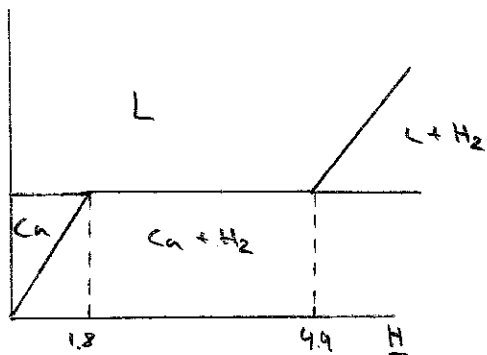
What is the maximum dissolved hydrogen we can have to avoid pore formation?

We have Cu melt with 0.01 wt-% O.



The solubility product of $2H + O \rightarrow H_2O$ is:

$$C_H^2 C_O = 2 \cdot 10^{-11} P_{H_2O} \quad (1)$$



Diffusion of O and H is fast so the Lever rule is valid.

$$C_H^L = \frac{C_H^0}{1-f(1-k_H)} \quad (2) \quad , \quad C_O^L = \frac{C_O^0}{1-f(1-k_O)} \quad (3)$$

C_H^0 is what we are looking for!

k_H and k_O you get from phase diagram, $k_{port} = \frac{x^s}{x^L}$

$$k_H = \frac{1.8}{4.9} = 0.37 \quad , \quad k_O = \frac{0.0035}{0.39} = 0.009$$

Get f from (3), $C_O^L = 0.39$

$$0.39 = \frac{0.01}{1-f(1-0.009)} \Rightarrow f = 0.983$$

From (1) we can get C_H^L

$$C_H^L = \left(\frac{2 \cdot 10^{-11} P_{H_2O}}{C_O^L} \right)^{1/2} \left\{ \begin{array}{l} \text{at } p=1 \text{ atm} \\ \text{there is risk} \\ \text{for vapor formation} \end{array} \right\}$$

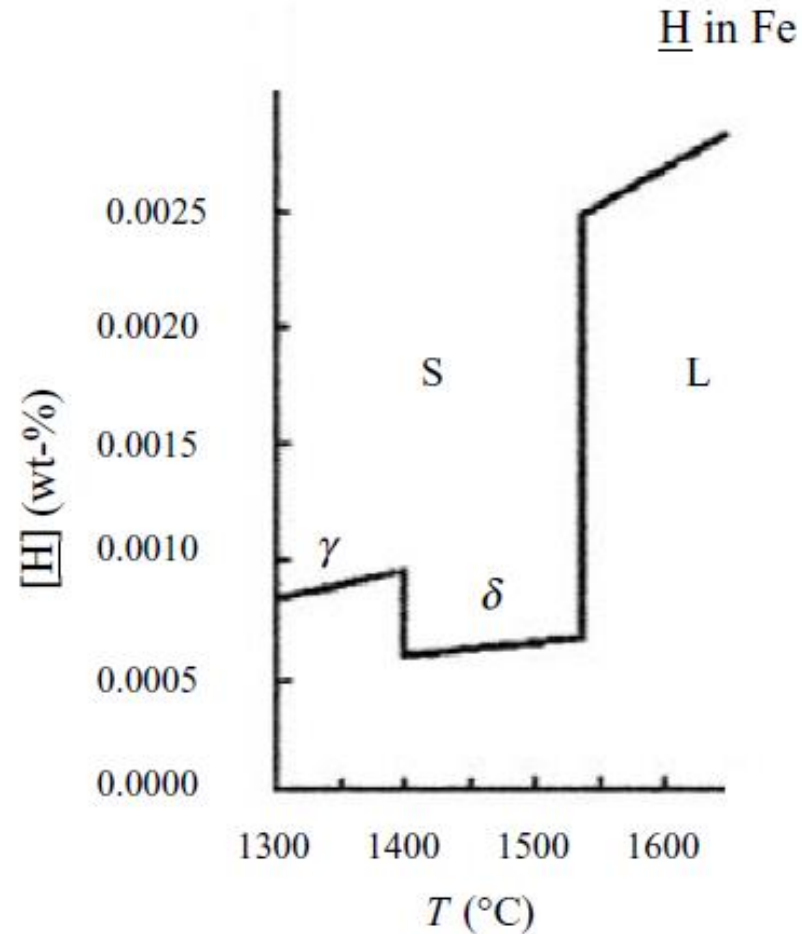
$$C_H^L = \left(\frac{2 \cdot 10^{-11} \cdot 1}{0.39} \right)^{1/2} \quad \text{2p}$$

From (2) we can solve C_H^0

$$C_H^0 = C_H^L (1-f(1-k_H)) = \left(\frac{2 \cdot 10^{-11} \cdot 1}{0.39} \right)^{1/2} (1-0.983(1-0.37)) = 2.7 \cdot 10^{-6} \quad [\text{wt-\%}]$$

If we have 2.7 ppm H in the melt there is a risk of getting pores. 5p

Problem 9.5



9.5 At a steelworks, steel with 0.050 % C is cast. The gas precipitation during the solidification process of rimming steel is determined by the sum of the partial pressures of the dissolved gases.

Describe graphically how the oxygen and hydrogen concentrations have to vary to ensure that the gas precipitation starts immediately after the casting.

Hint B314

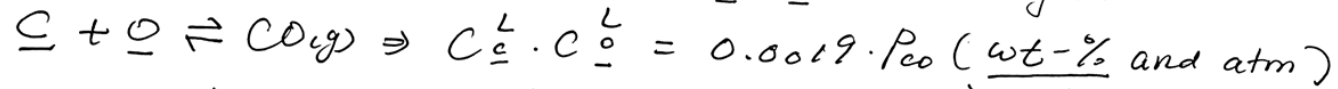
The equilibrium between the concentrations of O and C in the melt and the pressure of CO gas outside the melt is assumed to be described by the relation on page 280:

$$c_{\underline{C}}^L c_{\underline{O}}^L = 0.0019 p_{\text{CO}} \quad (\text{wt-\% and atm}).$$

The solubility of hydrogen in iron at equilibrium with 1 atm hydrogen as a function of temperature is illustrated in Figure 9.23 on page 277.

(9.5) Initial carbon content 0.05%. (wt-%)

The equilibrium between dissolved \underline{C} , \underline{O} and $CO_{(gas)}$



- ① Gas precipitation starts immediately after precipitation $\Rightarrow f_s = 0$ when precipitation of gas starts
- ② Precipitation of both hydrogen gases and CO gases are considered. When $P_{CO} + P_{H_2} \geq 1 \text{ atm}$. there are risks of gas precipitation. Limiting condition is $P_{CO} + P_{H_2} = 1 \text{ atm}$.
- ③ During solidification, dissolved gas could be segregated to the melt. The final dissolved gas concentration is related to the initial concentration in melt by lever rule, since H, C, O atoms are small (interstitials), they diffuse quickly in both liquid and solid phases, and is more easily to reach equilibrium concentrations indicated by phase diagram.

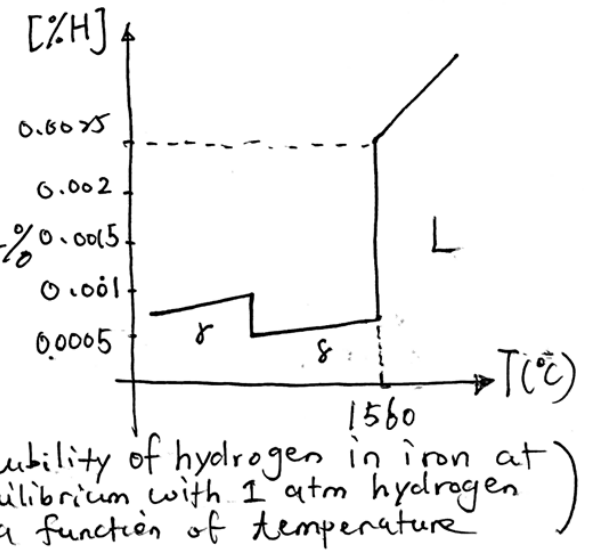
④ For hydrogen gas, we apply Sievert's law:

$$C_H^L = \text{constant} \times \sqrt{P_{H_2}}$$

To find the constant, we can use the point at melting point of iron: 1560°C , $[\%H] = 0.0025 \text{ wt-\%}$

$$\text{constant} = \frac{C_H^L}{\sqrt{P_{H_2}}} \Big|_{T=1560^\circ\text{C}} = \frac{0.0025}{\sqrt{1}} = 0.0025 \frac{\text{wt-\%}}{\sqrt{\text{atm}}}$$

The diagram is constructed at $P_{H_2} = 1 \text{ atm}$



(9.5) ④ (cont'd) Thus, we can write, in general

$$p_{H_2} = \left(\frac{C_H^L}{0.0025} \right)^2$$

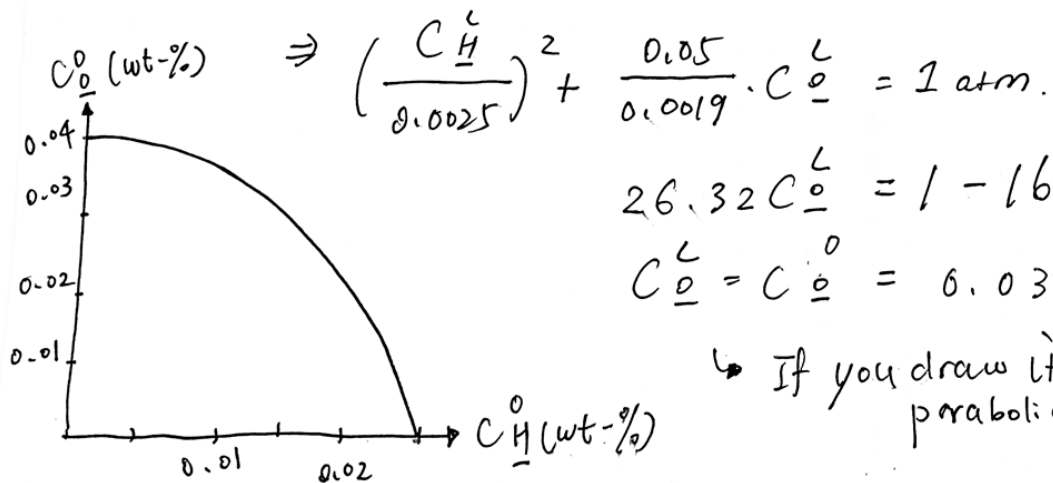
⑤ Since $f_s = 0$ when precipitation of both CO and H_2 gases begins:

$$C_C^L = \frac{C_C^0}{1 - f_s(1 - k_{part,C})}, \quad C_H^L = \frac{C_H^0}{1 - f_s(1 - k_{part,H})}, \quad C_O^L = \frac{C_O^0}{1 - f_s(1 - k_{part,O})}$$

$$f_s = 0, \text{ hence } C_H^L = C_H^0, C_C^L = C_C^0, C_O^L = C_O^0.$$

$$C_C^L = 0.05 \text{ wt-}\%, \quad p_{CO} = \frac{C_C^L \cdot C_O^L}{0.0019} = \frac{0.05}{0.0019} \cdot C_O^L.$$

$$⑥ \quad p_{H_2} + p_{CO} = 1 \text{ atm}$$



$$26.32 C_O^L = 1 - 160000 (C_H^L)^2 = 1 - 16000 (C_H^0)^2$$

$$C_O^L = C_O^0 = 0.038 - 607.9 (C_H^0)^2$$

↳ If you draw it out, it would be a parabolic shape like this!

Problem 9.6

9.6 A steel melt contains 0.040 wt-% O and 0.030 wt-% C. Manganese is added to the melt in order to prevent CO precipitation. The temperature of the melt is 1500 °C.

Calculate the minimum Mn concentration required to prevent formation of gaseous CO.

Hint B128

The partition coefficients of O and C are 0.054 and 0.20, respectively. The partition coefficient of Mn is 0.67. The solubility product of MnO in the melt can be written as:

$$K_{\text{MnO}} = c_{\text{Mn}}^{\text{L}} c_{\text{O}}^{\text{L}} = \exp \left[- \left(\frac{12760}{T} - 5.68 \right) \right] (\text{wt-}\%)^2$$

(9.6) Initial dissolved oxygen in steel melt = 0.04 wt-%
 " carbon " = 0.03 wt-%

Temperature of melt is 1500°C.

One wishes to have MnO precipitation instead of forming CO gas.
 Calculate minimum Mn content (initially in the melt!) that
 would prevent CO-gas formation

- ① $C_{\underline{C}}^L \cdot C_{\underline{O}}^L = 0.0019 \cdot p_{CO}$, when $p_{CO} = 1 \text{ atm}$ (Only consider CO precipitation and thus partial pressures of other gases need not be considered) there is risk of CO precipitation. $\Rightarrow C_{\underline{C}}^L \cdot C_{\underline{O}}^L = 0.0019 \cdot 1$. — (a)
- ② \underline{C} , \underline{O} are segregated into the melt during solidification, adopt lever rule, and plug their expressions into (a)

$$\left(\frac{C_{\underline{C}}^0}{1 - f_s(1 - k_{\text{part}, \underline{C}})} \right) \left(\frac{C_{\underline{O}}^0}{1 - f_s(1 - k_{\text{part}, \underline{O}})} \right) = 1.$$

\Rightarrow After solving for $f_s = 0.236$ (there are 2 solutions but $f_s \leq 1$)

$$k_{\text{part}, \underline{O}} = 0.054, \quad C_{\underline{O}}^0 = 0.03 \text{ wt-\%}$$

$$k_{\text{part}, \underline{C}} = 0.2, \quad C_{\underline{C}}^0 = 0.04 \text{ wt-\%}$$

(9.6) (cont'd)

③ The equilibrium solubility product of MnO:

$$K_{MnO} = C_{\underline{Mn}}^L \cdot C_{\underline{O}}^L = \exp\left[-\left(\frac{12760}{T} - 5.68\right)\right] \text{ (wt-%)}^2$$

$$\text{At } T = 1500^\circ\text{C}, K_{MnO} = 0.2187.$$

$K_{MnO} \geq 0.2187$ in order for MnO to form.

$$(Mn + O \rightleftharpoons MnO), C_{\underline{Mn}}^L \geq \frac{0.2187}{C_{\underline{O}}^L}$$

④ $C_{\underline{O}}^L$ could be calculated from f_s using lever rule.

But we need to think a bit what f_s value to use.

At $f_s = 0.236$ precipitation of CO gas is already starting to happen. We need to choose a solid fraction slightly lower, before CO precipitation starts. Let's take 0.22, for example.

$$\text{Then } C_{\underline{O}}^L = \frac{C_{\underline{O}}^0}{1 - (0.22)(1 - 0.054)} = \frac{0.04}{0.792} \doteq 0.0505 \text{ (wt-\%)}$$

$$\textcircled{5} C_{\underline{Mn}}^L \geq \frac{0.2187}{0.0505} \geq 4.3 \text{ (wt-\%)}$$

(9.6) (Cont'd)

- ⑥ But recall that Mn would also segregate into liquid during solidification. C_{Mn}^L at 1500°C , $f_s = 22\% = 4.3 \text{ wt-\%}$
This concentration has already been increased by microsegregation.
Recover the initial concentration of Mn by Scheil rule!
(No longer lever rule, since Mn is not an interstitial element)

$$\left(\frac{C_{Mn}^L}{C_{Mn}^0} \right)^{\frac{-1}{1 - k_{part, Mn}}} = f_L = 1 - f_s = 1 - 0.22 = 0.78$$

$$k_{part, Mn} = 0.67$$

$$\left(\frac{4.3}{C_{Mn}^0} \right)^{(-2.7)} = 0.78$$

$$C_{Mn}^0 \doteq 3.92 \text{ (wt-\%)}$$

At least 3.92 wt-% of Mn has to be present in the initial steel melt to prevent CO gas precipitation at 1500°C .