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

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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

Two relevant parameters for grain boundary (GB) cementite:
- GB cementite thickness
- GB cementite continuity

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])

1st approach: Precipitate nucleation and growth – Model

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]

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

- 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

[5] Miesenberger et al., unpublished research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

\[ G_L = hN_L \]

\[ N_L = N_{L0} \exp \left( \frac{-E_{\text{eff}}}{k_B T} \right) \]

$G_L$: Cementite thickening rate  \hspace{1cm} N_L$: Ledge production rate

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

\[ E_{\text{eff}} = \alpha \ln \left( \frac{t}{\tau_0} + 1 \right) \]

$\alpha$: energy factor  \hspace{1cm} \tau_0$: incubation time for the 1st ledge = $1/N_{L0}$

- $(\alpha, \tau_0)$ 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 $E_{\text{eff}}$

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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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

\[ d_{2D} = \frac{2}{\pi} \int_0^{\frac{\pi}{4}} \left( (R + d) \cos \cos \left( \frac{R \sin \sin \theta}{R + d} \right) - R \cos \cos \theta \right) \, d\theta \]

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