

## Lecture 20: Eutectoid Transformation in Steels: *kinetics of phase growth*

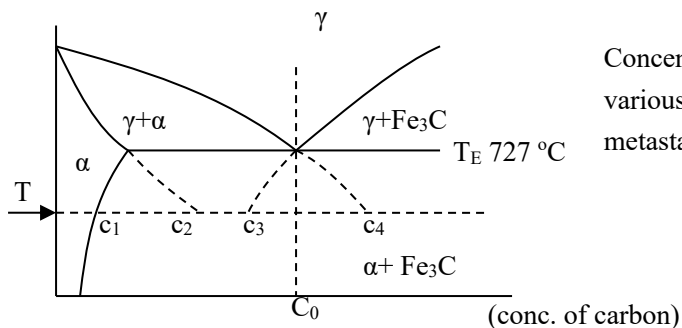
### Today's topics

- The growth of cellular precipitates requires the portioning of solute to the tips of the precipitates in contact with the advancing grain boundary. This can occur in one of the two ways: either by diffusion through the lattice ahead of the advancing cell front, or by diffusion in the moving boundary. *Today's topic: how to describe these diffusion kinetics relating to the phase growth rate?*
- For cellular transformation, *the diffusion distance does not increase with time*. This is distinct from the case of particle growth that we described in Lectures 16-18, where as the time proceeds, the radius of particle increases, and the concentration difference between the bulk phase and the particle interface decreases. Consequently, the diffusion flux to the growing particle becomes small, implying that *the diffusion distance becomes greater*.

### *In last Lecture:*

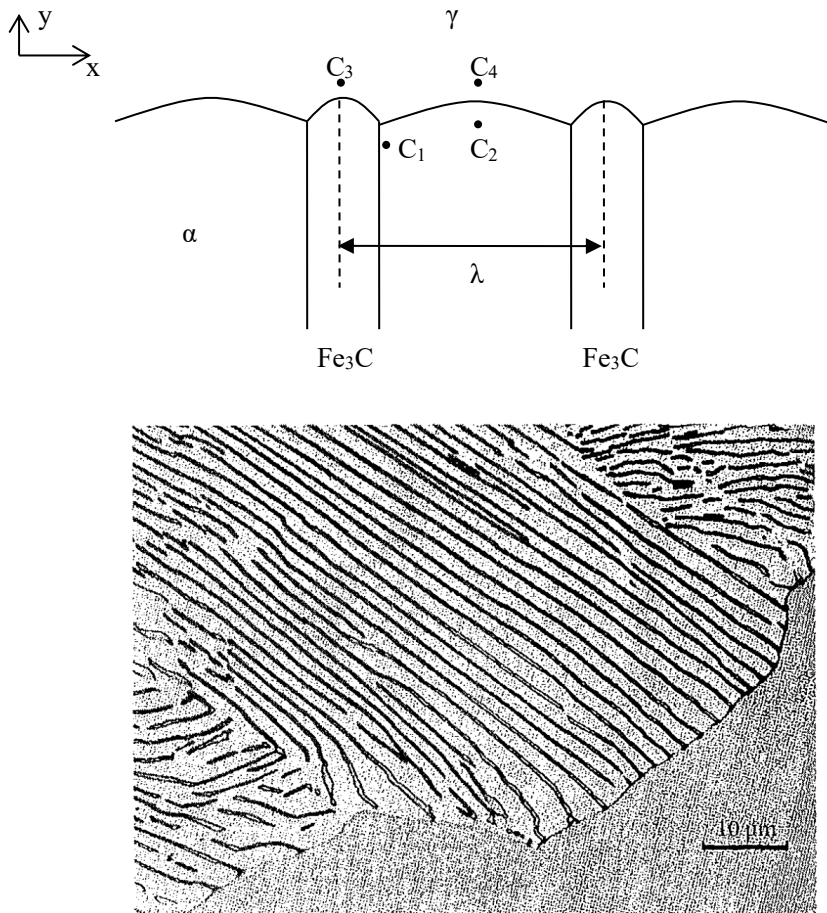
We went through the general description of the eutectoid transformation of Fe-C alloy from austenite to pearlite,  $\gamma\text{-Fe} \rightarrow \alpha\text{-Fe} + \text{Fe}_3\text{C}$  or Austenite  $\rightarrow$  Ferrite + Cementite. This phase transformation represents a typical type of **cellular precipitation**, where the two new phases are in equilibrium, and form simultaneously at the expense of the parent phase.

The following phase diagram describes the eutectoid transformation of Fe-C alloy.



Concentrations  $C_1, C_2, C_3, C_4$  are various equilibrium ( stable as well as metastable ) concentrations of carbon.

The concentrations of carbon in the different phases near the interfaces as illustrated in this diagram:



**FIGURE 5.60**

Pearlite colony advancing into an austenite grain. (After Darken, L.S. and Fisher, R.M., in *Decomposition of Austenite by Diffusional Processes*, Interscience, New York, 1962.)

- The pearlite cells grow along y-direction.
- Assume the rate of growth is controlled by diffusion of carbon to the  $\text{Fe}_3\text{C}$  plate. That is, the carbon atoms are removed from the matrix of  $\gamma$  (to form  $\alpha$ -Fe, or ferrite) and concentrate (to form  $\text{Fe}_3\text{C}$ , or cementite) --- *formation of ferrite and cementite are simultaneous, and coherent with the consumption of austenite phase.*
- The thickness (volume fraction) of  $\text{Fe}_3\text{C}$  is rather small because the initial concentration of carbon in austenite is low, only 0.8wt%.
- The spacing between two adjacent cementite plates is defined as  $\lambda$ .

We can define

J: as the diffusion flux of carbon,

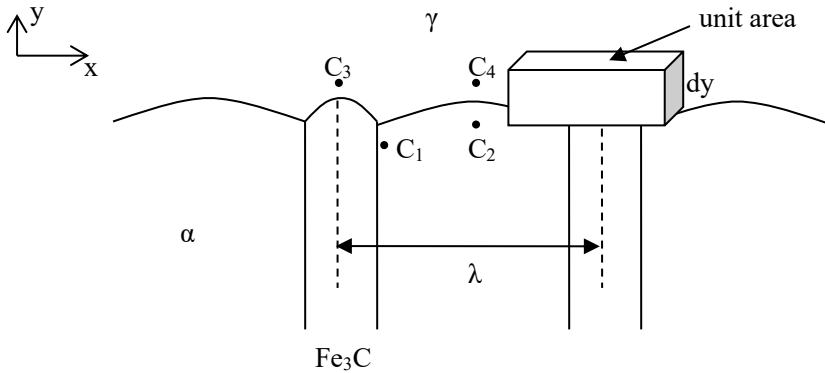
A: as the **effective diffusion area** through which carbon are removed to form one unit area of  $\gamma/\alpha\text{-Fe}_3\text{C}$  interface.

- Thus, in time  $dt$ , the amount of carbon removed is  $AJdt$ .
- One the other hand, during the same time, one unit area of  $\gamma/\alpha\text{-Fe}_3\text{C}$  interface moves by  $dy$ , yielding

the amount of carbon removed is  $1 \cdot dy (C_0 - C_1)$ .

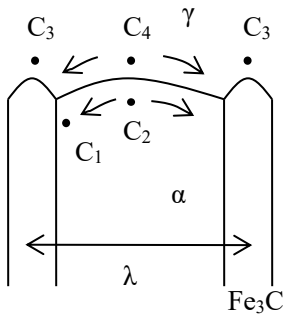
So,  $AJdt = dy (C_0 - C_1)$

The growth rate of interface,  $v = \frac{dy}{dt} = \frac{AJ}{C_0 - C_1}$



Now let's define A as the effective area of the diffusion path per unit area of  $\gamma$ - $\alpha$  interface, then,

- $A \cong 1$  for diffusion in the  $\gamma$  or  $\alpha$ , that is the width of the diffusion path is roughly the spacing between cementite plates ( $\lambda$ );
- $A \cong \frac{\delta}{\lambda}$  for diffusion along the  $\alpha$ - $\gamma$  interface, where  $\delta$  is the interface thickness.



$C_1 < C_2 < C_3 < C_4$ , try to understand this order by considering the diffusion diagram above.

Diffusion of Carbon can occur through  $\gamma$ ,  $\alpha$ , or  $\alpha/\gamma$  interface. *phase transformation is determined by the carbon diffusion to cementite.*

Diffusion flux  $J = D \frac{\Delta C}{L}$ , where L is the diffusion length, and  $\Delta C$  is always positive. Please recall the Fick's

first law:  $J = -D \cdot \frac{dc}{dx}$  (where dc is negative, along concentration gradient)

As shown, the two adjacent cementite plates are separated by a mean spacing,  $\lambda$ , and thus the mean diffusion length for the carbon atoms to reach the cementite phase is  $L = 1/2 \lambda$ .

Thus, we have  $J = D \frac{2\Delta C}{\lambda}$

Thereby, we can deduce the diffusion flux in the different phases

1. For diffusion in  $\gamma$ :  $\Delta C = C_4 - C_3$ , then,  $J_\gamma = D_\gamma \cdot \frac{\Delta C}{L} = \frac{2D_\gamma(C_4 - C_3)}{\lambda}$
2. For diffusion in  $\alpha$ :  $\Delta C = C_2 - C_1$ , then,  $J_\alpha = D_\alpha \cdot \frac{\Delta C}{L} = \frac{2D_\alpha(C_2 - C_1)}{\lambda}$
3. For diffusion along  $\alpha/\gamma$  interface:  $\Delta C = \left(\frac{C_4 + C_2}{2}\right) - \left(\frac{C_3 + C_1}{2}\right)$ , then,

$$J_{\alpha/\gamma} = D_{\alpha/\gamma} \frac{\Delta C}{L} = \frac{2D_{\alpha/\gamma}\Delta C}{\lambda}$$

Now, growth rate of phase interface ( $v$ ) caused by the carbon diffusion in different phases can be written as:

1. For diffusion in  $\gamma$ :  $v_\gamma = \frac{AJ_\gamma}{C_0 - C_1} = \frac{2D_\gamma(C_4 - C_3)}{\lambda(C_0 - C_1)}, (A=1)$
2. For diffusion in  $\alpha$ :  $v_\alpha = \frac{AJ_\alpha}{C_0 - C_1} = \frac{2D_\alpha(C_2 - C_1)}{\lambda(C_0 - C_1)}, (A=1)$
3. For diffusion along  $\alpha/\gamma$  interface:  $v_{\alpha/\gamma} = \frac{AJ_{\alpha/\gamma}}{C_0 - C_1} = \frac{2D_{\alpha/\gamma}\delta\Delta C}{\lambda^2(C_0 - C_1)}, (A = \delta / \lambda)$

Apparently, for diffusion in  $\gamma$  or  $\alpha$  phases,  $v \propto \frac{1}{\lambda}$

For diffusion along  $\alpha/\gamma$  interface,  $v \propto \frac{1}{\lambda^2}$ .

The three diffusion pathways described above, through  $\alpha$ , through  $\gamma$ , and along  $\alpha/\gamma$  interface, are parallel in contributing to the phase growth. The rate of phase transformation will be determined by whichever pathway provides the fastest flux flow of carbon atoms.

**Now let's study how  $\lambda$  and  $v$  varies with  $T$ :**

When a unit volume of  $\gamma$  converts into pearlite ( $\alpha\text{-Fe} + \text{Fe}_3\text{C}$ ), the change in Free energy is

$$\Delta G = \text{volumetric free energy} + \text{surface energy} = \Delta G_V + A_{\alpha/\text{Fe}_3\text{C}}\gamma_{\alpha/\text{Fe}_3\text{C}}$$

Where

- $\gamma_{\alpha/Fe_3C}$  is the interfacial energy between  $\alpha$ -Fe and  $Fe_3C$ ,
- $A_{\alpha/Fe_3C}$  = area of  $\alpha / Fe_3C$  interfaces per unit volume =  $\frac{2}{\lambda}$  (since the number of  $\alpha/Fe_3C$  interface per unit length is  $2/\lambda$ ).

Thus,  $\Delta G = \Delta G_V + \frac{2}{\lambda} \gamma_{\alpha/Fe_3C}$ ,

**Note:**  $\Delta G_V < 0$ , for  $T < T_E$

So, as  $\lambda$  decreases,  $\Delta G$  will becomes  $> 0$  (thermodynamically unfavorable for the phase transformation).

The smallest allowable value of  $\lambda$  ( $\lambda_{min}$ ) is the one, at which  $\Delta G = 0$ .

Then we have,  $\lambda_{min} = -\frac{2\gamma_{\alpha/Fe_3C}}{\Delta G_V}$

**Clearly, at  $\lambda < \lambda_{min}$ ,  $\Delta G > 0$ , thermodynamically unfavorable for the transformation.**

Now,  $\Delta G_V = \Delta S_V \Delta T = -|\Delta S_V| \Delta T, \Delta T = T_E - T$  (see Lecture 11)

Then,  $\lambda_{min} = \frac{2\gamma_{\alpha/Fe_3C}}{|\Delta S_V| \Delta T}$ , or  $\lambda_{min} \propto \frac{1}{\Delta T}$  (*one important point, implying that the lamellar structure*

*depends on the temperature you cool down*)

For growth rate,  $v$ , generally,

$$v \propto \frac{|\Delta G|}{T} \exp\left[-\frac{\Delta G_A}{RT}\right] \text{ (thermodynamic factor} \times \text{kinetics factor)} \quad \text{(see Lecture 2)}$$

Where  $\Delta G_A$  is the activation barrier for the diffusion.

Assuming that the phase transformation occurs by diffusion through either  $\alpha$  or  $\gamma$ , then

$$v \propto \frac{D}{\lambda}$$

So, the phase growth rate can be written as:

$$v = \Gamma \cdot \frac{D}{\lambda} \cdot |\Delta G|$$

Where  $\Gamma$  = a factor includes all other terms dependent on  $T$ , but not on  $\lambda$

From the above,  $\Delta G_V$  can be written in term of  $\lambda_{min}$ ,

$$\Delta G_V = -\frac{2\gamma_{\alpha/Fe_3C}}{\lambda_{min}}$$

Then, we have  $\Delta G = \Delta G_V + \frac{2\gamma_{\alpha/Fe_3C}}{\lambda} = 2\gamma_{\alpha/Fe_3C} \left( \frac{1}{\lambda} - \frac{1}{\lambda_{\min}} \right)$

Then,

$$v = \Gamma \cdot \frac{D}{\lambda} \cdot 2\gamma_{\alpha/Fe_3C} \left( \frac{1}{\lambda_{\min}} - \frac{1}{\lambda} \right)$$

Or

$$v = 2\Gamma D \gamma_{\alpha/Fe_3C} \left( \frac{\lambda - \lambda_{\min}}{\lambda^2 \lambda_{\min}} \right)$$

At a fixed temperature, the group of parameters before the parathesis remains a constant, so the equation can be simplified as

$$v = \text{const} \cdot \left( \frac{\lambda - \lambda_{\min}}{\lambda^2 \lambda_{\min}} \right) \quad (\text{be prepared to practice this equation in the homework})$$

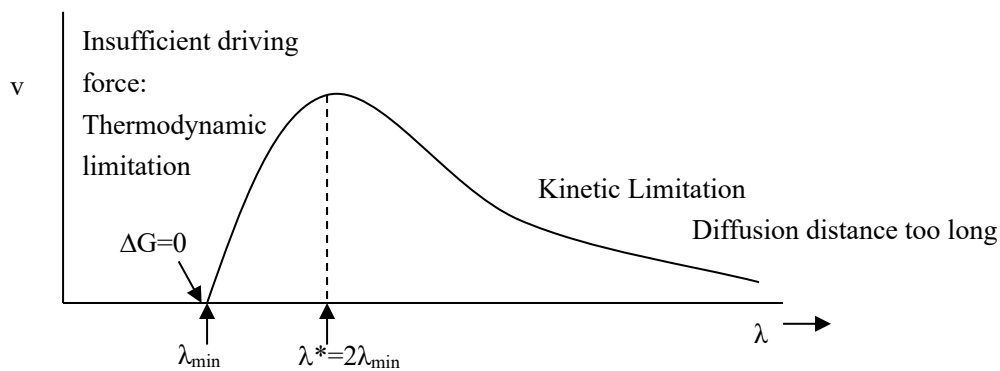
Now consider two limiting conditions:

1. when  $\lambda = \lambda_{\min}$ ,  $v = 0$
2. when  $\lambda \rightarrow \infty$ ,  $v \rightarrow 0$

Clearly, “v” must exhibit a maximum at some  $\lambda$  between  $\lambda_{\min}$  and the infinite spacing.

At the maximum,  $\frac{dv}{d\lambda} = 0$  or  $\frac{d}{d\lambda} \left( \frac{\lambda - \lambda_{\min}}{\lambda^2 \lambda_{\min}} \right) = 0$

This gives  $\lambda^* = 2\lambda_{\min}$  corresponding to the maximum growth rate as depicted below.



As shown above, at  $\lambda_{\min}$ ,  $\Delta G = 0$ .

$\lambda_{\min}$  is an intrinsic parameter that depends on the temperature you cool down,  $\lambda_{\min} \propto \frac{1}{\Delta T}$

$$\Delta G = \Delta G_V + \frac{2}{\lambda} \gamma_{\alpha/\text{Fe}_3\text{C}}$$

- *the smaller the diffusion length ( $\lambda$ ), the more positive the  $\Delta G$  will become (since  $\Delta G_V < 0$ ), the more unfavorable the transformation will then become --- falling into the **thermodynamic limited zone**.*
- On the other hand, if  $\lambda$  gets too large,  $v$  gets decreased, and eventually approaches zero when  $\lambda \rightarrow \infty$ , falling into the **kinetics limited zone**.