# Lecture 31: Principles of Solidification of Steel

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Key words: Solidification, planar growth, dendritic growth, casting, constitutional supercooling

**Preamble:**

Solidification is a phase transformation process in which liquid is transformed to solid when superheat and latent heat are removed. In this connection it is important to distinguish between solidification of pure metals and alloys. Pure metals solidify at constant temperature, whereas alloys solidify over a range of temperature. The following binary phase diagram illustrates the solidification in alloys:

**(a)**                                                                    **(b)**

*Fig. 31.1: Equilibrium phase diagram of a binary system (a) there is a complete solubility of the components in liquid and solid and (b) complete solubility of the components in the liquid phase and partial solubility in the solid phase.$\alpha$ and $\beta$ are solid solutions. Liquidus, solidus and solvus lines are shown by blue, green and black lines.*
***Vertical dotted line show the temperature changes that occurs during solidification of an alloy of composition $C_O$***

**Solidification variables**

Solidification behavior depends on parameters such as growth rate, temperature gradient, under cooling and alloy constitution. The temperature gradient (G) and growth rate (R) influence the solidification morphology and solidification substructure respectively.

Growth rate or solidification rate is the rate of advance of the solid/liquid interface into the liquid. The rate of movement of solidification front determines solute redistribution during solidification, scale of solidification substructure and the growth undercooling. Rapid solidification (faster movement of solid/liquid interface) minimizes the tendency of segregation of elements

Temperature gradients both in solid and liquid are important. Thermal gradient in liquid is more critical as compared with solid and is strongly affected by mixing in liquid. Temperature gradient in solid is diffusion dependent.

Undercooling is the difference between the liquid temperature of the alloy of nominal composition and the actual temperature.

The total undercooling $\Delta T$

$$\Delta T = \Delta T_{Th} + \Delta T_C + \Delta T_R + \Delta T_K.$$

$\Delta T_C = $ Constitutional undercooling

$\Delta T_k = $ Kinetic undercooling,

$\Delta T_R = $ Undercooling due to curvature at solid/liquid interface.

$\Delta T_{Th} = $ Thermal undercooling

$\Delta T_K$ and $\Delta T_R$ are usually negligible in casting. Thermal under cooling is required in solidification of pure metal where there is a significant nucleation barrier for liquid to solid transformation or when directional solidification is carried out at a lower rate where cellular structure forms. In the solidification of ingot and continuous casting where alloys are solidified, thermal undercooling is not of interest.

In solidification of alloy, the liquidus temperature of the melt is composition dependent. If the liquid composition deviates from the bulk composition, then the melt temperature may differ from the liquidus temperature of the overall alloy. The change in transformation temperature due to compositional effect is called constitution undercooling .

**Equilibrium solidification**

Equilibrium solidification of an alloy of any composition occurs when concentration of the liquid and that of solid follows the liquidus and solidus line of the phase diagram. Though it is an idealized concept, equilibrium solidification helps understanding the compositional changes that occur during solidification. Solidification of an alloy of a composition begins when the temperature reaches to the liquidus  line. Lowering of temperature changes the composition of elements both in liquid and solid phase. Composition of liquid and solid in the two phase region at any temperature is determined by a tie line. The tie line connects liquidus and solidus line at a temperature in the two phase region.

As equilibrium is assumed, at some temperature between $T_L$ (liquiudus temperature) and $T_S$ (solidus temperature)

$$C_S f_S + C_L f_2 = C_0 .$$

according to lever rule.  $f_l$ and $f_s$ are liquid and solid fraction respectively.

**Non equilibrium solidification**

Assumption of complete mixing does not prevail in actual solidification process. Diffusion in the solid is a slow process. Fluid flow in liquid will govern the concentration gradient of the solute in the liquid. Only faster mixing can minimize the concentration gradients, otherwise concentration gradients will be present in the liquid also. The presence of gradients in the solid and liquid during solidification makes the solidification process to deviate from the equilibrium. This means that in the actual solidification of alloy the concentration of solute in the liquid and solid rarely follows the liquidus and solidus lines of the respective phase diagram

Consider solidification of an alloy of composition $C_o$ at temperature T (see figure 31.1) in which there is no mixing in the solid but mixing in liquid is sufficiently large so as to have no composition gradient in the liquid. In other words liquid has a uniform composition at every stage of solidification. This can be illustrated by plotting concentration of solute Vs distance both in the solid and liquid

Figure 31,2: Concentration vs. distance profile in solid and liquid in one dimensional solidification

At the onset of solidification $C_L = C_O$ and $C_S = K_e\ C_O, where\ K_e$ is the partition coefficient, which is shown in the figure 31.2 at X=0. As the solidification proceeds the composition of liquid follows the liquidus line (see figure 31.1) but there will be gradient of solute since no mixing is assumed in solid. Figure 31.2 shows the variation of concentration of solute in the solid by a green line. In the figure $C_S^*$ is the interfacial concentration. As the solidification proceeds more and more solute will be rejected in the liquid but no gradient of the solute will be built-up in the liquid since complete mixing is assumed. Mass balance of solute when a small amount of solid $df_s$ forms and causes solute to increase in liquid $dC_L$

$$(C_L - C_S^*)\ df_s = f_L dC_L \qquad (1)$$

$$f_s + f_L = 1\ \text{and}\ K_e = \frac{C_S^*}{C_L} \qquad (2)$$

By 1 and 2 and integrating the equate on. $C_L = K(1 - f_s)^{K_e - 1}$ \hfill 3)

At begin of solidification $f_s = O$ and $C_L = C_O$ we get $K = C_O$, therefore we get

$$C_L = C_o(1 - f_s)^{K_e - 1} \qquad (4)$$

Equation 4 is Sheil's equation. $K_e$ is segregation coefficient. The role of partition coefficient of an element on solidification becomes clear from equation 4. At $K_e$ = 1, $\frac{C_L}{C_o}$ = 1 at all $f_s$. However, when $K_e$ is < 1, $\frac{C_L}{C_o}$ > 1for all values of $f_s$. The value of $K_e$ is given for some elements in iron in table.

| Element | $\delta$-iron | $\gamma$- iron |
|---------|---------------|----------------|
| C | 0.13 | 0.36 |
| S | 0.02 | 0.02 |
| P | 0.13 | 0.06 |
| O | 0.02 | 0.02 |
| N | 0.28 | 0.54 |
| H | 0.32 | 0.45 |
| Mn | 0.84 | 0.95 |
| Ti | 0.14 | 0.07 |

A more practical situation for solidification would be no mixing in either solid or in liquid. As the solid/liquid interface advances into the liquid, solute concentration builds up near the interface since no mixing in the liquid is assumed. There will be gradient of concentration in the liquid as illustrated in the figure 31.3.

**Figure 31.3: Concentration versus distance profile. In the figure $\delta$ is boundary layer thickness in which gradient of concentration persists**

**Microstructure development**

Nucleation and growth behavior, both determine development of microstructure in solidification of alloys. In alloys, nucleation of solid is not an issue since nucleating sites are present. Growth behavior is important.

*Growth behavior*

The solute redistribution at the solid/liquid interface governs the stability of the solidification front. The solidification begins with the planar solid/liquid interface .During growth the morphological stability of the planer solid/liquid interface is governed by thermal and composition gradients at the interface

**Figure 31.4: Constitutional super cooling during plane front alloy solidification, (a) concentration profile of the solute enriched layer ahead of the planar solidification front, (b) condition for a stable planar front solidification and (c) condition for unstable planar solid/liquid front.**

In figure 31.4a the variation in composition as a function of distance from the planar solid/liquid interface is depicted. By referring to the phase diagram such as one shown in figure 31.1b, a curve of equilibrium liquidus temperature versus distance from the S/L interface corresponding to figure 31.3a can be determined and such a curve is shown in figure 31.4b and c. (It must be noted that the equilibrium liquidus temperature depends on the solute; as the solute segregates, the liquidus temperature will be lower than when there is no segregation.)

Two conditions are possible based on the actual temperature distribution in the liquid imposed by temperature gradient arising from the heat flow conditions:

**Condition 1:** Actual thermal gradient is steeper than equilibrium liquidus temperature at the interface due to the compositional gradient. Under this condition any perturbation developed at the solid/interface will remelt and the planar front will remain stable.

**Condition 2:** If, however, actual thermal gradient is smaller, as shown in figure 31.4c, then the liquid ahead of the interface is supercooled since the actual temperature ahead of the interface is lower than the equilibrium liquidus temperature. Any perturbation of the plane front can no longer melt but instead will grow. Under these conditions the planar growth is no longer stable, this is due to constitutional super cooling and is responsible for cellular or dendrite solidification.

The compositional gradient for steady state plane front growth can be determined by mass balance consideration at the planar interface to

$$\frac{G_L}{R} < \frac{\Delta T_O}{D_L}$$
5)

In the equation 5 $\Delta t_O$ is the liquidus and solidus temperature difference at composition $C_O$, $D_L$ is the diffusion coefficient of solute in liquid, $G_L$ is thermal gradient in the liquid. Several parameters affect the conmstitutional supercooling. Decrease in the imposed temperature gradient increases the tendency for planar solidification.

In addition to gradient, growth rate is also important. For a given gradient,(G), the growth rate (R) also plays an important role in determining solidification structure. Higher temperature gradient and smaller growth rate I.e. when G/R is large plane front solidification prevails. As G/R decreases, plane front can no longer be stable. Low G/R favors dendridic solidification. Solutes with a smaller partition coefficient create conditions for instable plane front solidification, since more solute will be rejected in the liquid.

Thus as the extent of constitutional super cooling ahead of the solid/liquid interface increases, the morphology of interface changes from planar to cellular and to dendrite

**References:**

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