Iron Making and Steel Making
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Module – 10
Lecture – 47
Casting Fundamentals – Segregation

We are discussing casting fundamentals; we have already discussed heat transfer in casting and in this lecture we will be discussing the Segregation.

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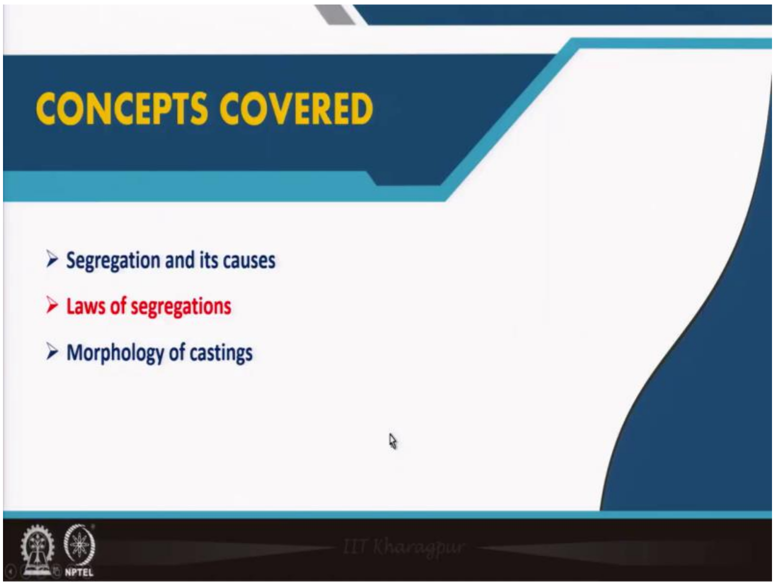

CONCEPTS COVERED

- Segregation and its causes
- Laws of segregations
- Morphology of castings

So, the topics covered will include causes of segregation and different laws of segregation for quantification of solute concentration in liquid with progress of solidification, and finally morphology of the casting during solidification.

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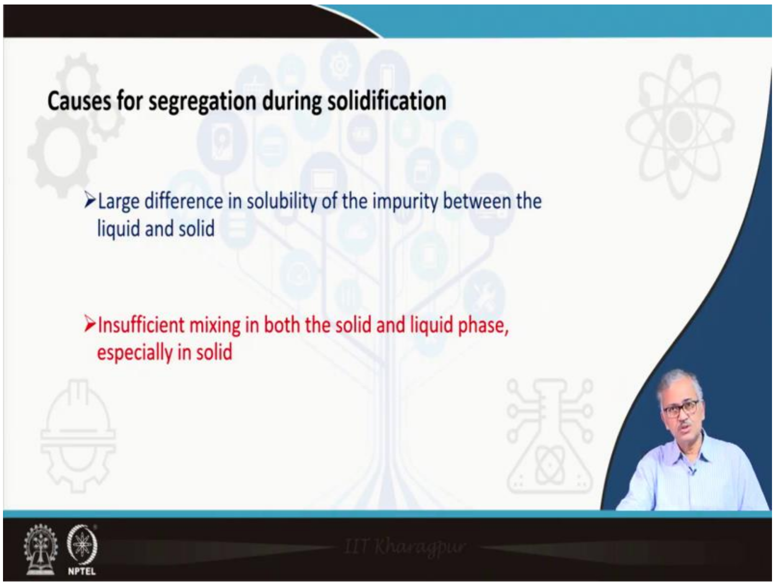

Causes for segregation during solidification

- Large difference in solubility of the impurity between the liquid and solid
- Insufficient mixing in both the solid and liquid phase, especially in solid

Segregation is defined as the deviation of solute concentration from is average concentration. In cast structure, where the solute concentration is higher than the average concentration, called the positive segregation and where the concentration is lower than the average concentration, is called the negative segregation.

There are two major factors that causes the segregation. The first factor is that the solute solubility in solid is much lower compared to that in liquid; in other words large amount of solutes could be accommodated in the liquid compared to its condensed state like solid. So, during solidification solute is rejected at the solid-liquid interface and with progress of solidification the liquid become richer and richer in impurities. So, the first liquid to solidify (at the skin of a solidifying ingot) will have the minimum composition and the last liquid to solidify (at the core of ingot) will have high solute concentration. Such solute partitioning at solid-liquid interface is determined by the equilibrium partition coefficient, Ke, defining a ratio of the concentration of solute in solid to that in the liquid under equilibrium.

And, the second factor is mixing in liquid as well as in solid. If solute after being rejected at the solid-liquid interface, cannot move either on the solid or on the liquid side, interface will get progressively enriched in solute and finally will solidify with large positive segregation. On the contrary if solute can disperse in liquid and solid from interface, the extent of interface enrichment will reduce and extent of segregation will be controlled.

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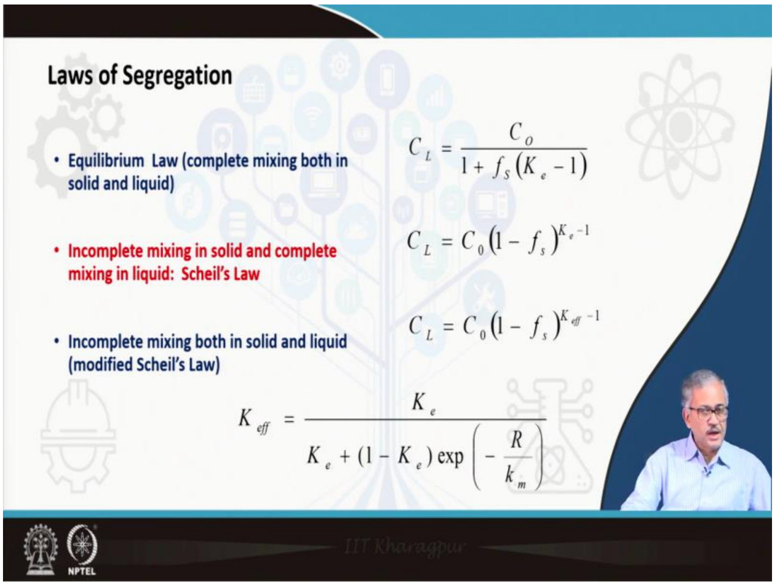

Laws of Segregation

- Equilibrium Law (complete mixing both in solid and liquid) $C_L = \dfrac{C_0}{1 + f_S(K_e - 1)}$
- Incomplete mixing in solid and complete mixing in liquid: Scheil's Law $C_L = C_0(1 - f_s)^{K_e - 1}$
- Incomplete mixing both in solid and liquid (modified Scheil's Law) $C_L = C_0(1 - f_s)^{K_{eff} - 1}$

$$K_{eff} = \frac{K_e}{K_e + (1 - K_e)\exp\left(-\dfrac{R}{k_m}\right)}$$

Now, let us discuss the laws of segregations, which are used to quantify the solute concentration in liquid during progress of solidification under different conditions of mixing in the solid, liquid, and in both.

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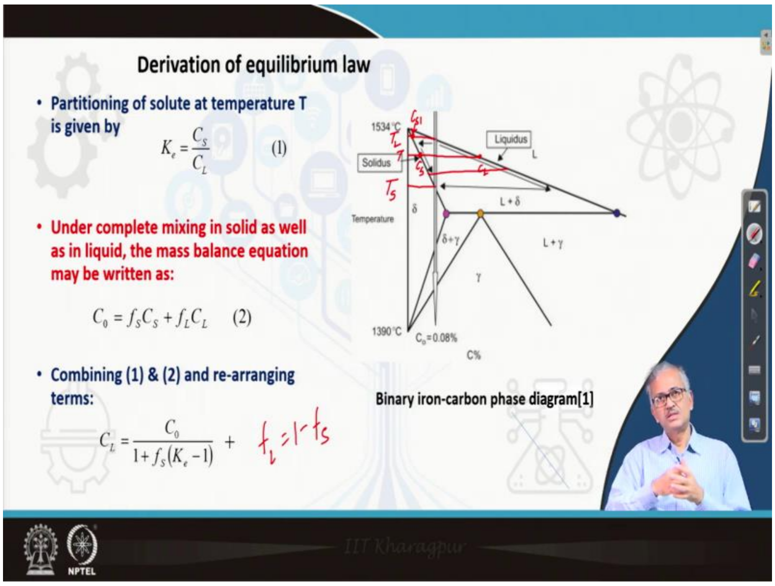

Derivation of equilibrium law

- Partitioning of solute at temperature T is given by

$$K_e = \frac{C_S}{C_L} \qquad (1)$$

- Under complete mixing in solid as well as in liquid, the mass balance equation may be written as:

$$C_0 = f_S C_S + f_L C_L \qquad (2)$$

- Combining (1) & (2) and re-arranging terms:

$$C_L = \frac{C_0}{1 + f_S(K_e - 1)} + \quad f_L = 1 - f_s$$

Binary iron-carbon phase diagram[1]

Equilibrium law: It consider complete mixing of solute in solid and liquid; in other words the rejected solute at the solid liquid interface, gets completely mixed up in the solid and liquid. At any instant of time during solidification, solute partitioning between solid and liquid takes place following equilibrium partitioning and there exists no concentration gradients in solid and liquid. Lever rule may be applied to estimate the solute concentration in liquid based on initial liquid composition (C_0), partition coefficient (K_e) and fractional solidification(f_s). Figure 47.1 shows the solidification of alloy of composition 0.08%C in a Fe-C binary alloy. The horizontal line ABC indicate the solute (C_S) and liquid composition(C_L) a temperature T, at points A and C, respectively. BC represents the solid fraction (F_S) and AB represents the liquid fraction(f_L) at temperature T.

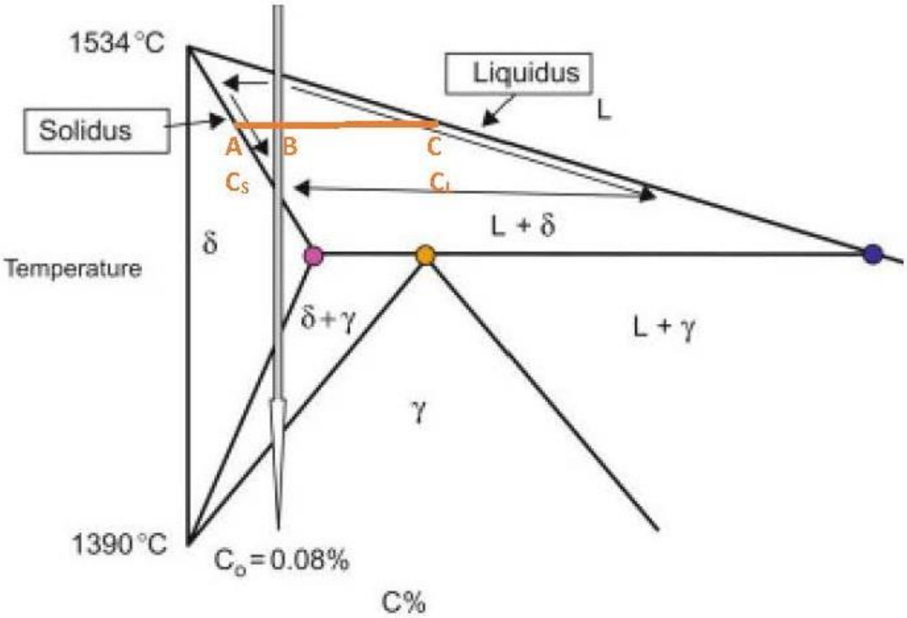

Figure 47.1: The binary Fe-C phase diagram showing the solidification of alloy of composition 0.08%C.

Applying the lever rule:

$$C_0 = f_S C_S + f_L C_L$$

(27.1)

Equilibrium partition coefficient may be defined as:

$$K_e = \frac{C_S}{C_L}$$

(47.2)

Combining equations (1) &(2) and rearranging terms:

$$C_L = \frac{C_0}{1 + f_S(K_e - 1)}$$

(47.3)

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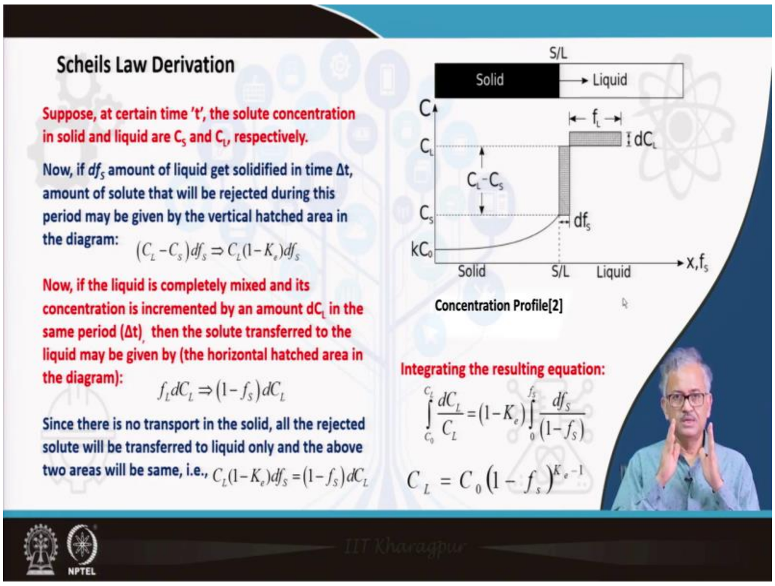

Scheils Law Derivation

Suppose, at certain time 't', the solute concentration in solid and liquid are C_S and C_L, respectively.

Now, if df_S amount of liquid get solidified in time Δt, amount of solute that will be rejected during this period may be given by the vertical hatched area in the diagram: $(C_L - C_S)df_S \Rightarrow C_L(1-K_e)df_S$

Now, if the liquid is completely mixed and its concentration is incremented by an amount dC_L in the same period (Δt), then the solute transferred to the liquid may be given by (the horizontal hatched area in the diagram): $f_L dC_L \Rightarrow (1-f_S)dC_L$

Since there is no transport in the solid, all the rejected solute will be transferred to liquid only and the above two areas will be same, i.e., $C_L(1-K_e)df_S = (1-f_S)dC_L$

Concentration Profile[2]

Integrating the resulting equation:

$$\int_{C_0}^{C_L} \frac{dC_L}{C_L} = (1-K_e)\int_0^{f_S} \frac{df_S}{(1-f_S)}$$

$$C_L = C_0(1-f_s)^{K_e - 1}$$

Scheil's law: This law is based on the assumption of complete mixing in liquid and no mixing in solid. In fact, solute cannot be mixed into the solid, because the mechanism of transport of solute from the interface to the solid side will be purely by diffusion. And, if we consider the time scale of solidification, it is much less compared to the timescale in diffusion. So, no mixing in solid, is a reasonable practical assumption. Liquid mixing on the other hand is reasonable; because rate of diffusion in liquid is much faster and again liquid could be stirred introducing another two faster modes of transport like convection and eddy diffusion.

Under this assumptions the concentration profile will look like:

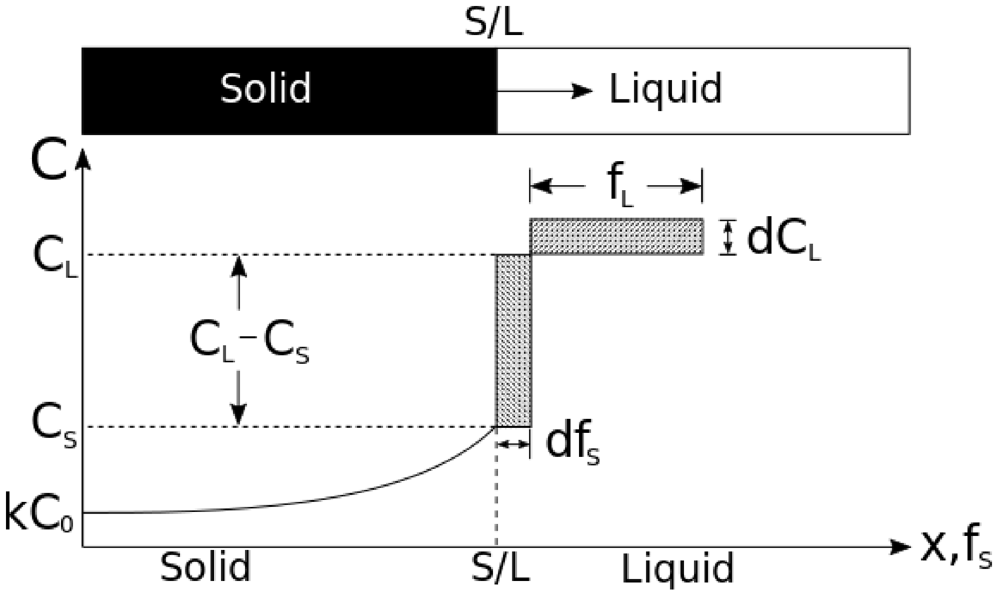

Figure 47.2: Concentration profile of solute under complete mixing in liquid and no mixing in solid

No gradient in the liquid is shown by a horizontal line and there is a partitioning of solute concentration at the interface and then the solute concentration in the solid follows a parabolic profile. Now a mass balance with df_S fractional solidification can be established as:

Amount of solute rejected during solidification = Solute transferred to the liquid

The solute rejected is represented by the vertical hatched area in the figure and mathematically it may be represented as:

$$(C_L - C_S)\,df_S \Rightarrow C_L(1-K_e)df_S \tag{47.4}$$

Similarly, solute transferred to the liquid may be represented by the horizontal hatched area in the figure and mathematically may be represented as:

$$f_L dC_L \Rightarrow (1-f_S)\,dC_L \tag{47.5}$$

Where dC_L represents the increment in solute concentration in the liquid.

Equating (47.4) and (47.5) and rearranging:

$$C_L(1-K_e)df_S = (1-f_S)\,dC_L$$

(47.8)

Equation (47.8) may be integrated for $f_S=0$ to f_S and C_L from C_0 to C_L, as follows:

$$\int_{C_0}^{C_L} \frac{dC_L}{C_L} = (1-K_e)\int_0^{f_S} \frac{df_S}{(1-f_S)}$$

(47.9)

Finally, the integral form of the equation becomes:

$$C_L = C_0(1-f_s)^{K_e-1}$$

(47.10)

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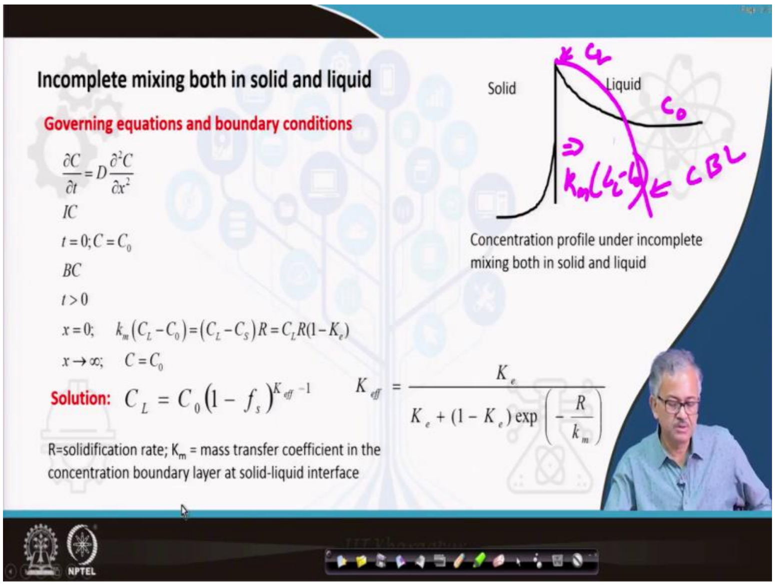

Incomplete mixing both in solid and liquid

Governing equations and boundary conditions

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

IC

$t=0; C=C_0$

BC

$t>0$

$x=0;\quad k_m(C_L-C_0)=(C_L-C_S)R=C_LR(1-K_e)$

$x\to\infty;\quad C=C_0$

Solution: $C_L = C_0(1-f_s)^{K_{eff}-1}$ $\qquad K_{eff} = \dfrac{K_e}{K_e+(1-K_e)\exp\left(-\dfrac{R}{k_m}\right)}$

R=solidification rate; K_m = mass transfer coefficient in the concentration boundary layer at solid-liquid interface

Concentration profile under incomplete mixing both in solid and liquid

Incomplete mixing in solid is pragmatic assumption, but complete mixing in liquid is hypothetical; it is unlikely that the concentration boundary layer at the solid liquid interface to be complete mixed and concentration gradient will exist there. Therefore a most realistic assumption should be no mixing in solid and incomplete mixing in liquid.

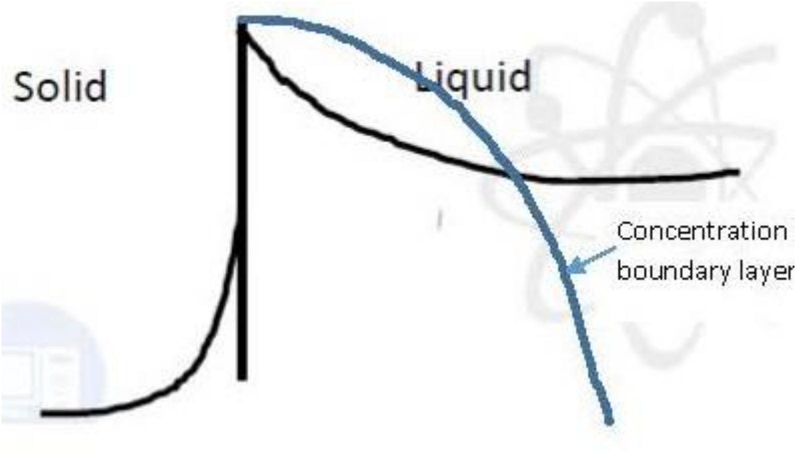

Figure 47.4: Concentration profile of solute under incomplete mixing both in solid and liquid.

Figure 47.4 represents the concentration profile of solute under incomplete mixing in liquid and no mixing in solid. The species transport equation in the concentration boundary layer with initial and boundary conditions may be given as:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

IC

$t = 0; C = C_0$

BC

$t > 0$

$$x = 0; \qquad k_m\left(C_L - C_0\right) = \left(C_L - C_S\right)R = C_L R(1 - K_e)$$

$$x \to \infty; \qquad C = C_0$$

The boundary condition at x= 0 represents the mass balance statement as: solute crossing the concentration boundary layer (per unit area per unit time) = solute rejected (per unit area per unit time) when the solid liquid interface move at a speed, R.

The analytical solution of the above formulation may be given as:

$$C_L = C_0\left(1 - f_s\right)^{K_{eff} - 1} \tag{47.11}$$

Where,

$$K_{eff} = \frac{K_e}{K_e + (1-K_e)\exp\left(-\frac{R}{k_m}\right)}$$

(47.12)

Here, R is the rate of movement of solid-liquid interface and K_m is the mass transfer coefficient in the concentration boundary layer.

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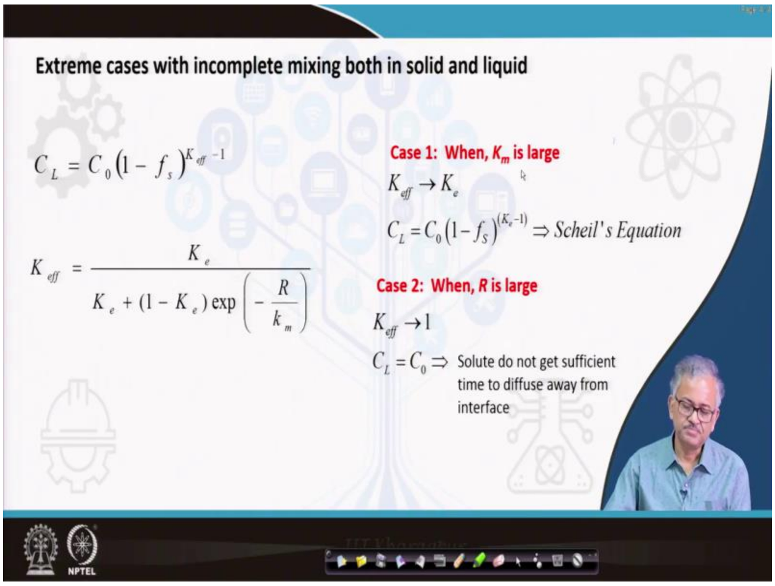

Extreme cases with incomplete mixing both in solid and liquid

$$C_L = C_0(1-f_s)^{K_{eff}-1}$$

$$K_{eff} = \frac{K_e}{K_e + (1-K_e)\exp\left(-\frac{R}{k_m}\right)}$$

Case 1: When, K_m is large

$K_{eff} \to K_e$

$C_L = C_0(1-f_S)^{(K_e-1)} \Rightarrow Scheil's\ Equation$

Case 2: When, R is large

$K_{eff} \to 1$

$C_L = C_0 \Rightarrow$ Solute do not get sufficient time to diffuse away from interface

Now, let us consider two extreme cases: Case 1 when K_m is very large

$$K_{eff} \to K_e$$

$$C_L = C_0(1-f_S)^{(K_e-1)}$$

This situation basically representing a condition of complete mixing when there exists no concentration gradient in the concentration boundary layer, and therefore the equation (47.12) reduces to Scheil's equation.

Another extreme case (Case 2), when R is large.

$$K_{eff} \rightarrow 1$$
$$C_L = C_0$$

When the rate of solidification is very high, solute does not get sufficient time to come out of solid structure and as a result no segregation takes place.

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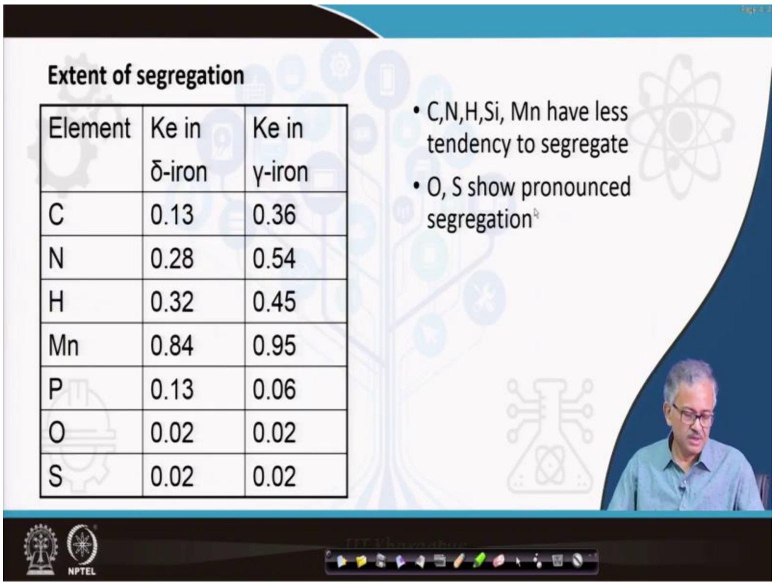


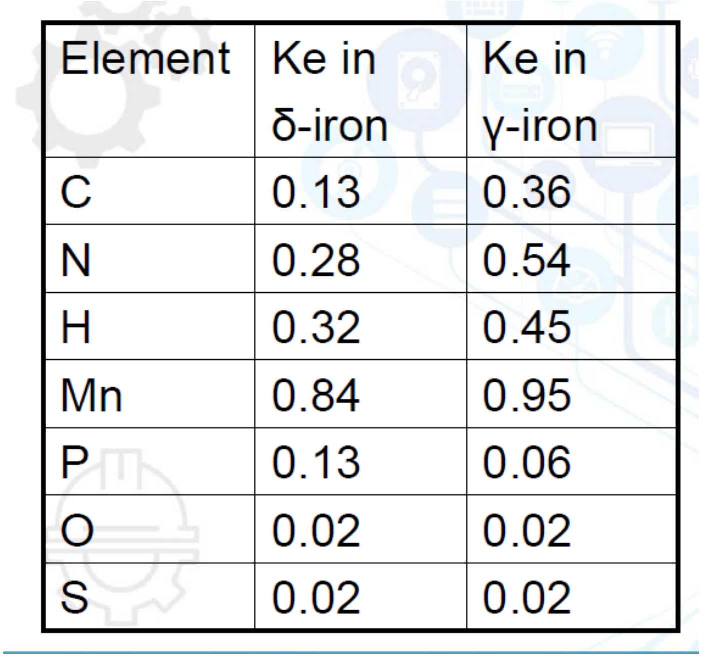
Extent of segregation

Element	Ke in δ-iron	Ke in γ-iron
C	0.13	0.36
N	0.28	0.54
H	0.32	0.45
Mn	0.84	0.95
P	0.13	0.06
O	0.02	0.02
S	0.02	0.02

- C,N,H,Si, Mn have less tendency to segregate
- O, S show pronounced segregation

Now, the extent of segregation depends on the solubility difference of solute between solid and liquid, or the equilibrium partition coefficient, K_e. If K_e is near to 1, no segregation is likely to take place and extent of segregation will be large when K_e is far way from 1.

Table 47.1: Equilibrium partition coefficient in delta and gamma iron for various elements



Element	Ke in δ-iron	Ke in γ-iron
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H	0.32	0.45
Mn	0.84	0.95
P	0.13	0.06
O	0.02	0.02
S	0.02	0.02

From the Table 47.1 it is seen that C, N, H, Mn are less likely to segregate; while S and O are likely to segregate to large extent.

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Types of segregations

- Two types of segregation
  - Macro-segregation
    - ➢It is difficult to annihilate by annealing and it is considered as defect.
    - ➢Produces by bulk movement of solutes under liquid convection
  - Micro-segregation
    - ➢Inter-dendritic segregation (so called coring)
    - ➢Produced by dendritic solidification. Solute accumulates in the interdendritic region surrounded by solute depleted crystals, dendrites
    - ➢Can be easily removed by annealing, when the solute will diffuse to the solute depleted dendrites, where solubility for solute increases at higher temperature

Types of segregation: Two types of segregations are there; one is called the macro segregation, which are the localized segregation and it is difficult to annihilate such segregation by annealing and it is considered as a defect. Macro segregation are generated by the liquid convections. In this case solute rejected at the solid liquid interface are taken away by liquid convection from a location of higher velocity to a location of low velocity intensity and deposits there causing macro-segregation.

The other kind of segregation is called the micro-segregation that is usually observed into the inter-dendritic space. When the dendrites grow, then the liquid get enriched in the inter-dendritic region and such inter-dendritic segregation is called micro-segregation.

And, this micro segregation can be easily eliminated by heating it. On heating the solute migrates from inter-dendritic region to the dendrites, eliminating the difference in concentration of solute between dendritic and inter-dendritic regions.

But since macro segregation is localized, solute needs to be transported through a long distance to low solute regions, making it difficult to annihilate this type of segregation by heating.

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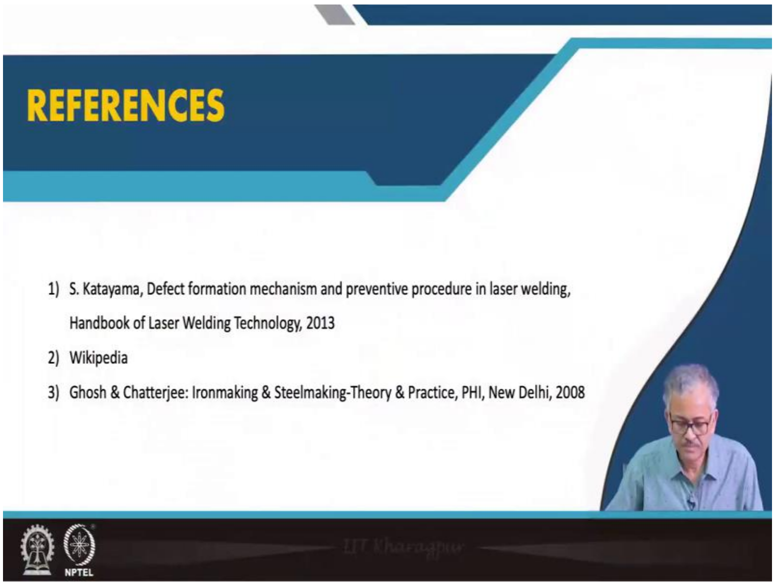

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2) Wikipedia
3) Ghosh & Chatterjee: Ironmaking & Steelmaking-Theory & Practice, PHI, New Delhi, 2008

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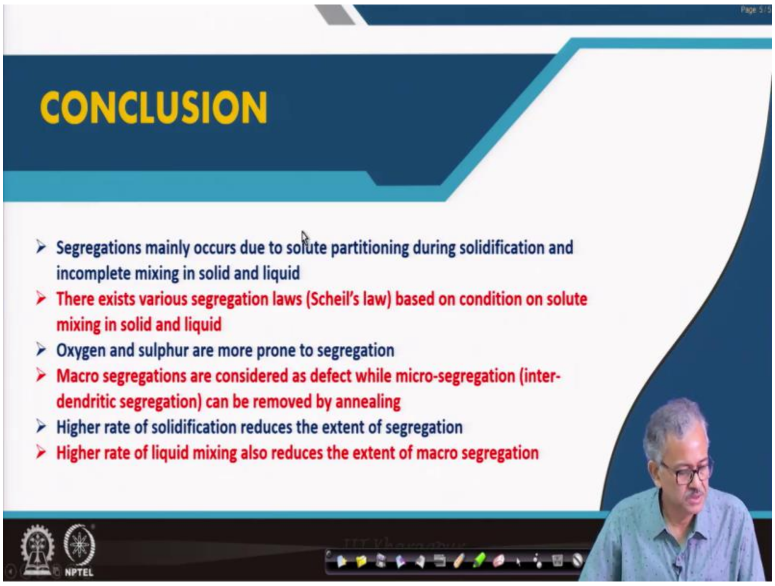

CONCLUSION

- Segregations mainly occurs due to solute partitioning during solidification and incomplete mixing in solid and liquid
- There exists various segregation laws (Scheil's law) based on condition on solute mixing in solid and liquid
- Oxygen and sulphur are more prone to segregation
- Macro segregations are considered as defect while micro-segregation (inter-dendritic segregation) can be removed by annealing
- Higher rate of solidification reduces the extent of segregation
- Higher rate of liquid mixing also reduces the extent of macro segregation

Conclusion: Solute partitioning during solidification and incomplete mixing in solid and liquid causes segregation. There are various segregation laws to quantify the solute concentration in liquid during the course of solidification at various fractional solidification depending on the extent of mixing in solid and liquid. Scheil's law yields the handy solution with near realistic assumption with complete mixing in liquid and no mixing in solid (Equation 47.10).

Oxygen and sulfur are more prone to segregation, because their equilibrium partition coefficient is far away from unity.

There are two types of segregation. Macro-segregation occurs due liquid convection that carries the solute from a region of higher velocity intensity to a location of lower velocity intensity and deposits there and develops localized segregation. Segregation in the inter-dendritic region is called the micro-segregation. Micro-segregation may be annihilated by annealing or heating when the solute migrates from inter-dendritic region to adjacent dendritic region that are depleted in solute. In macro-segregation the solute rich and solute depleted regions are localized and requires large time for solute migration, making it difficult to remove such segregation in reasonable amount of time. Therefore, macro-segregation is considered as defect.