



# Displacive versus diffusional transformations - the determining factors

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## 1. Background – some remarks

There is no “versus”!

It is generally accepted that a transformation may be both displacive and diffusion controlled!

But: Many authors mean diffusionless when they say displacive.



## Two "versus":

- Reconstructive/displacive
  - refers to the details of the crystallographic changes at the phase interface.
- Diffusional/diffusionless
  - Refers to if there is a change in composition at the phase interface



## Displacive transformations:

- Interface migration by coordinated motion of atoms (transformation dislocations)
- Coherent or semi-coherent interfaces
- Crystallographic orientation relationships
- Shape changes

## Reconstructive

- Incoherent interfaces
- Interface migration by random jumps of atoms
- No crystallographic orientation relationships



# Examples of reactions involving FCC→BCC in steels

Reaction	Displacive	Reconstructive	Diffusional	Diffusionless
Allotriomorphic		X	X	
Widmanstätten	X		X	
Martensitic	X			X
Massive		X		X
Bainitic	X		X	
Pearlite		X	X	



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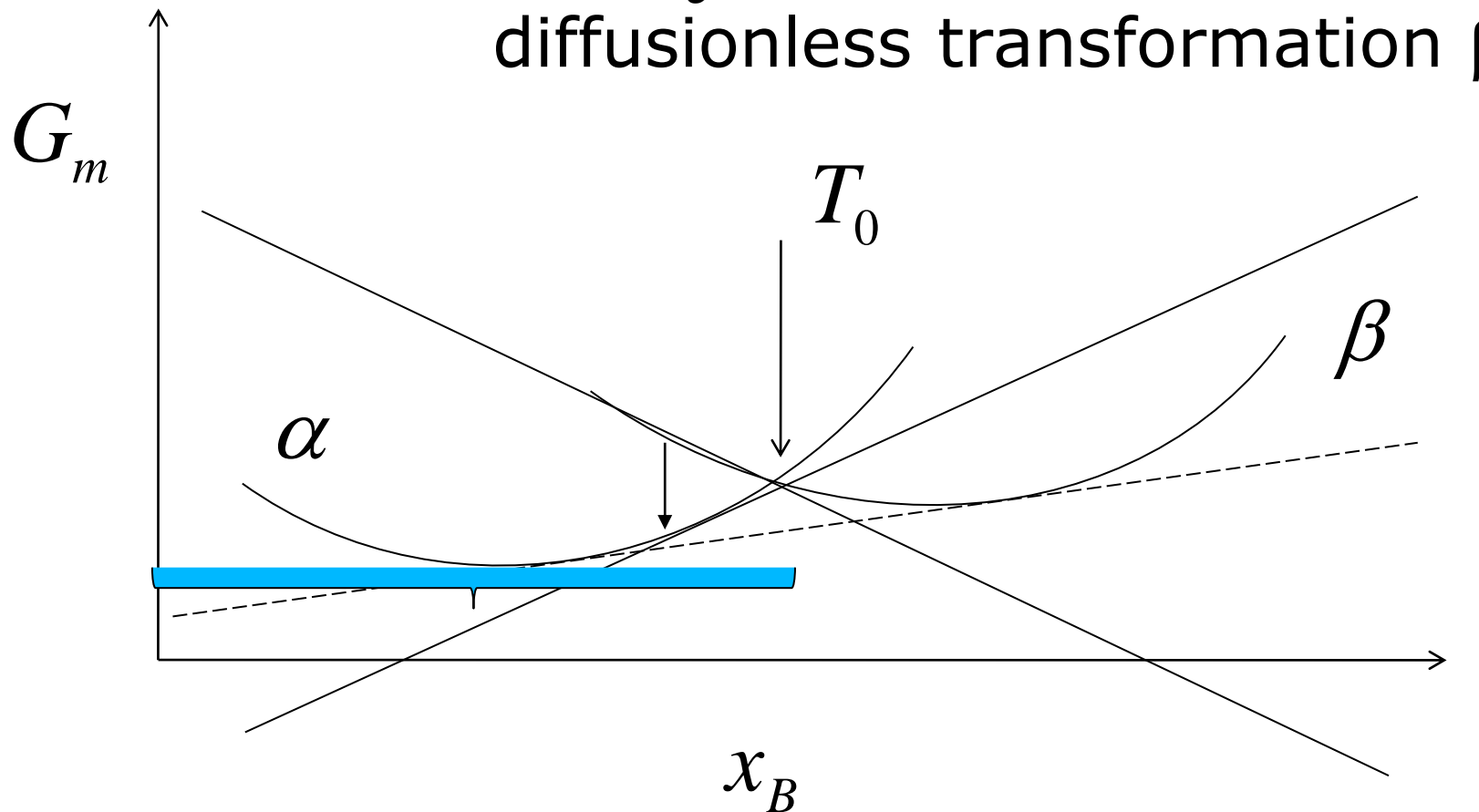


# What determines if a transformation is diffusional or diffusionless?

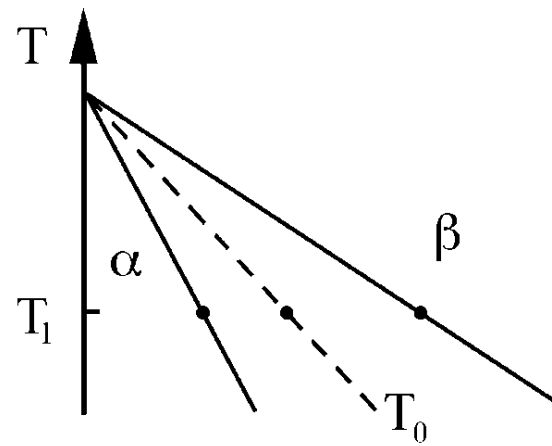
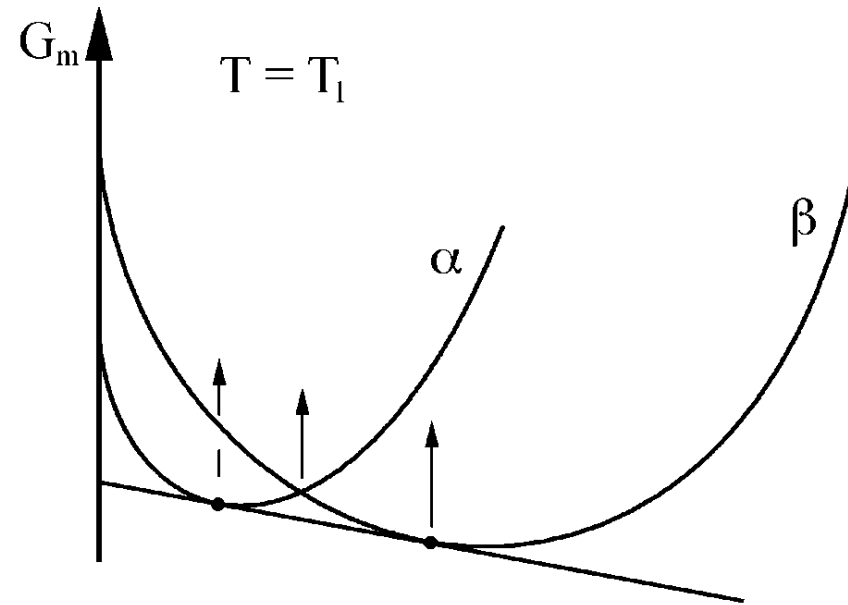
Thermodynamic limits  
Kinetic limits

## 2. Thermodynamic limits

The  $T_0$  line: Thermodynamic limit for diffusionless transformation  $\beta \rightarrow \alpha$ .





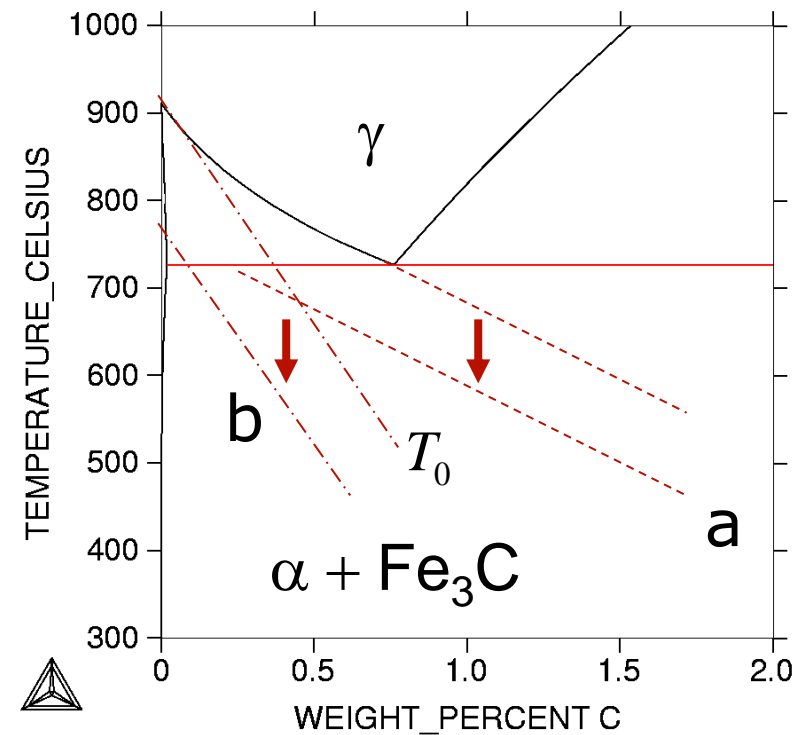




Deviation from local equilibrium during  $\gamma \rightarrow \alpha$  in Fe-C when some extra driving force (undercooling) needed.

Temperature for start of reaction.

- a) Diffusion control
- b) Diffusionless





## 3. Kinetic limits

Even if a transformation is thermodynamically possible the kinetics may be such that it cannot occur.

Depends on the balance between the different processes e.g. long-range diffusion and interfacial reactions.

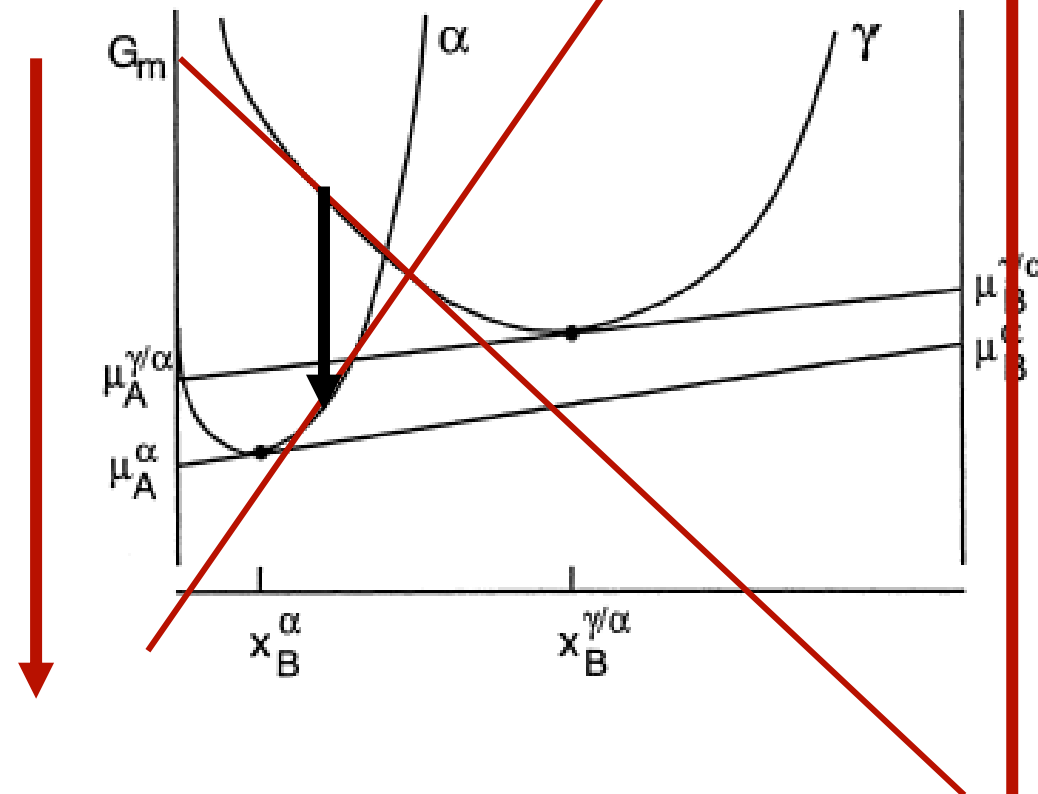
The local state of the migrating phase interface must be understood.

# The local state at phase interface

## Conventional view:

-atoms jump individually from the parent phase across the phase interface and attach to the growing phase.

Problem: All atoms must have a lower chemical potential in the growing phase. This is not the case during a diffusionless transformation.





## 4. Modelling of local state at a sharp phase interface

Hillert 1960 (FCC  $\rightarrow$  BCC in Fe-C)

Aziz 1982 (for solidification)

Ågren 1989 (FCC  $\rightarrow$  BCC in Fe-C)

Olson et al. 1989 (FCC  $\rightarrow$  BCC in Fe-C)

Two processes coupled in series at the interface

- change in composition (trans interface diffusion)
- change of crystalline structure (intrinsic interface mobility)



## These models all predict:

Diffusion controlled growth at high temperatures (low driving forces) – the growing phase has a different composition.

Transition to diffusionless growth at low temperatures (high driving forces) – the growing phase has the same composition as the parent phase.



# Modeling the local state of the moving phase interface

Response functions (Baker and Cahn 1971) For example in a binary system  $\gamma \rightarrow \alpha$ :

$$f_1(x_B^\gamma, x_B^\alpha, v, T) = 0$$

$$f_2(x_B^\gamma, x_B^\alpha, v, T) = 0$$

Simplest case: **Local equilibrium.**

- The interfacial properties do not enter into the problem except for the effect of interfacial energy of a curved interface (Gibbs-Thomson) and the interface velocity does not enter.

$$\Delta\mu_A^{\gamma/\alpha} = \mu_A^\gamma(x_B^\gamma, T) - \mu_A^\alpha(x_B^\alpha, T) = 0$$

$$\Delta\mu_B^{\gamma/\alpha} = \mu_B^\gamma(x_B^\gamma, T) - \mu_B^\alpha(x_B^\alpha, T) = 0$$

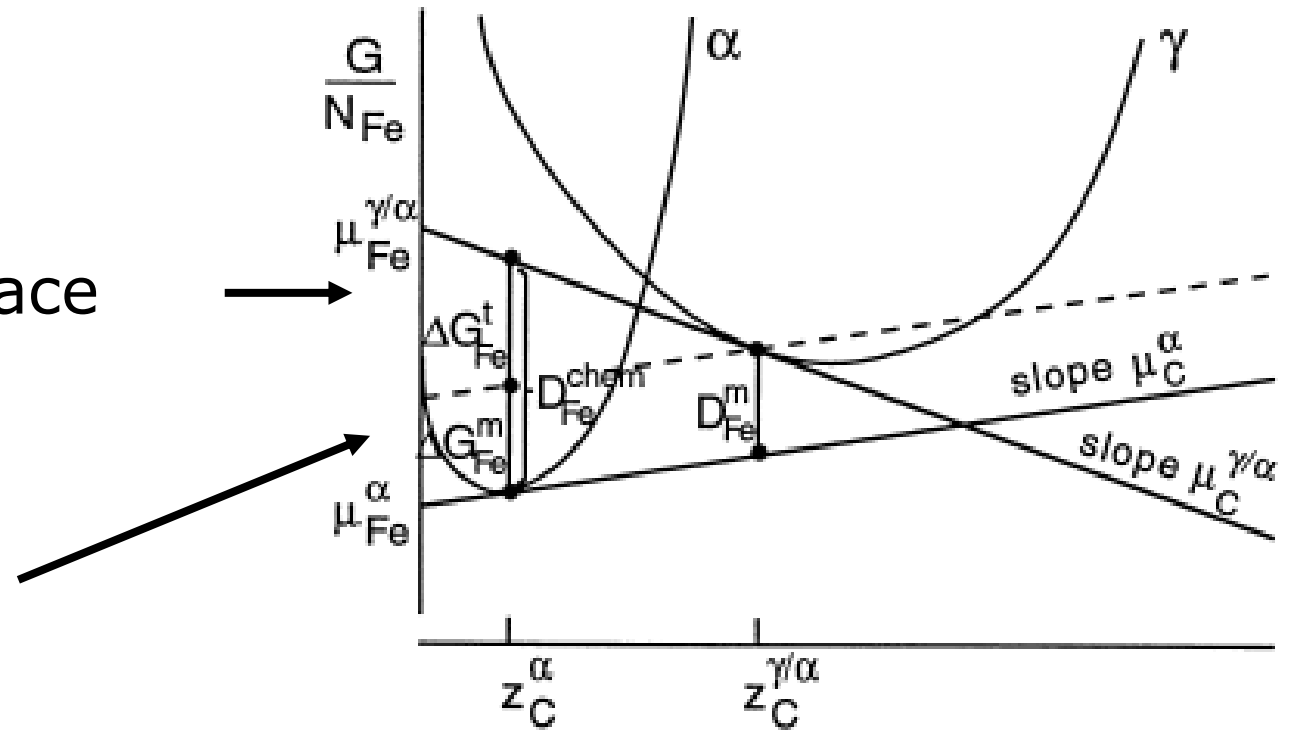


# Deviation from local equilibrium during $\gamma \rightarrow \alpha$ in Fe-C.

Carbon diffuses across interface from  $\alpha$  to  $\gamma$ .

Driving force for trans-interface diffusion:

Driving force for change of crystalline lattice:

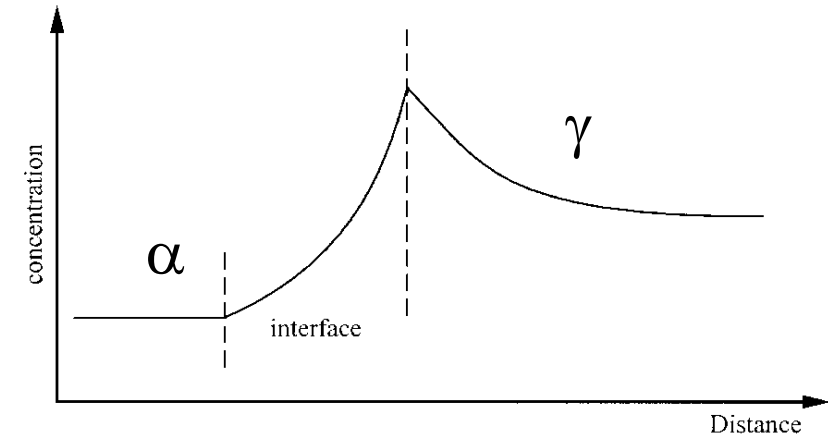


All quantities expressed per mole of Fe atoms.

$$z_C = N_C / N_{Fe} = x_C / x_{Fe}$$



# Trans-interface diffusion



$$J_C^t = -L_{CC}(\mu_C^{\gamma/\alpha} - \mu_C^\alpha) = -L_{CC}\Delta\mu_C^{\gamma/\alpha}$$

The Gibbs energy dissipation from this process

$$-\dot{G} = -J_C^t \Delta\mu_C^{\gamma/\alpha} = \frac{v}{V_s} \Delta G_{Fe}^t$$

$\Delta G_{Fe}^t$  is the driving force for trans-interface diffusion per mole of Fe. Under steady state at the phase interface:

$$\Delta G_{Fe}^t = -\left(z_C^{\gamma/\alpha} - z_C^\alpha\right)\Delta\mu_C^{\gamma/\alpha}$$



# Finite interface mobility

The total available chemical driving force is (per mole Fe):

$$\Delta G_{Fe}^{chem} = (\mu_{Fe}^{\gamma/\alpha} - \mu_{Fe}^{\alpha}) + z_C^{\alpha} (\mu_C^{\gamma/\alpha} - \mu_C^{\alpha}) = \Delta\mu_{Fe}^{\gamma/\alpha} + z_C^{\alpha} \Delta\mu_C^{\gamma/\alpha}$$

and the driving force to overcome the finite interface mobility is obtained from:

$$\Delta G_{Fe}^{chem} = \Delta G_{Fe}^m + \Delta G_{Fe}^t \quad \text{i.e.} \quad \Delta G_{Fe}^m = \Delta G_{Fe}^{chem} - \Delta G_{Fe}^t :$$

$$\Delta G_{Fe}^m = \Delta\mu_{Fe} + z_C^{\gamma/\alpha} \Delta\mu_C = \frac{v}{M} V_s$$



## The response functions become:

$$f_1(z_C^{\gamma/\alpha}, z_C^\alpha, v) = \Delta\mu_C^{\gamma/\alpha}(z_C^{\gamma/\alpha}, z_C^\alpha) + \frac{v}{V_s L_{CC}} (z_C^{\gamma/\alpha} - z_C^\alpha) = 0$$

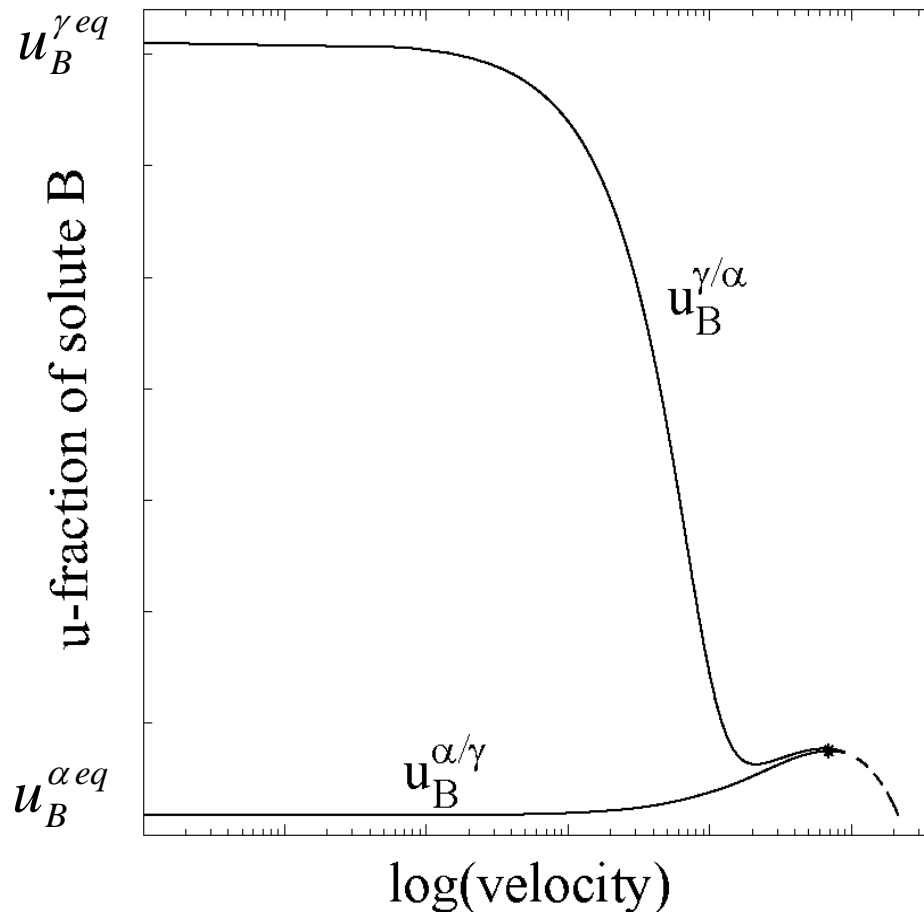
$$f_2(z_C^{\gamma/\alpha}, z_C^\alpha, v) = \Delta\mu_{Fe}^{\gamma/\alpha}(z_C^{\gamma/\alpha}, z_C^\alpha) - \frac{v}{V_s} \left( \frac{V_s^2}{M} + \frac{z_C^{\gamma/\alpha}}{L_{CC}} (z_C^{\gamma/\alpha} - z_C^\alpha) \right) = 0$$

$\Delta\mu_C^{\gamma/\alpha}(z_C^{\gamma/\alpha}, z_C^\alpha)$  and  $\Delta\mu_{Fe}^{\gamma/\alpha}(z_C^{\gamma/\alpha}, z_C^\alpha)$  may be described by suitable thermodynamic models of the  $\gamma$  and  $\alpha$  phase, respectively.

The composition on each side of interface may be calculated for a given interface velocity.

In the limit of very low velocity we recover local equilibrium.

# 5. Transition diffusional/diffusionless growth

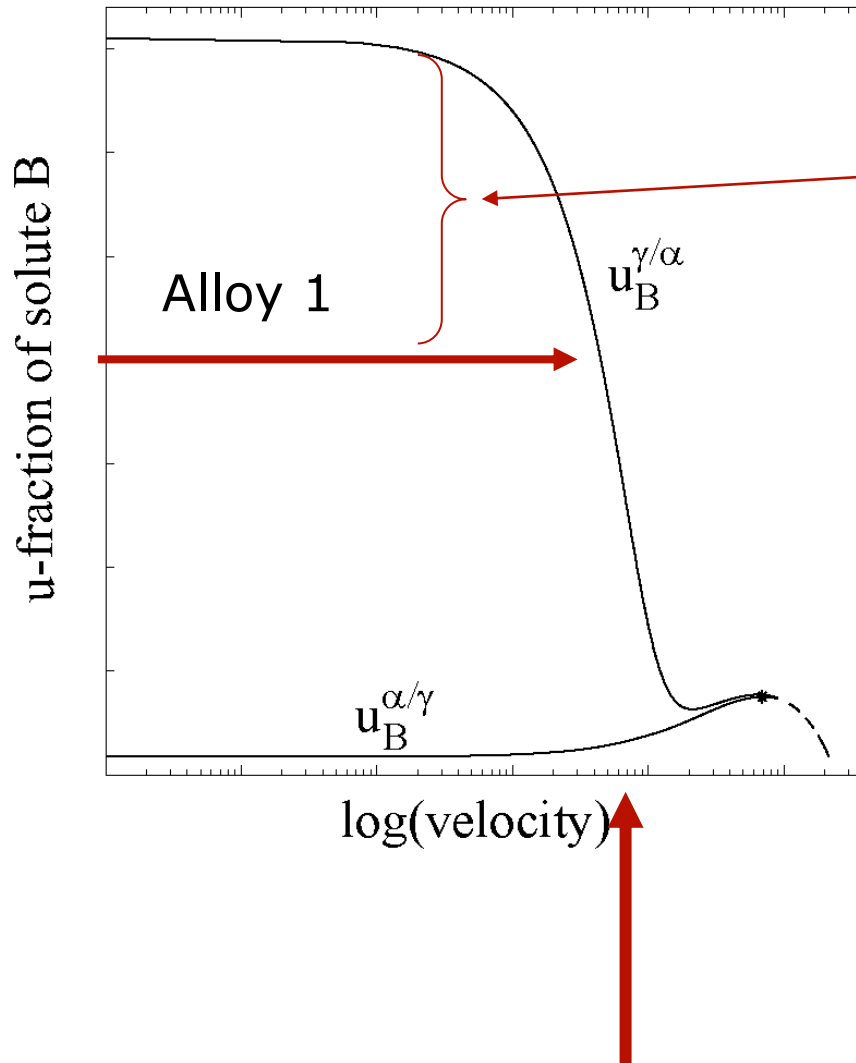


The compositions on each side of the phase interface depend on interface velocity and they approach each other.

$$u_B^\alpha = f(T, v) \rightarrow u_B^{\alpha eq} \quad \text{as } v \rightarrow 0$$

$$u_B^\gamma = g(T, v) \rightarrow u_B^{\gamma eq} \quad \text{as } v \rightarrow 0$$

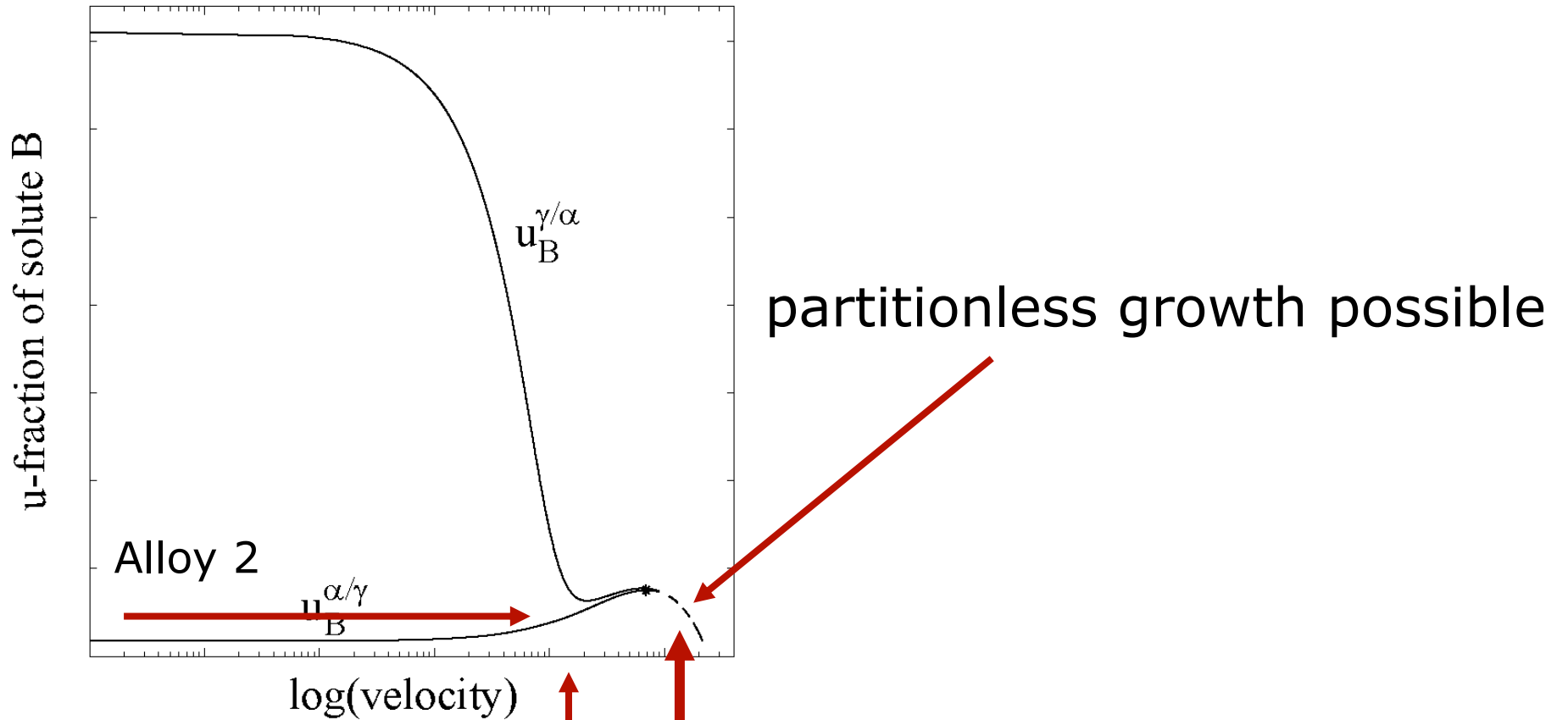
Above a critical velocity transformation turns partitionless.



Driving diffusion in  $\gamma$

Non-parabolic growth in early stages.

Maximum possible growth rate for alloy 1



partitionless growth with spike  
in  $\gamma$  possible

Maximum possible (partitionless) growth rate  
for alloy 2



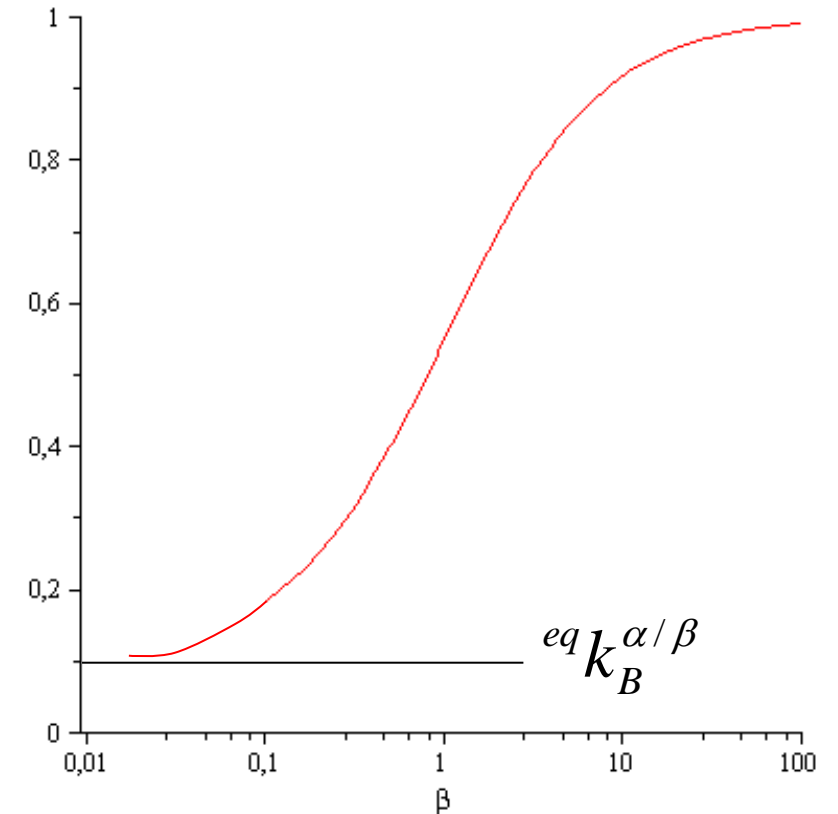
## Aziz model for transinterface diffusion(1982)

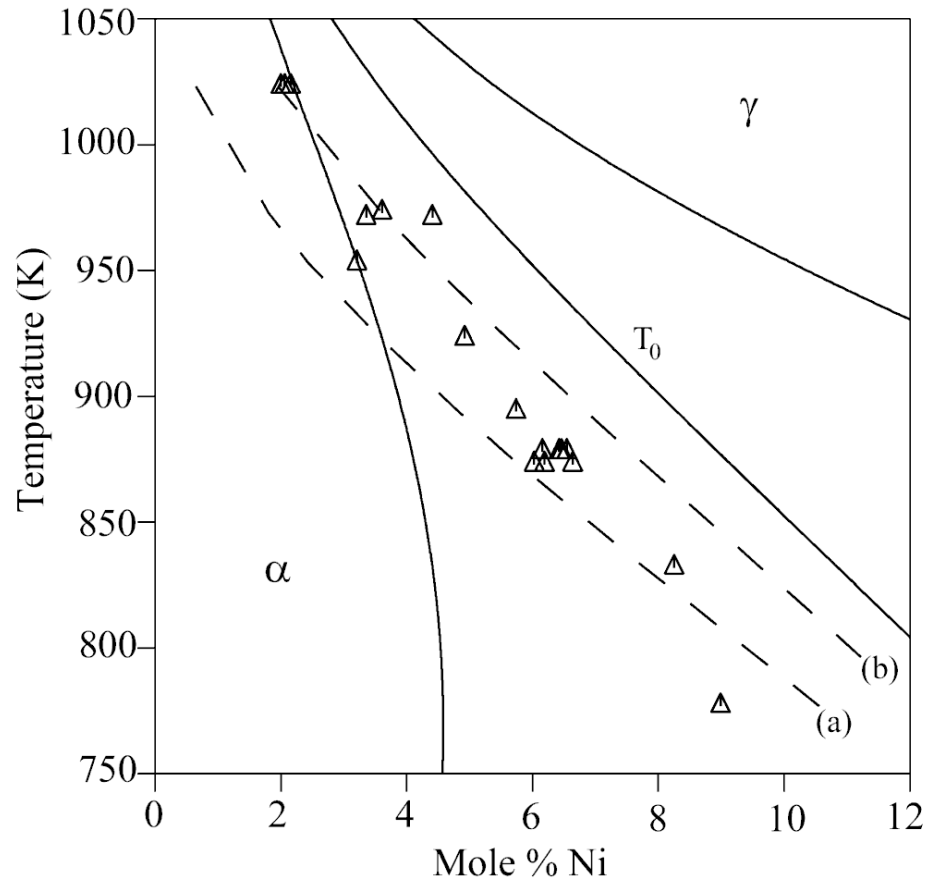
Similar as the previous sharp interface model but:

$$\frac{x_B^\alpha}{x_B^\gamma} = k_B^{\alpha/\gamma} = \frac{\beta + {}^{eq}k_B^{\alpha/\gamma}}{\beta + 1} \quad \beta = \frac{v}{D^i / \lambda}$$

$D^i$  : diffusivity in interface

$\lambda$  : Thickness of interface





Calculated limit of the massive transformation in Fe-Ni alloys (dashed lines) calculated for two different assumptions on properties of interface.

(Odqvist et al. 2002)

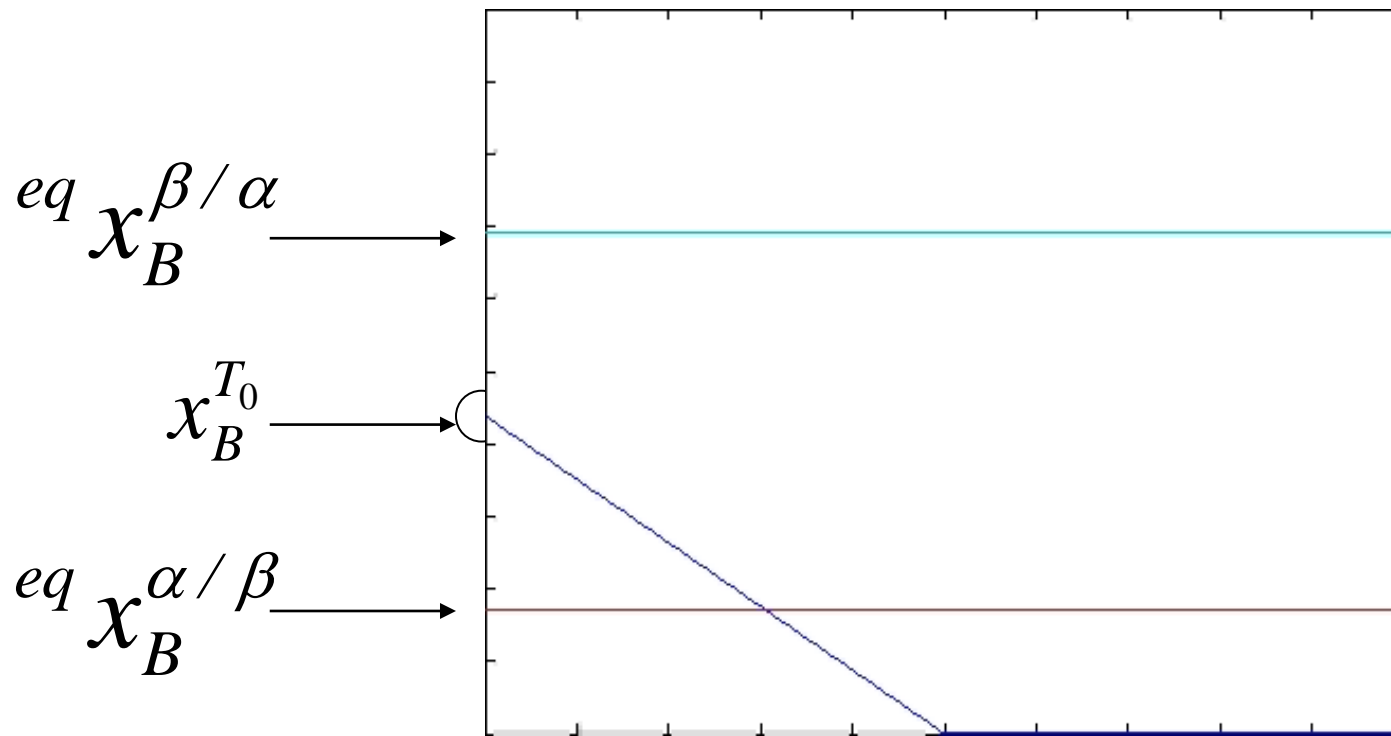
Exp: Borgenstam and Hillert 2000



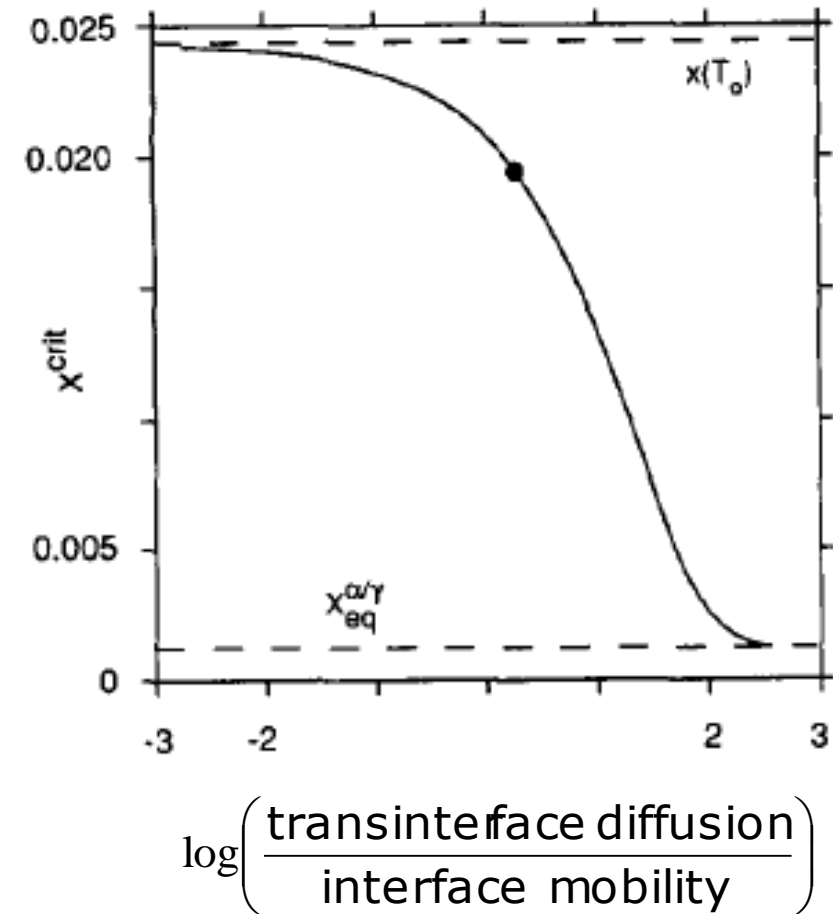
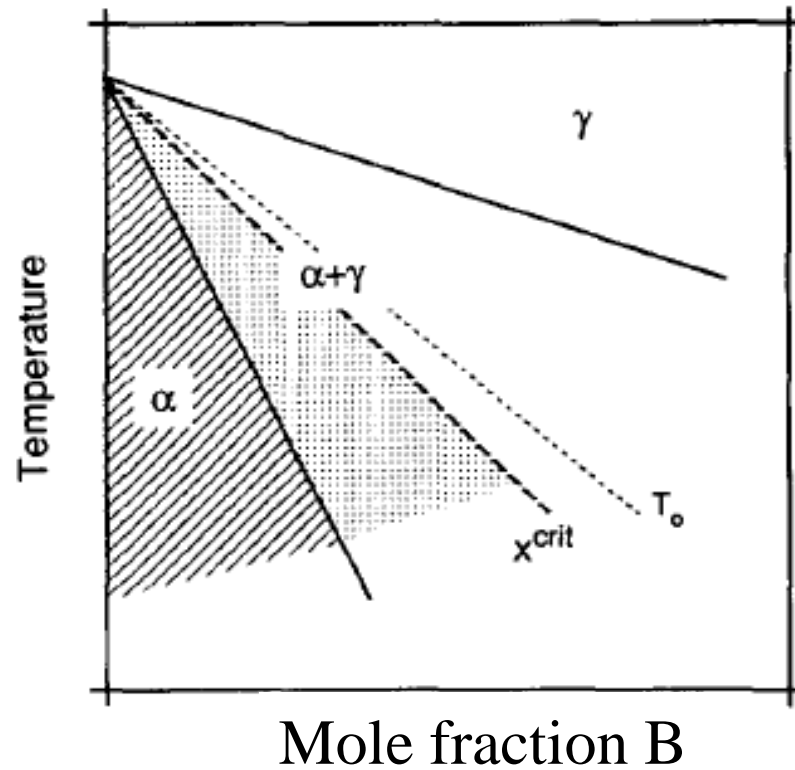


# Simulation of diffusional growth with composition gradient (Larsson 2005)

$\alpha$  nucleates here



# Kinetic limit for partitionless transformation



Jönsson and Ågren 1990



## One conclusion:

It is not possible to have a slow (compared to rate of diffusion) diffusionless reaction, i.e. a diffusionless reaction has to be very fast compared to the rate of diffusion.



## 6. Application to bainite in steel

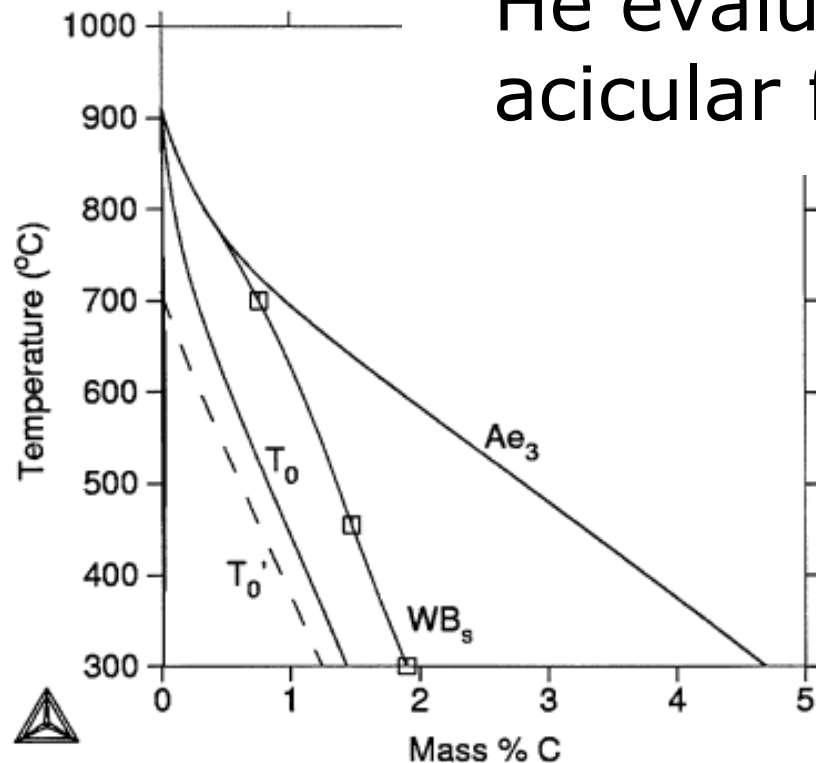
- the crystallographic aspects are those of a displacive transformation.
- the microstructure formed at low temperatures looks similar to martensite

But ...

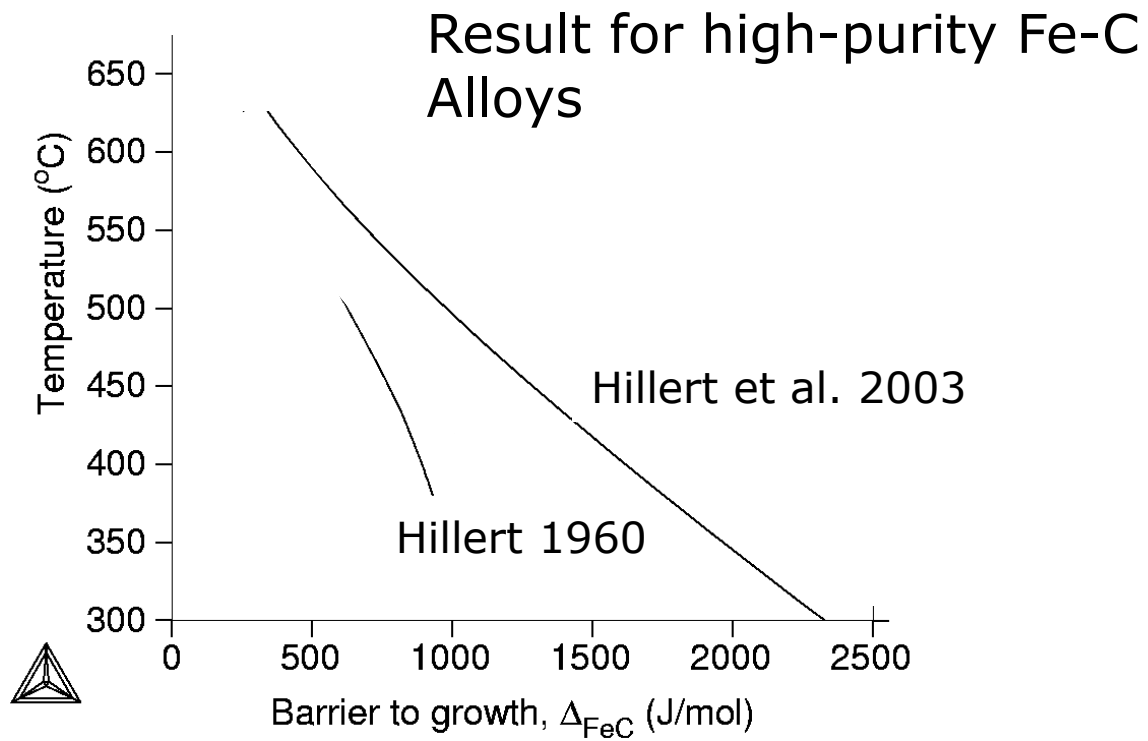
- The kinetics is much slower and similar to what is expected for C-diffusion control.

# Thermodynamic limit for bainite

1960 – Hillert analyzed experimental growth rates of Widmanstätten ferrite and upper bainite in high-purity Fe-C. He evaluated the temperature where acicular ferrite could start growing.

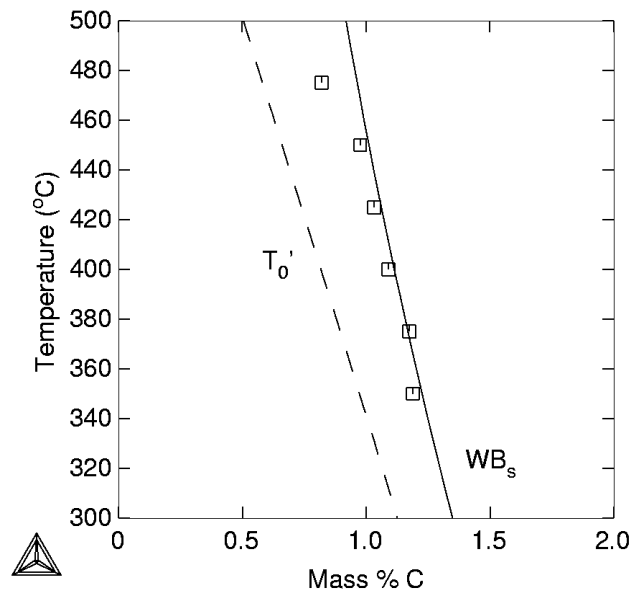


# Assume C partitioning:



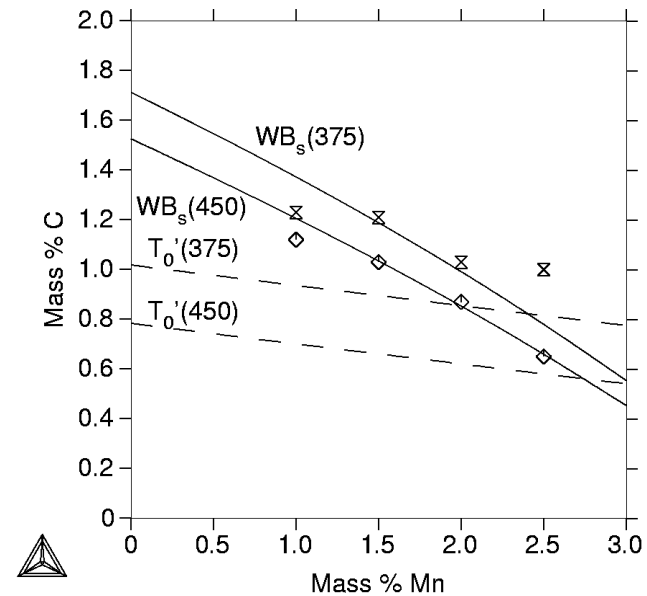
For alloys assume the same barrier and para equilibrium

1.51Si 1.51 Mn.



Exp. data from Sugimoto et al (2000)

1.51Si



Exp. data from Sugimoto et al (2002)



## Conclusions

A reaction that is slow enough to allow diffusion can never be diffusionless.

A displacive reaction can be diffusional or diffusionless.

The bainitic reaction is an example of displacive reaction that is controlled by the rate of carbon diffusion.