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Modelling of grain boundary cementite growth kinetics in hypereutectoid steels by conventional and autocatalytic ledge growth approaches

Marko Vogric [1,2], Ernst Kozeschnik [2], Jiří Svoboda [3], Sabine Zamberger [4], Erwin Povoden-Karadeniz [1,2]

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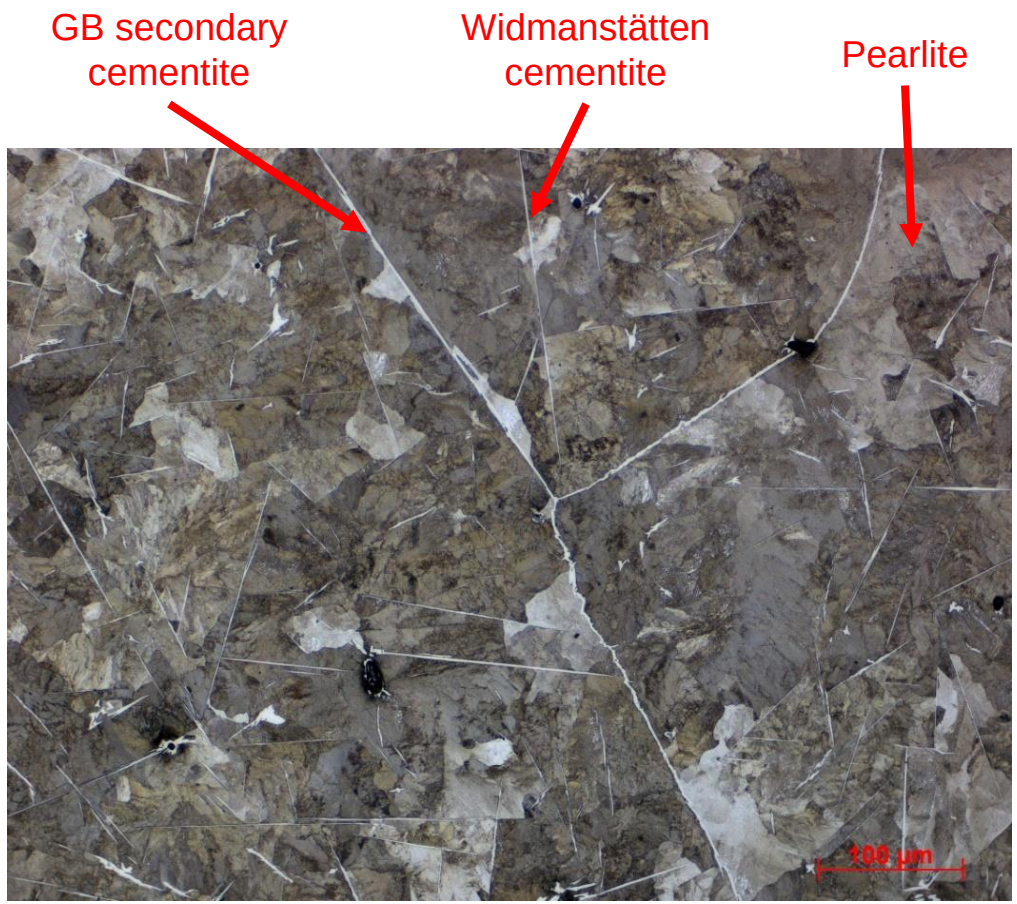
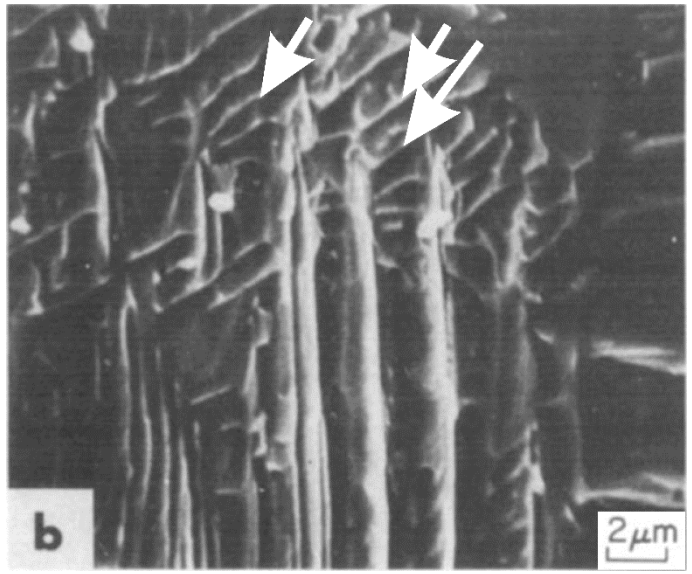
[1] Christian Doppler Laboratory for Interfaces and Precipitation Engineering CDL-IPE, TU Wien, Vienna, Austria
[2] Institute of Materials Science and Technology, TU Wien, Vienna, Austria
[3] Institute of Physics of Materials, Academy of Science of the Czech Republic, Brno, Czech Republic
[4] voestalpine Forschungsservicegesellschaft Donawitz GmbH, Leoben, Austria

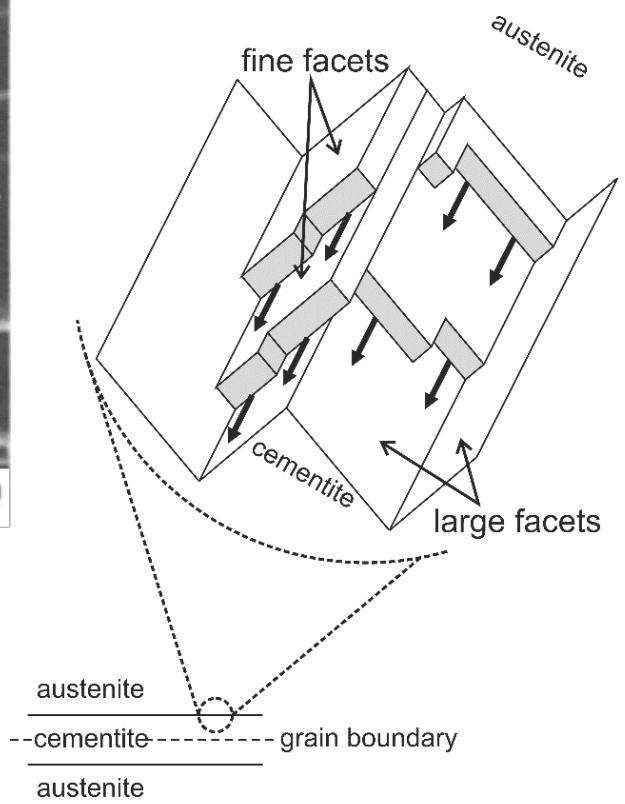
The microstructure of hypereutectoid steels



Bright field light microscopy micrograph of an as-cast hypereutectoid steel (1.2wt%C – 1wt%Mn – 1wt%Cu), 200x magnification



SEM micrograph of cementite ledges [1]



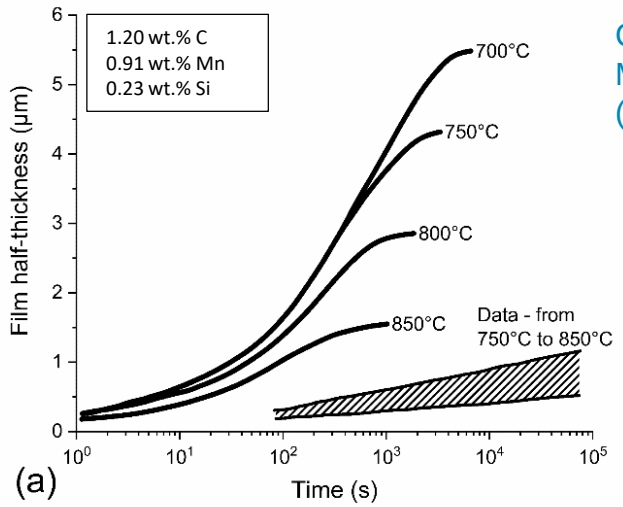
Schematic representation of the stepped austenite/cementite interface

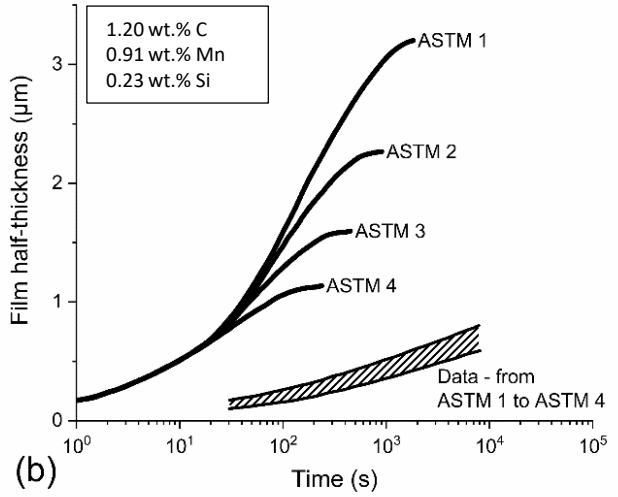
Two relevant parameters for grain boundary (GB) cementite:

- **GB cementite thickness**
- GB cementite continuity

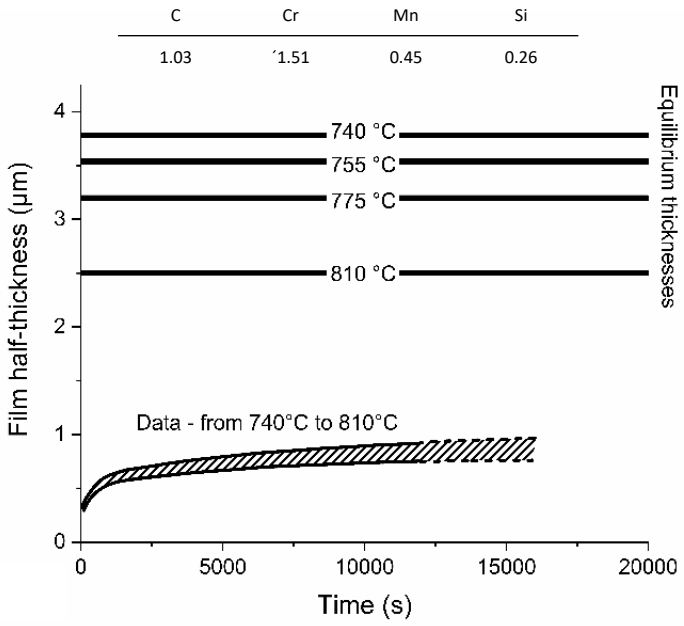
[1] Ando, Krauss, Acta Metall., 29, 1981, 351-363

State of the art – GB cementite thickening

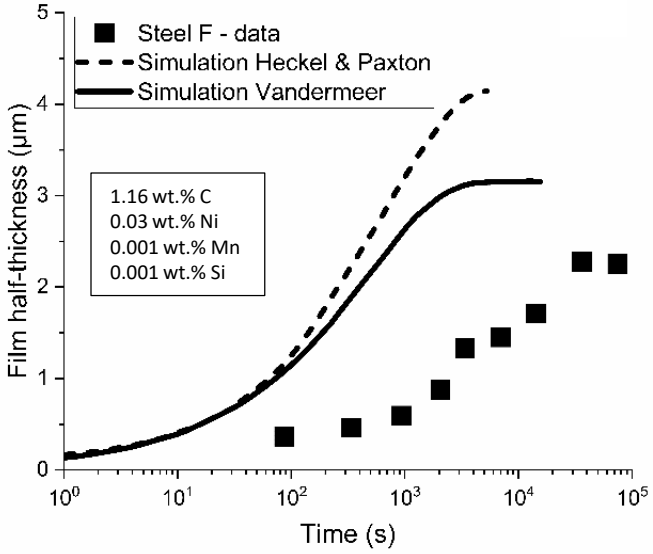




Cementite half-thickness for a Fe–C–Mn–Si steel for different temperatures (a) and grain sizes (b) (redrawn from [1])



Experimental vs. equilibrium cementite half-thickness for a AISI 52100 steel (redrawn from [2])



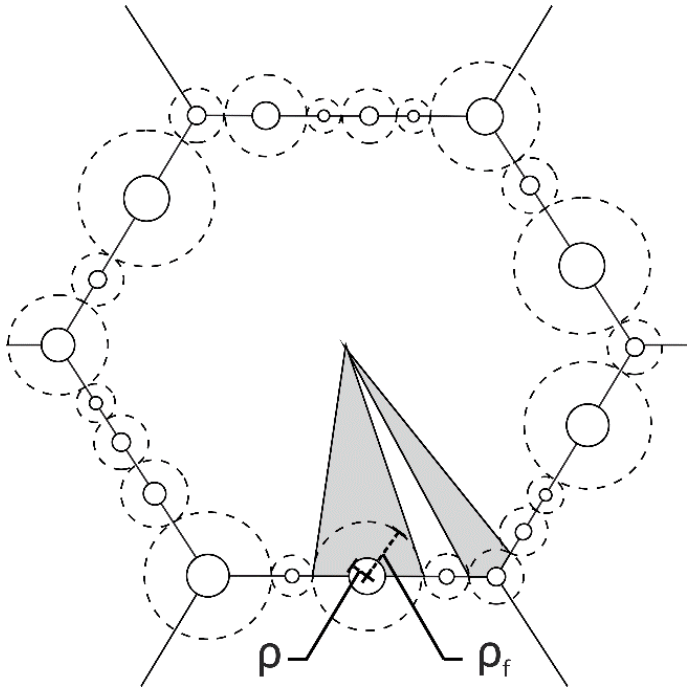
Experimental cementite half-thickness for an almost pure Fe–C steel and simulations by the Heckel & Paxton [1] or Vandermeer [3] models (redrawn from [3])

[1] Heckel, Paxton, Trans. AIME, 218, 1960, 799-806

[2] Ando, Krauss, Acta Metall., 29, 1981, 351-363

[3] Spanos et al., Metall. Trans. A, 22, 1991, 1367-1380

1st approach: Precipitate nucleation and growth – Model



Schematic precipitate distribution and diffusion fields

Precipitation of cementite spheres at austenite GB:

- Classical nucleation theory

$$J = NZ\beta^* exp\left(\frac{-G^*}{k_B T}\right) exp\left(\frac{-\tau}{t}\right)$$

- SFFK model for size & chemical evolution of precipitates [1,2]
- Conical diffusion fields & fast GB diffusion [3]
- Interface energy calculated from the Generalized Broken Bond model [4]
- Energy gain at heterogeneous nucleation sites [5]

$$\Delta G_{nucl} = \frac{4}{3}\pi\rho^3 \Delta G_{vol} + 4\pi\rho^2\gamma - \Delta G_{het}$$

- Nuclei composition control criterion: maximum nucleation rate
- Reduced nucleation site efficiency

➡ growth-controlled evolution of precipitates, no influence of coarsening

Simulations on the software MatCalc (v6.04) with mc_fe open thermodynamic & diffusion databases

[1] Svoboda et al., Mater. Sci. Eng. A, 385, 2004, 166-174

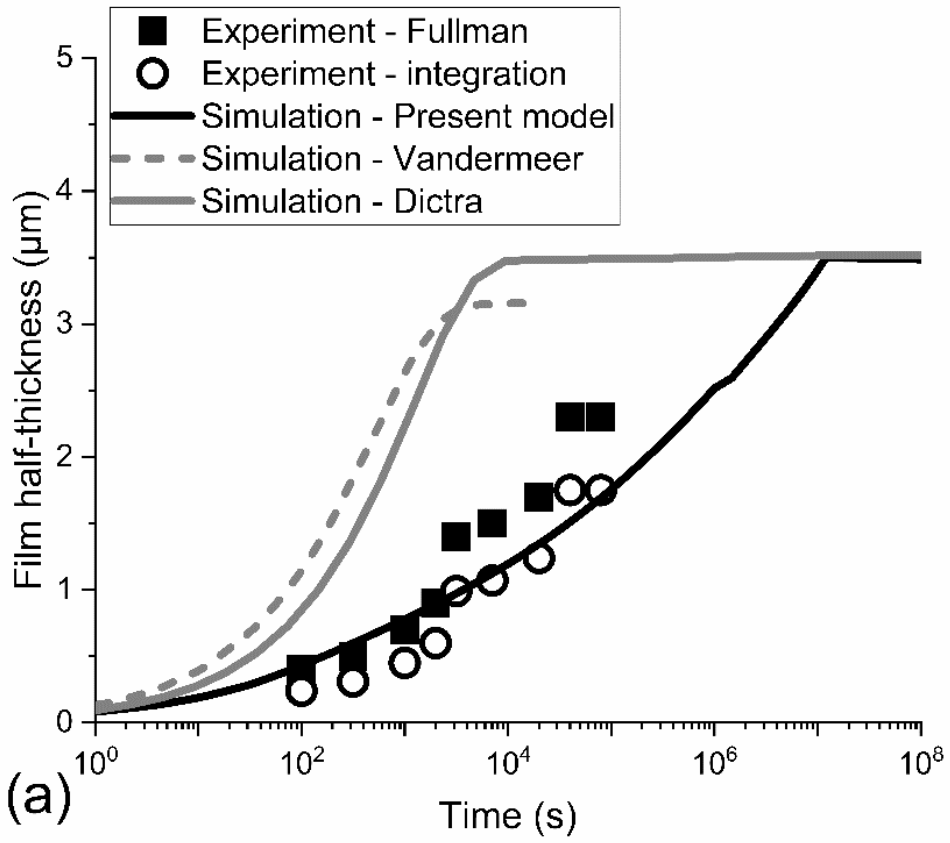
[2] Kozeschnik et al., Mater. Sci. Eng. A, 385, 2004, 157-165

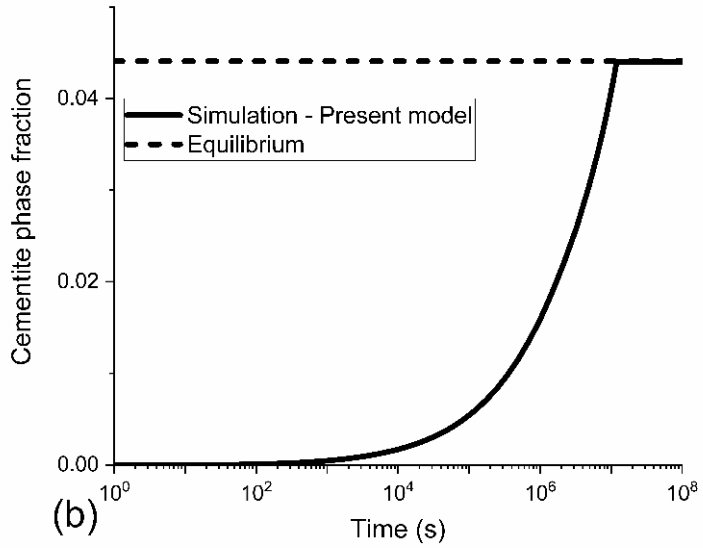
[3] Kozeschnik et al., Model. Simul. Mater. Sci. Eng., 18, 2010, 015011

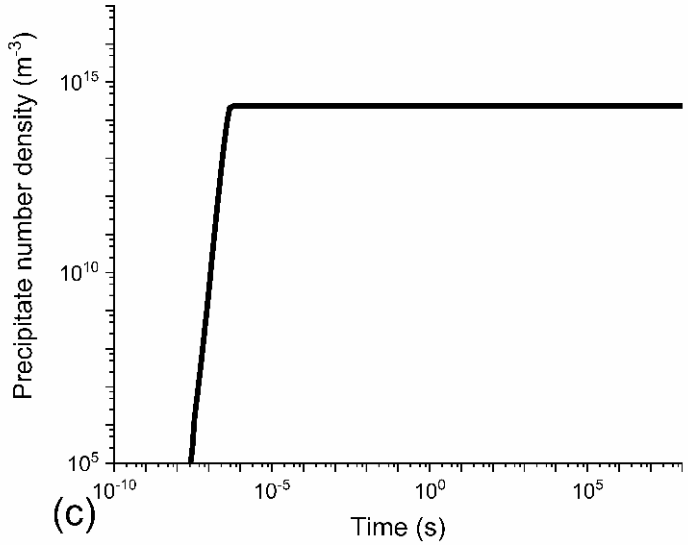
[4] Sonderegger, Kozeschnik, Metall. Mater. Trans. A, 40, 2009, 499-510

[5] Miesenberger et al., unpublished research

1st approach: Precipitate nucleation and growth – Results

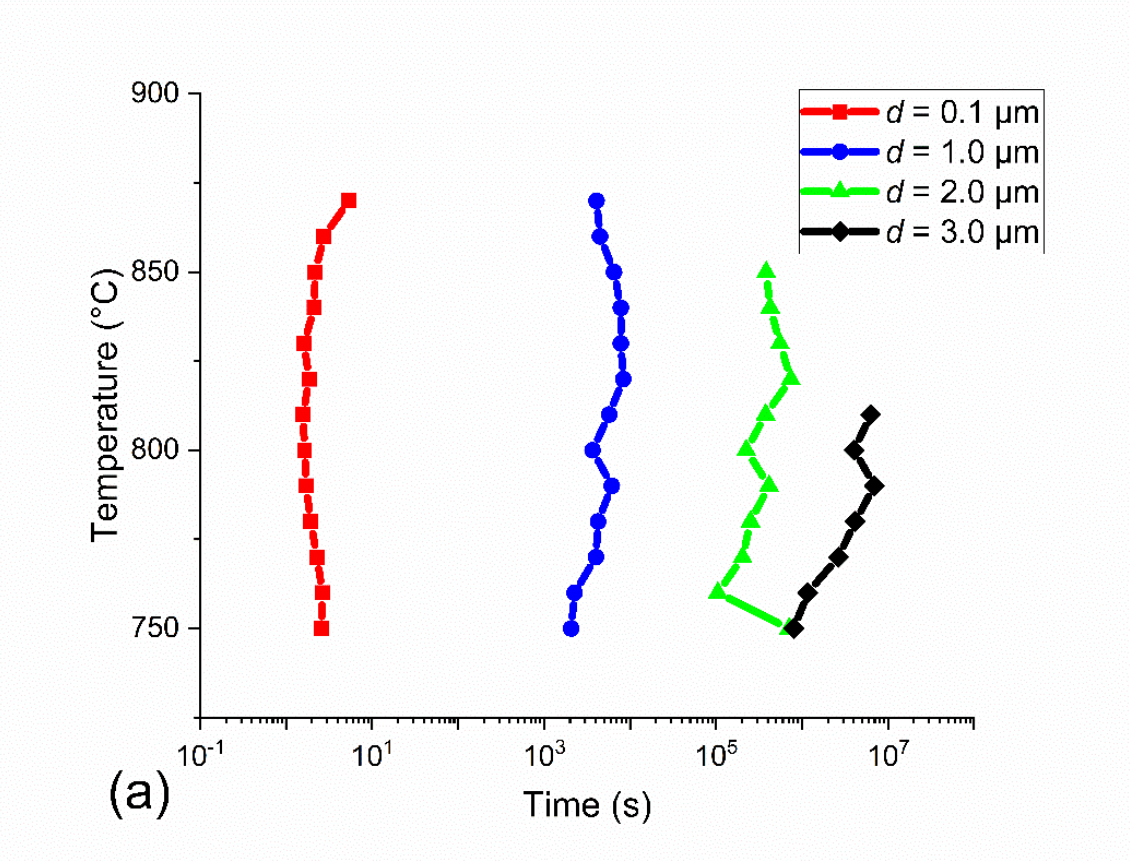


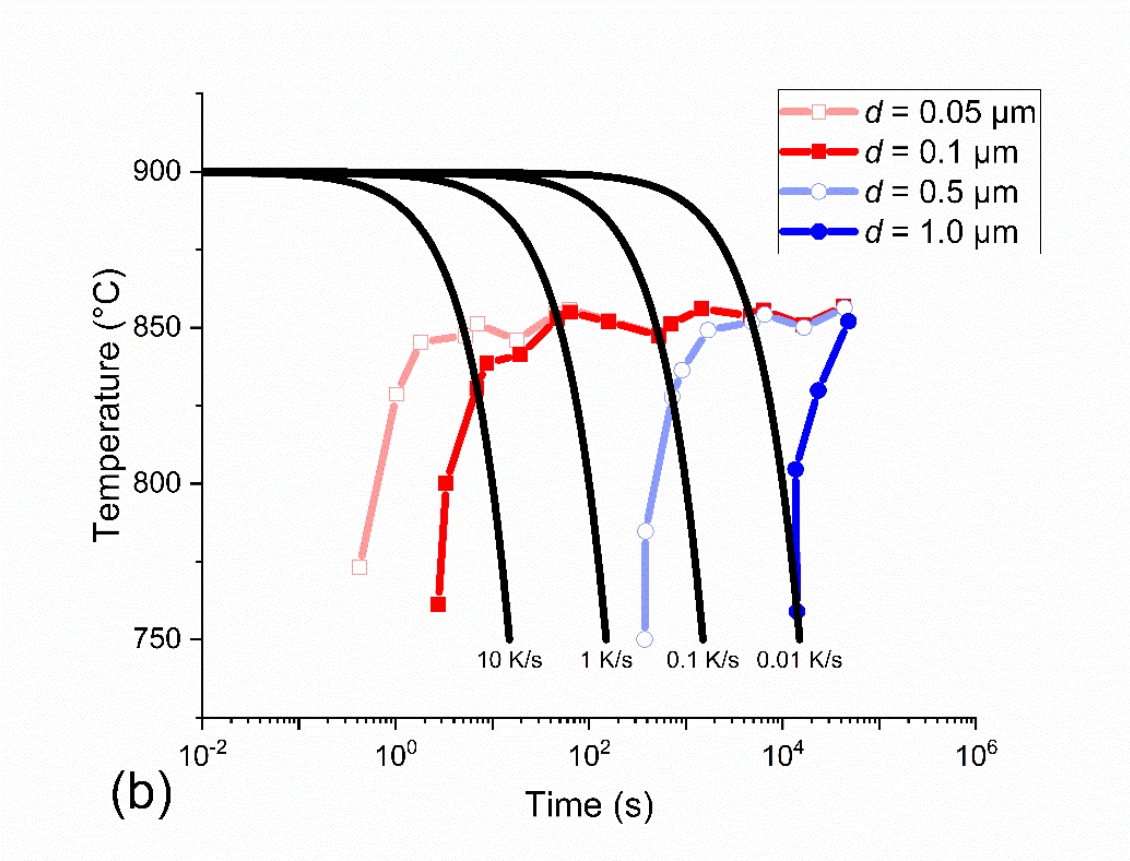




Experimental and simulated time evolution of grain boundary cementite half-thickness (a); Equilibrium and simulated cementite phase fraction (b); Simulated precipitate number density (c)

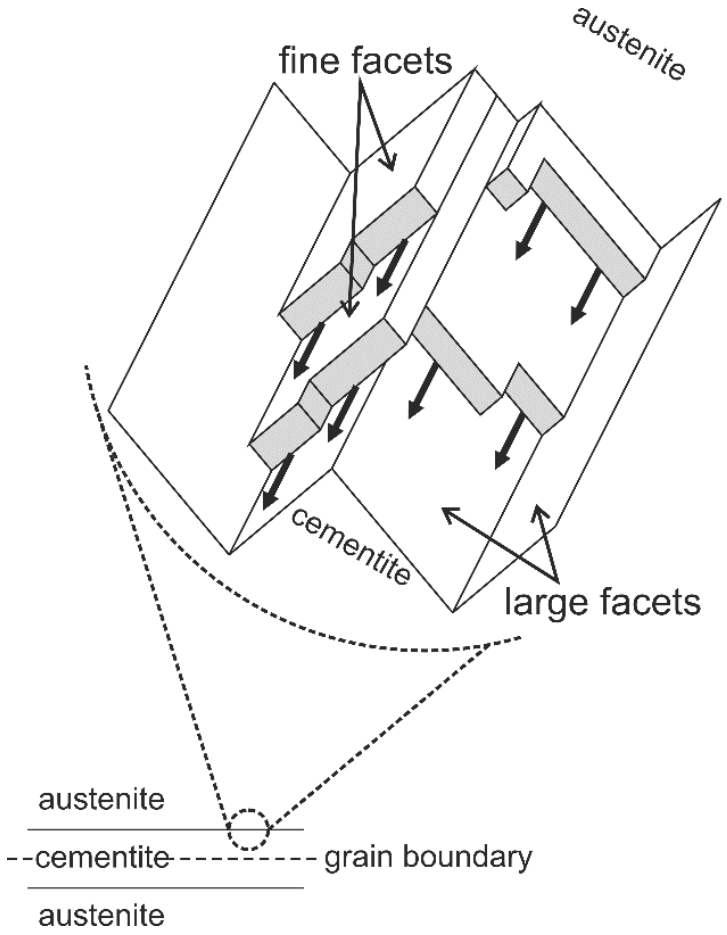
1st approach: Precipitate nucleation and growth – Predictive TTP/CCP diagrams





Simulated TTP (a) and CCP (b) diagrams for different values of half-thickness *d*

Second approach: Autocatalytic ledgewise growth – Model



Control of the thickening kinetics by the ledge formation rate:

- Assuming all ledges have the same height h = 7 nm

$$G_{\mathrm{L}} = hN_{\mathrm{L}}$$

$$N_{\mathrm{L}} = N_{\mathrm{L0}} \exp\left(\frac{-E_{\mathrm{eff}}}{k_{\mathrm{B}}T}\right)$$

G_L : Cementite thickening rate N_L : Ledge production rate

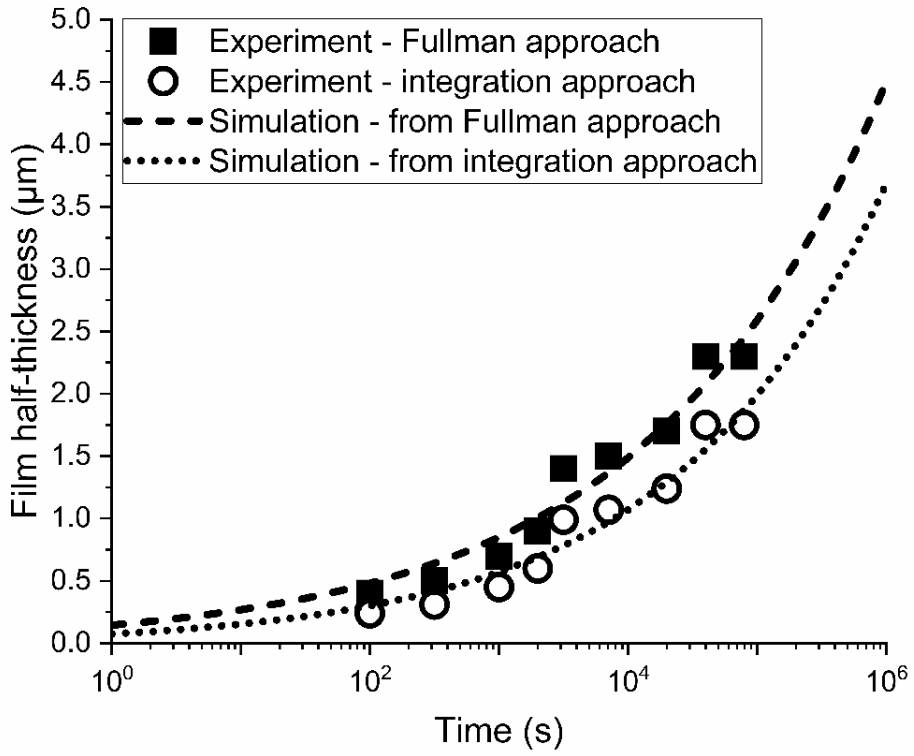
- E_{eff} is the effective energy barrier to ledge nucleation

$$E_{\mathrm{eff}} = \alpha \ln\left(\frac{t}{\tau_0} + 1\right)$$

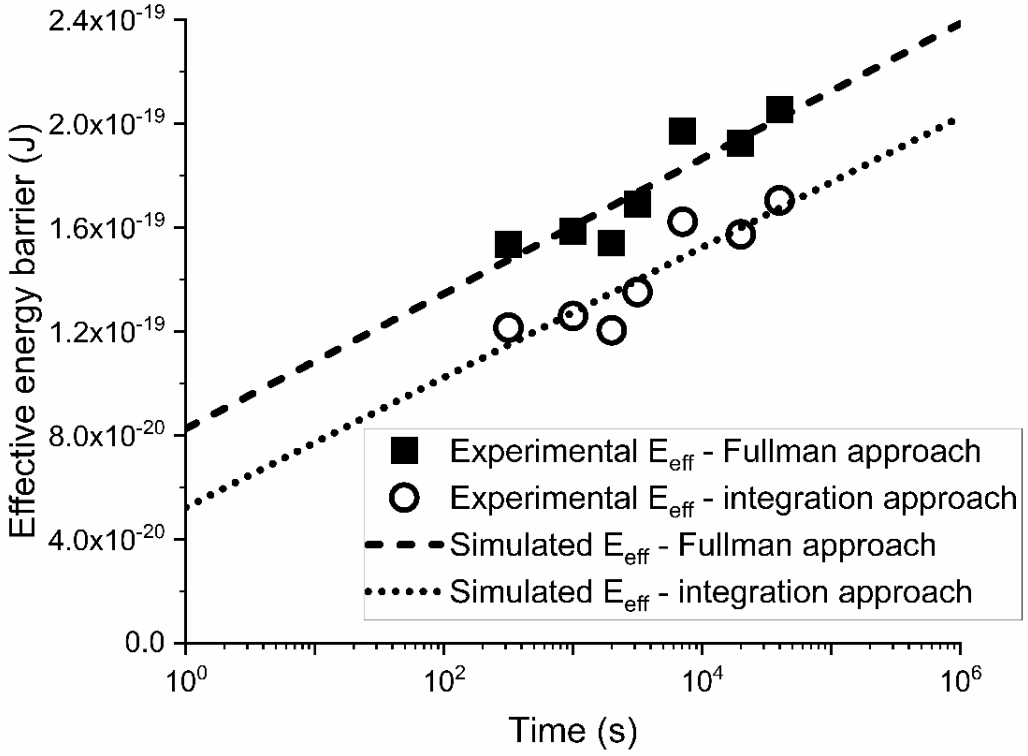
α : energy factor τ_0 : incubation time for the 1st ledge = $1/N_{L0}$

- (α, τ_0) determined from experimental data

Second approach: Autocatalytic ledgewise growth – Results



Experimental and simulated half-thickness from the Fullman and integration conversion approaches



Experimental and simulated effective energy barrier from the Fullman and integration conversion approaches

Conclusion & Outlook

Two modeling approaches:

- SFFK model for nucleation and growth of cementite GB precipitates
- Control of cementite thickness by ledge nucleation rate, dependent on time-dependent E_{eff}

Both models deliver significantly improved results compared to previous published models.

Next steps: linking ledge nucleation control to austenite & cementite thermodynamic and thermokinetic parameters

⇨ Understanding austenite/cementite interface evolution, local thickness variations or breaks in GB cementite continuity.

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MatCalc The Materials Calculator

MatCalc Engineering

voestalpine ONE STEP AHEAD.

Appendix: 2D/3D half-thickness conversion

Fullman approach [1]:

- Assuming spherical grains, homogeneous thickness and disc-like shape for the GB films
- BUT expression defined for derivation of disc thickness, not film thickness

$$d_{2D} = 2d$$

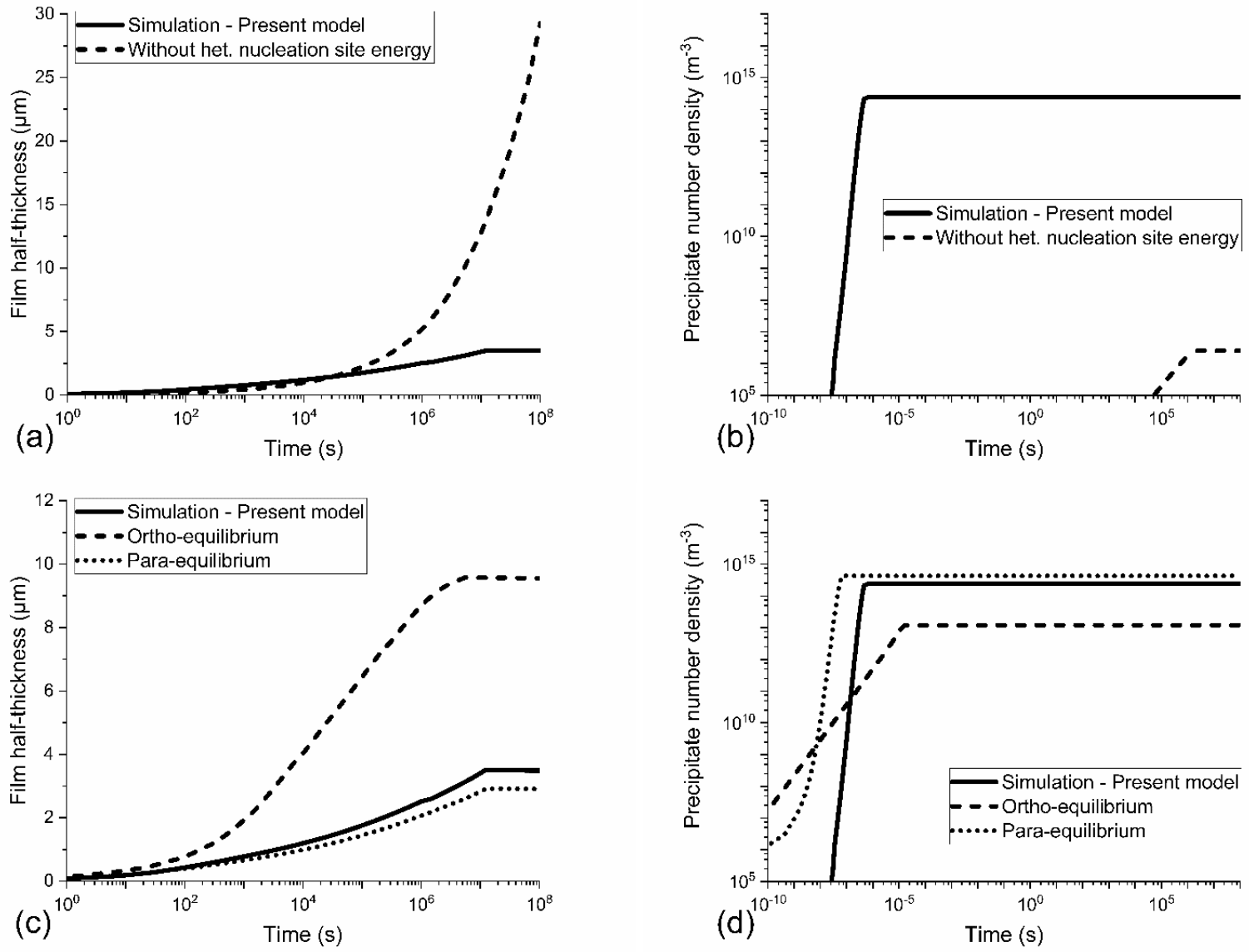
Integration approach:

- Assuming spherical grains and homogeneous thickness
- Based on the integration of the film half-thickness over the quarter of a circle perimeter

$$d_{2D} = \frac{2}{\pi}\int_0^{\frac{\pi}{2}}\left((R+d)\cos\cos\left(\frac{R\sin\sin\theta}{R+d}\right) - R\cos\cos\theta\right)d\theta$$

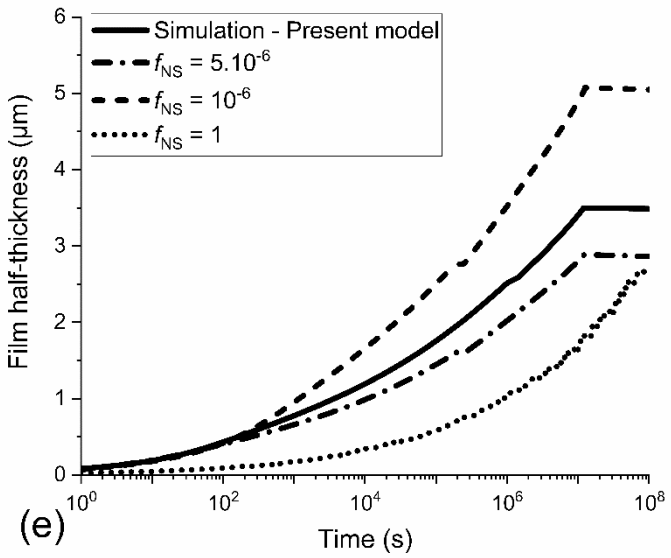
[1] Fullman, JOM, 5, 1953, 447-452

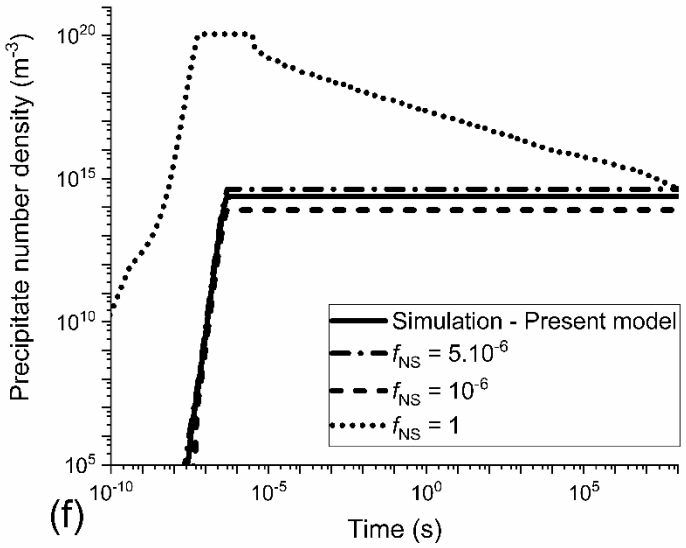
Appendix: 1st model – Influence of model parameters (1/2)

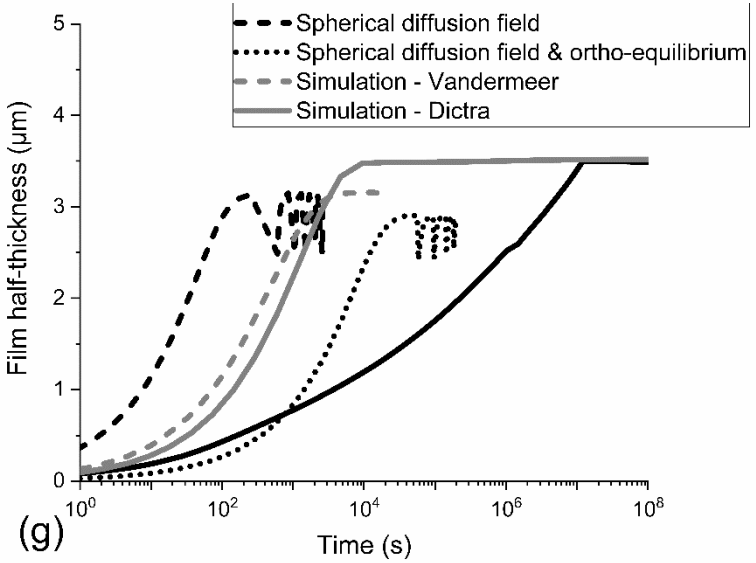


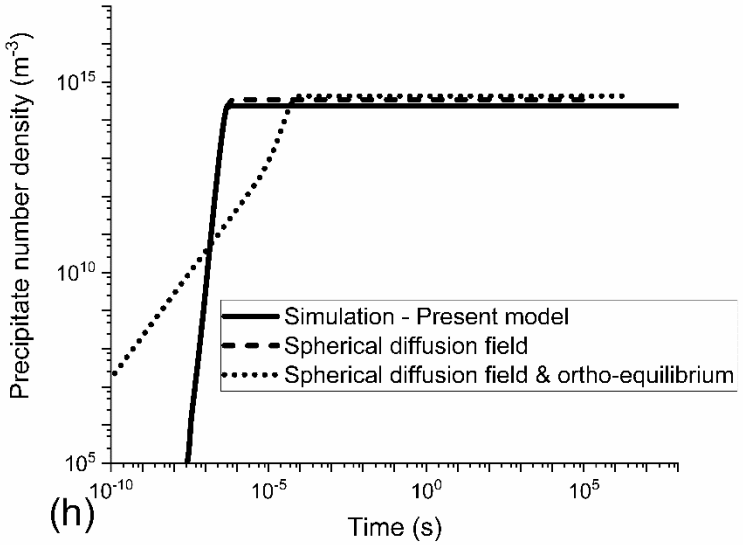
Simulated half-thickness and precipitate number density with or without energy gain at heterogeneous nucleation sites (a,b) and for different nuclei composition criteria (c,d)

Appendix: 1st model – Influence of model parameters (2/2)









Simulated half-thickness and precipitate number density for different values of nucleation site efficiency (e,f) and for different diffusion field geometries (g,h)