Effect of bainite reaction and carbides precipitation on the carbon redistribution during Q&P process

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June 27, 2017

Outline

1. Experimental results

2. Modeling effect of competitive reactions in the carbon redistribution

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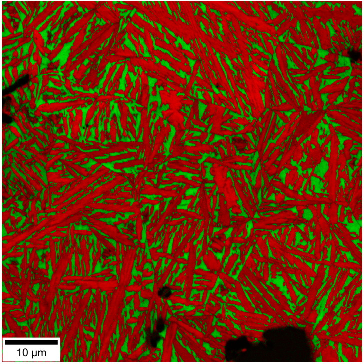
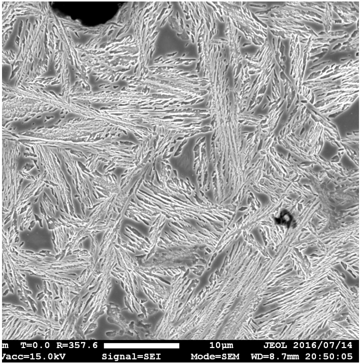
Experimental results

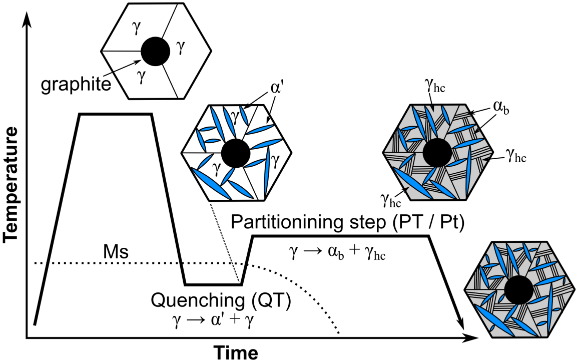
- Cast iron literature: ADI (austempered ductile iron), α_b + high carbon γ
- Microstructure confers very good ductility and high strength (TRIP effect)





Experimental results

- Cast iron literature: ADI (austempered ductile iron), α_b + high carbon γ
- Microstructure confers very good ductility and high strength (TRIP effect)
- Q&P has been proposed as alternative to produce similar microstrutures



Experimental results

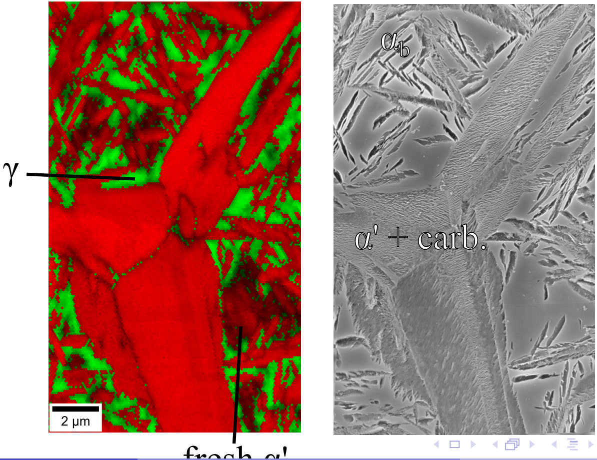
Element	C	Si	Mn	Cu
Comp. as-cast (wt.%)	3.5	2.5	0.2	0.4
Comp. @ 880 °C (wt.%)	**0.76**	2.54	0.21	0.39

- Quenching at 170 °C ($\approx$ 50% martensite)
- Partitioning at 300, 375, and 450 °C up to 2h

Experimental results

- Final microstructures constitutes of tempered martensite, bainitic ferrite, and austenite
- Carbides in α' and α_b are observed for times as short as 30 s @ 375 °C

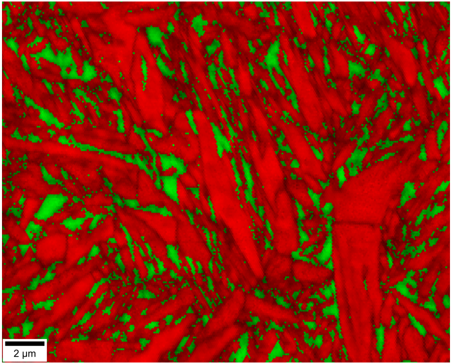
170/375 °C - 30 s

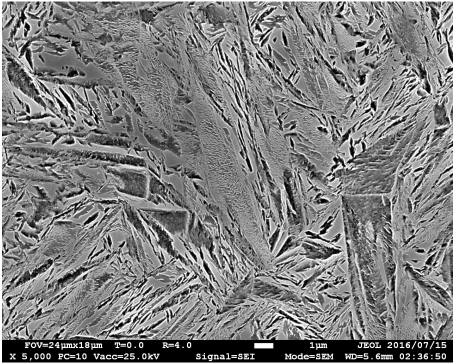


Experimental results

- For longer times fresh martensite is no longer formed during final cooling

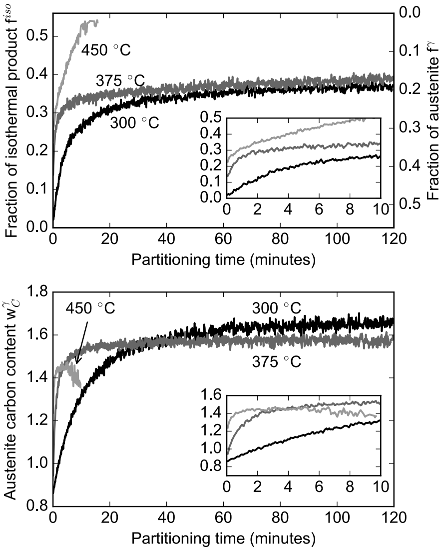
170/375 °C - 15 min





Experimental results

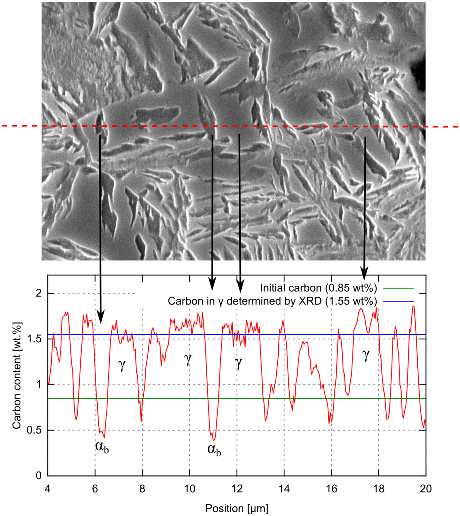
- In situ XRD shows γ carbon enrichment followed by bainite reaction



Experimental results

170/375 °C - 15 min

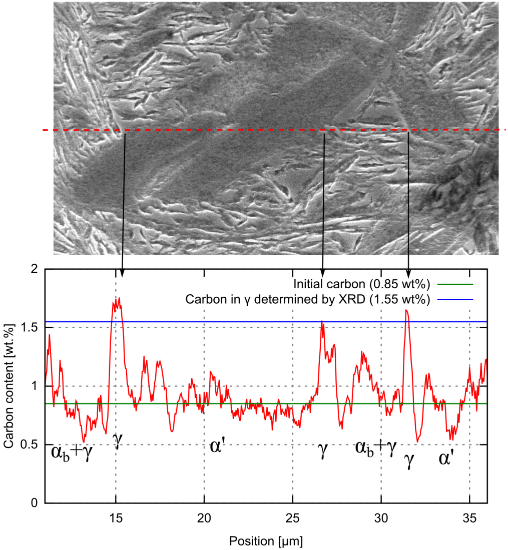
- Carbon partitioning locally observed by EPMA
- Results in good agreement with XRD data



Experimental results

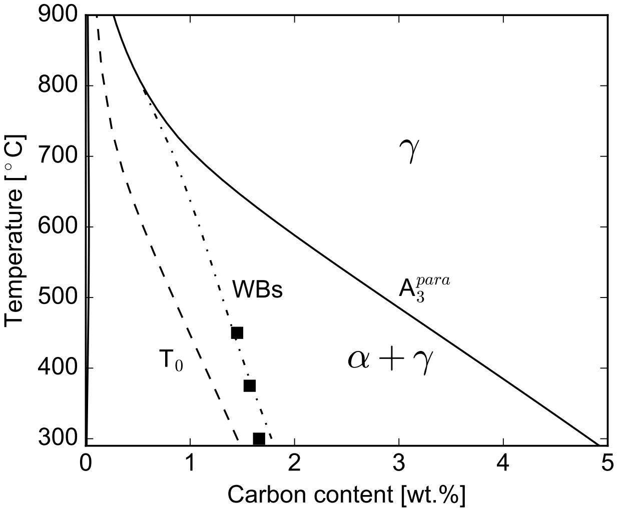
170/375 °C - 15 min

- Carbon partitioning locally observed by EPMA
- Results in good agreement with XRD data
- Average C in a α' is still high due to presence of carbides



Results - WBs theory

- Maximum austenite carbon content achieved during partitioning step agrees with Hillert's WBs limit (Hillert, 2004)



Summary - experimental results

- As a big part of carbon remains trapped inside the martensite plates in the form of carbides, results strongly suggest that bainite reaction is main mechanism of carbon enrichment of austenite
- Bainite reaction easily occurs in this alloy because of low Mn and presence of martensite, which accelerates the reaction

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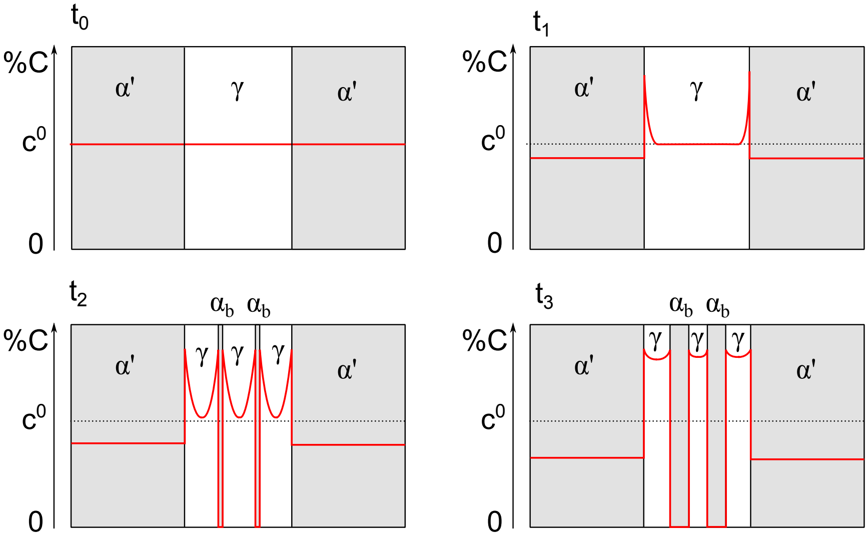

t0
%C
c0
0
α'
γ
α'
t1
%C
c0
0
α'
γ
α'
t2
%C
c0
0
α'
αb αb
γ γ γ
α'
t3
%C
c0
0
α'
αb αb
γ γ γ
α'

- Could soft impingement of diffusion fields slow down the carbon partitioning from martensite to austenite?
- This problem is addressed by means of numerical simulations by solving 1D diffusion equations (using Finite Differences Method – FDM)
- Problem is divided in 2 parts...
  - α'/γ carbon partitioning
  - formation of bainitic ferrite (α_b)
- ...then couple them together

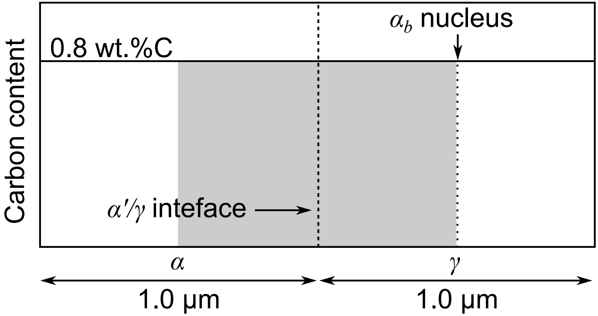
Approach for α'/γ C partitioning

- Mujahid and Bhadeshia, 1992; Hillert et al, 1992; Santofimia et al., 2008, 2009
- Thermodynamical data obtained from TCFE8 for Fe-2.54Si-0.21Mn-0.39Cu-C system
- $\mu_C^\alpha = \mu_C^\gamma$ (CCE, Speer et al, 2003), mass balance at the interface $J_C^\alpha = J_C^\gamma \Rightarrow D_C^\alpha \nabla c_i^\alpha = D_C^\gamma \nabla c_i^\gamma$
- Immobile α'/γ interface
- Fick's 2nd law numerically solved in austenite using finite differences method.

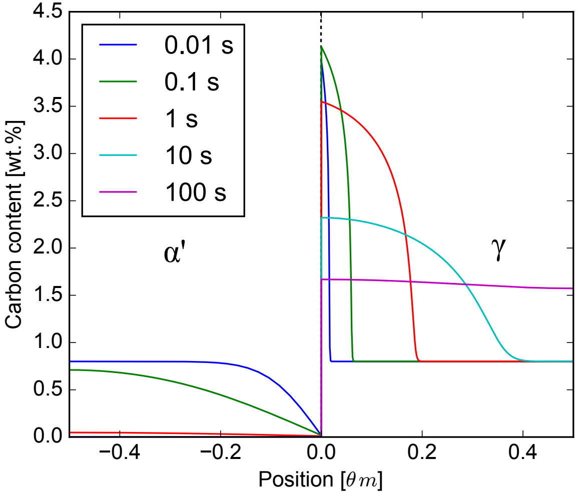
$$\frac{\partial c}{\partial t} = \frac{d}{dz}\left(D\frac{dc}{dz}\right)$$

α'/γ C partitioning

- **T = 375 °C; c_0 = 0.80 wt.%**
- Martensite plate with half-width = 0.5 μm according to martensite microstruture of cast iron

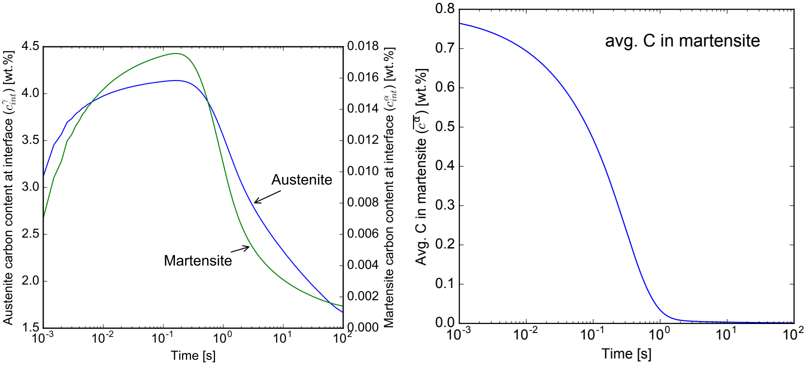


T = 375 °C; 0.80 wt.%



- Drop of carbon in α' at the interface; spike of carbon in γ

T = 375 °C; 0.80 wt.%

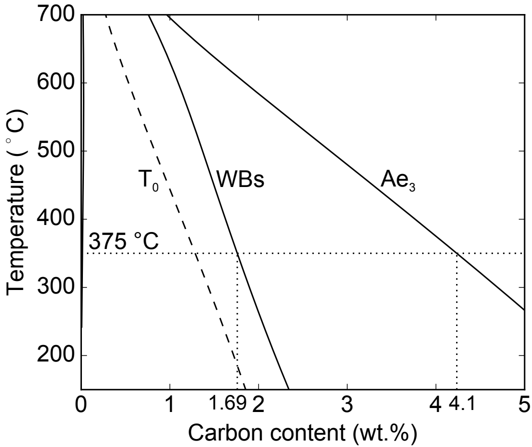


- Carbon partitioning controlled by diffusion of carbon in α'

Approach for formation of bainitic ferrite

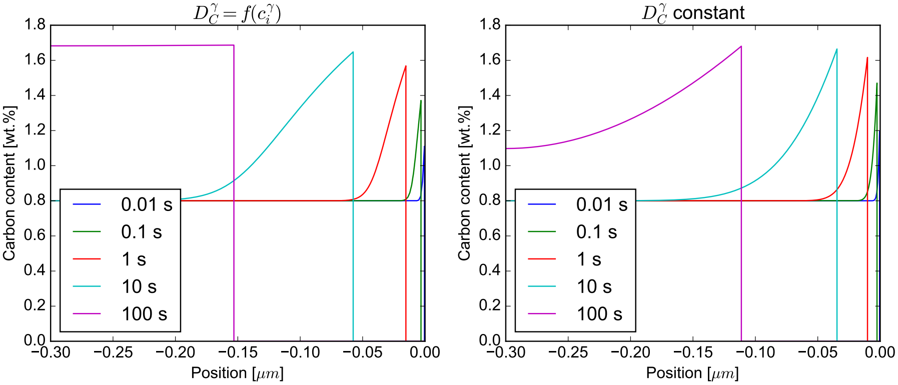
- Plate thickening
- Interface movement calculated using mixed-mode approach ($v = M\Delta G/V_m$)
  $M = 2 \times 10^{-4} \exp\left[\frac{-140\,000}{RT}\right]$ ($m^4 J^{-1} s^{-1}$) (Gamsjäger et al, 2006)
- C profiles are obtained solving Fick's second law
- Boundary condition at interface is established by the Stefan problem:
  $v\left(x_C^{\gamma/\alpha} - x_C^{\alpha/\gamma}\right) = J_C^{\gamma} - J_C^{\alpha}$

- Experimental data don't agree with paraequilibrium limits
- Very good agreement is obtained when comparing with Hillert's WBs theory (extra energy necessary for formation of bainitic ferrite is added to free energy curves)
- Modified chemical potentials following WBs was employed to calculate ΔG



Formation of bainitic ferrite

- **T = 375 °C**; c_0 **= 0.80 wt.%**
- Kinetics is faster when considering effect of carbon on D_C^γ



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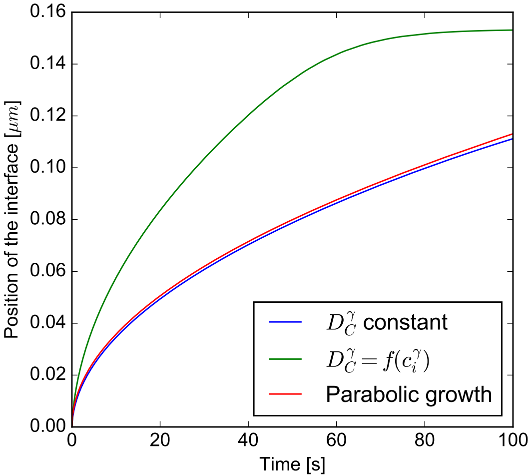
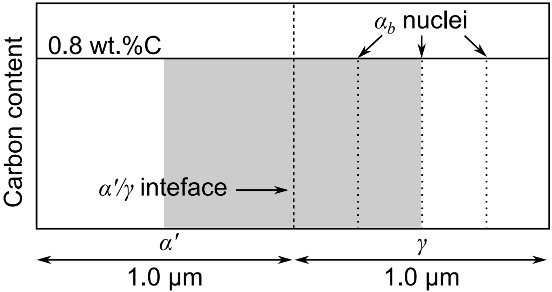


Coupling α'/γ carbon partitioning and bainite reaction

- Geometry estimated following microstructural characterization
- Martensite plate width: $1\,\mu m$; Untransformed austenite pool: $0.3\,\mu m$ (much coarser than in low carbon steels)
- **T = 375 °C; c_0 = 0.80 wt.%**



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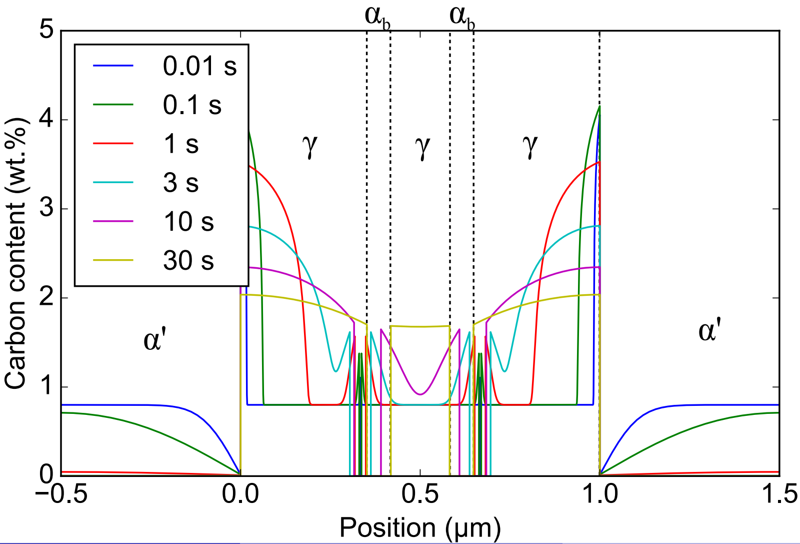
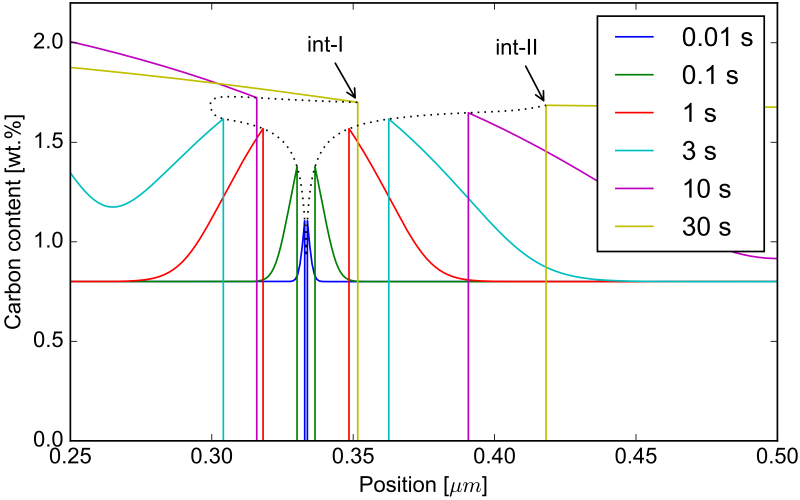


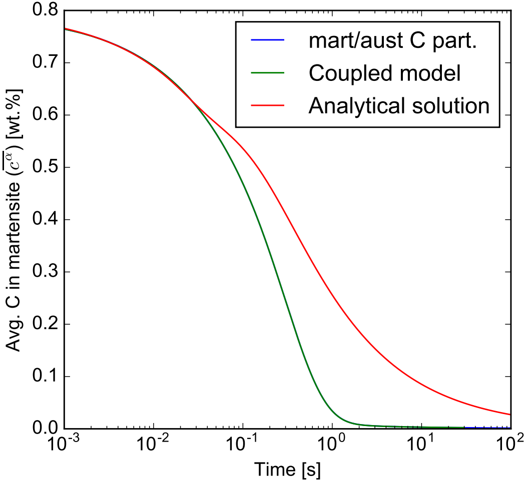
Coupling α'/γ carbon partitioning and bainite reaction

- Soft impingement leads to negative ∇c at vicinity of α_b/γ interface. This causes reversion of movement of interface



Coupling α'/γ carbon partitioning and bainite reaction

- Presence of bainitic ferrite doesn't affect kinetics of carbon partitioning from α' to γ, as c_i^{α} rapidly drops to 0.



Modifying coupled model to include carbides precipitation

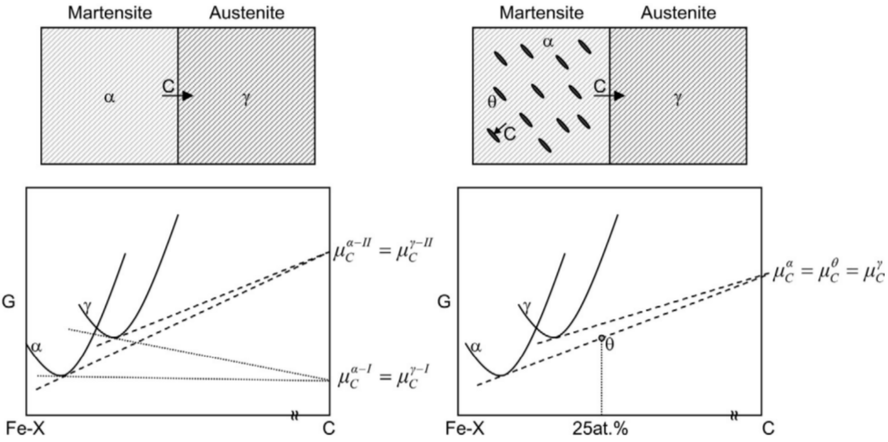
- Boundary conditions at α'/γ are problematic. Presence of carbides in α' might affect interfacial compositions
- Toji, Miyamoto and Raabe, 2015[1]: CCEθ. Carbides (cementite) are in metastable equilibrium with martensite and martensite

$$\mu_i^{\alpha'} = \mu_i^{\theta} \qquad \text{where } i = (C, Si, Mn, Fe)$$
$$\mu_C^{\alpha'} = \mu_C^{\theta} = \mu_C^{\gamma}$$

- CCEθ has a unique solution. So CCEθ condition imply in fixed compositions at the interface.

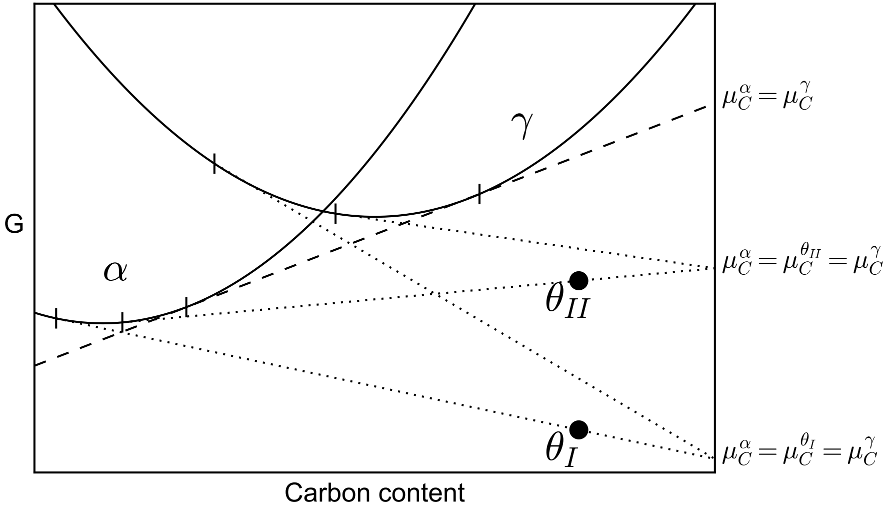
[1] Toji, Y., Miyamoto, G. & Raabe, D. Acta Mater. 86, 137–147 (2015).

CCEθ



Martensite
Austenite
α
C
γ
G
α
γ
$\mu_C^{\alpha-II} = \mu_C^{\gamma-II}$
$\mu_C^{\alpha-I} = \mu_C^{\gamma-I}$
Fe-X
C
Martensite
Austenite
α
θ
C
C
γ
G
γ
α
θ
$\mu_C^{\alpha} = \mu_C^{\theta} = \mu_C^{\gamma}$
Fe-X
25at.%
C

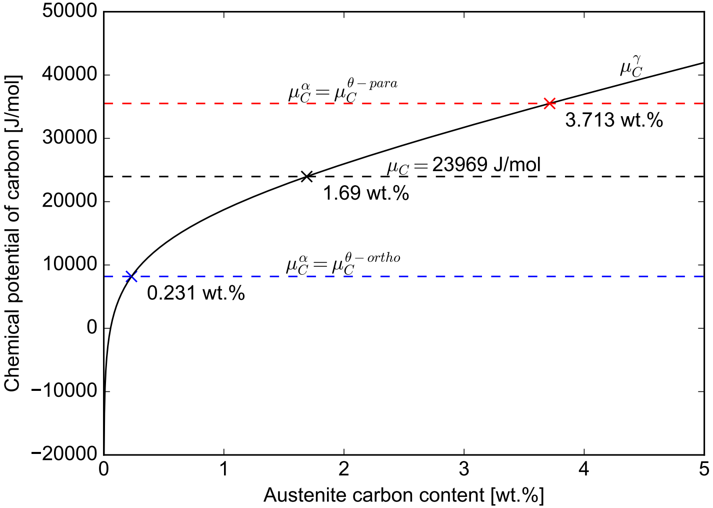
CCEθ



G
α
γ
θ_{II}
θ_I
$\mu_C^\alpha = \mu_C^\gamma$
$\mu_C^\alpha = \mu_C^{\theta_{II}} = \mu_C^\gamma$
$\mu_C^\alpha = \mu_C^{\theta_I} = \mu_C^\gamma$
Carbon content

Computing effect of carbides using CCEθ

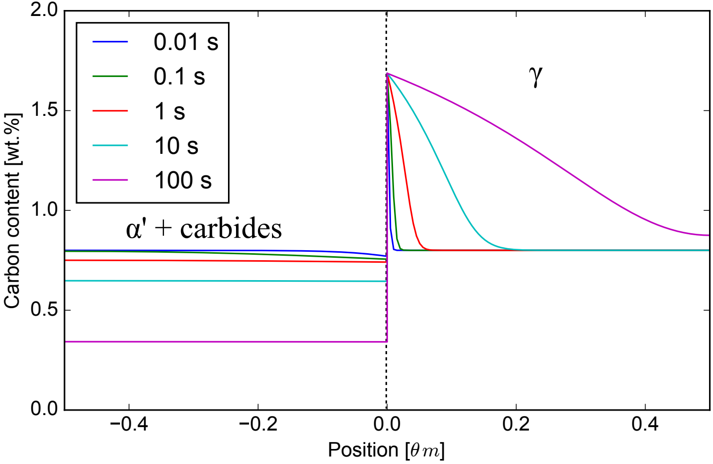
- CCEθ para, ortho cementite. Carbon content in austenite not reliable.



Computing effect of carbides using CCEθ

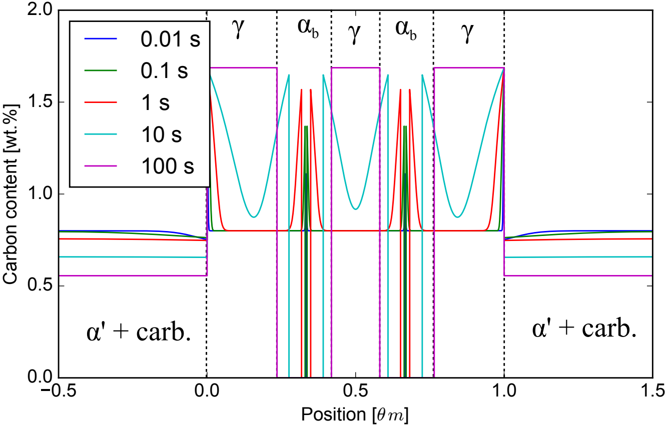
- $c_{int}^{\gamma} = 0.231\,\mathrm{wt.\%}$ is too low (would lead to decarburization of γ); $c_{int}^{\gamma} = 3.713\,\mathrm{wt.\%}$ is too high.
- Free energy of carbides could be wrong. No evidence that carbides are cementite; transition carbides are more probable (no thermodynamical data for them, though).
- Let's consider that the CCEθ condition provide a austenite composition equal to the value determined for the metastable equilibrium between bainitic ferrite and austenite, i.e., $1.69\,\mathrm{wt.\%}$.
- CCEθ is established at before partitioning step begins (as auto-tempering carbides).

Computing effect of carbides using CCEθ



Coupling α'/γ carbon partitioning and bainite reaction and carbides

- No reversion of the growth of the bainitic ferrite (no negative Δc)
- Stationary state established after 100 s. Carbon trapped in martensite ($c^{avg} \approx 0.55\,\mathrm{wt.\%}$)



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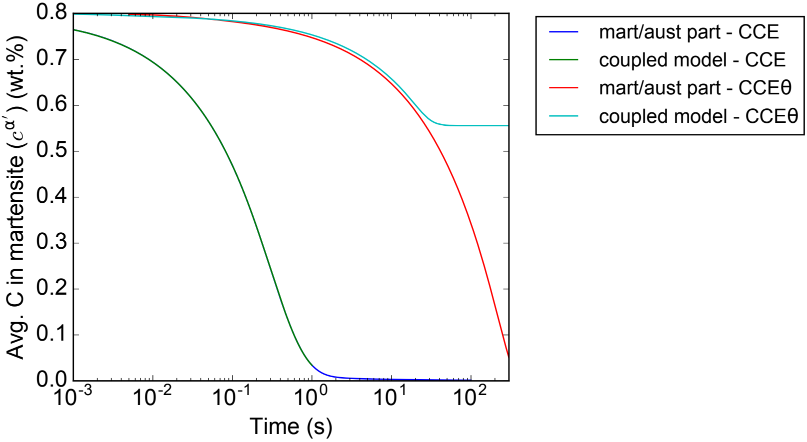

Summary

- Kinetics of decarburization of martensite plate varies with assumed boundary condition
- CCE: Controlled by diffusion of carbon in martensite; Bainite has no effect in the mart/aust carbon partitioning
- CCEθ: Controlled by diffusion of carbon in austenite; Bainite causes carbon partitioning to cease, trapping carbon inside martensite as undissolved carbides

Thank you!