Theory guided and experimentally validated Materials Design

Gamsjäger ERNST (Austria)

Training School "Solutions for Critical Raw Materials in extreme conditions: from fundamental science to industrial innovations", Sofia, 6 - 8 February 2018
Lecture overview

• **Motivation:**
  Materials at extreme conditions → Microstructural changes → Material properties → Influence and possible substitution of CRMs

• **Thermodynamics and kinetics of microstructural changes**
  - Phase transformations and
  - Grain growth and coarsening.

• **Experimental verification**
  - High temperature laser scanning confocal microscopy (HT-LSCM),
  - Dilatometry,
  - In-situ high temperature X-ray diffraction.

• **Conclusions**
Motivation: Materials at extreme conditions

**EXTREME CONDITIONS:**
- **Temperature:** From mK to the melting point
- **Pressure:** From vacuum to several GPa
- **Corrosion**
- **Radiation (high level nuclear waste)**

**REQUIREMENTS:**
- Tensile Strength and impact strength, Creep resistance.
- High hardness and yield strength
- Good oxidation and corrosion properties
- Leach resistance, pouring temperature, no formation of yellow phases (molybdates)
Motivation: Materials at extreme conditions I

- Linepipe steels

turkstream.info
Motivation: Materials at extreme conditions II

- Large steam turbines
  (e.g. high temperature exposed, creep-resistant steels)

- High speed steels
  (e.g. Böhler S290)

Tools used under extreme compressive stresses (e.g. Precision blanking tools for high-strength materials.)

\[ \eta_C = 1 - \frac{T_2}{T_1} \]

Solidification of a high speed steel (S290)

Cooling rate: 0.08 K/s          Cooling rate: $10^4$ K/s (powder metallurgy)

Mass fractions in %:
2.0C, 0.3Mn, 0.4Si, **3.8Cr**, **2.5Mo**, 4.8V, **14.3W**, **11.0Co**.

*Mechanical properties: excellent toughness & machinability*

Improved heat treatment during tempering \(\rightarrow\) reduction of Co?
Grain growth (X80 linepipe steel)

Microstructures at high temperatures

$t_1 = 110s$

$t_2 = 610s$
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• Conclusions
Thermodynamic description of multi-particle systems

**System:** $6 \cdot 10^{23}$ particles

**Equations of motion**

- **Equilibrium thermodynamics**
  - $\mu = \mu(T, x)$

- (T, p const.)

  **Gibbs energy** $G = \text{min.}$

- **Balance equations and other constraints**
  - (Lagrange multipliers)

- **Equilibrium**

**Thermodynamics**

- of irreversible processes
  - $\mu_{\text{RVE1}} \neq \mu_{\text{RVE2}}$

- $\dot{q} = -\frac{D}{RT} \nabla \mu$

- **Dissipation** $Q = \text{max.}$

- **Evolution equations**
Phase transformations

\[ \text{\(\alpha\)-phase} \quad \text{\(\beta\)-phase} \]

\(\text{Va}\) substitutional components A, B, C

\(\text{\(\uparrow\\)}\) interstitial components
Maxima and Minima
(subject to constraints: Lagrange multipliers)

Determine: Extremum of $F(x_1, x_2, \ldots, x_N)$

$m$ constraints $g_j(x_1, x_2, \ldots, x_N) = 0$

$j = 1, 2, \ldots, m$; $(m < N)$

By Lagrange multipliers $\lambda_j$:

Extremum of $F + \sum_{j=1}^{m} \lambda_j g_j$

$N + m$ equations
for $m$ unknown $\lambda_j$
$N$ unknown $x_i$

Lagrange: Théorie des Fonctions Analytiques (p. 198, 1797)
Phase equilibrium
(binary system)
Phase equilibrium
(binary system)

Molar Gibbs energy of the system: \( g = g(x^\alpha, x^\beta, \xi) \)

\[
g = \xi g^\alpha + (1 - \xi) g^\beta
\]

Minimum!

Constraint: \( x_0 = \xi x^\alpha + (1 - \xi) x^\beta \)

\[
\Lambda = \xi g^\alpha + (1 - \xi) g^\beta + \lambda \left( x_0 - \xi x^\alpha - (1 - \xi) x^\beta \right)
\]

\[
\frac{\partial \Lambda}{\partial x^\alpha} = \frac{\partial \Lambda}{\partial x^\beta} = \frac{\partial \Lambda}{\partial \xi} = 0
\]

\[
\dot{\lambda} = \frac{\partial g^\alpha}{\partial x^\alpha} = \frac{\partial g^\beta}{\partial x^\beta} = \frac{g^\beta - g^\alpha}{x^\beta - x^\alpha}
\]

Principle of maximum dissipation $Q$

\[
\dot{G} = \sum_{i=1}^{N} \frac{\partial G}{\partial q_i} \dot{q}_i
\]

\[
Q = \sum_{i=1}^{N} \sum_{k=1}^{N} B_{ik} \dot{q}_i \dot{q}_k
\]

The extremal principle asserts that the rates $\dot{q}_i$ of the characteristic variables correspond to a maximum of the Gibbs energy dissipation $Q$ constrained by the energy balance $\dot{G} = -\dot{G}$ and by $m$ further constraints.

\[
\sum_{i=1}^{N} a_{ik} (q_1, ... , q_N) \dot{q}_i = 0
\]

\[
\frac{\partial}{\partial \dot{q}_i} \left[ \dot{G} + \lambda (Q + \dot{G}) + \sum_{k=1}^{m} \beta_k \sum_{i=1}^{N} a_{ik} \dot{q}_i \right] = 0
\]

\[
\frac{\partial}{\partial q_i} \left[ \dot{G} + \frac{Q}{2} + \sum_{k=1}^{m} \beta_k \sum_{i=1}^{N} a_{ik} \dot{q}_i \right] = 0
\]

\[
\sum_{j=1}^{N} B_{ij} \dot{q}_j + \sum_{k=1}^{m} a_{ik} \beta_k = -\frac{\partial G}{\partial q_i}
\]
Contact conditions at the sharp interface

Assumption: The amount of lattice vacancies is negligibly small, and so is the flux $j_{va}$.

Mass balance at the interface:

$[[a]] = a^o - a^n$

Substitutional diffusion:

$[[x_i/\Omega)]v = [[j_i]]$

$\sum_{i=1}^{s} j_i = -j_{va} \approx 0$
Contact conditions at the sharp interface

\[ \dot{G}_{\text{int}} = - \sum_{i=1}^{N} \frac{v}{\Omega} \cdot x_i^I[[\mu_i]] \]
\[ x_i^I = x_i^0 - \frac{j_i^0}{v} \Omega \]
\[ \dot{G}_{\text{int}} = \sum_{i=1}^{N} j_i^0[[\mu_i]] - \sum_{i=1}^{N} \frac{x_i^0}{\Omega} v[[\mu_i]] \]
\[ Q_{\text{int}} = \frac{v^2}{M} \]

Fluxes of the substitutional components \((i = 1, \ldots, s)\)

\[ \frac{\partial}{\partial j_i^0} \left[ \dot{G}_{\text{int}} + \frac{Q_{\text{int}}}{2} + \kappa \left( \sum_{k=1}^{s} j_k \right) \right] = 0 \quad \rightarrow \quad \kappa = -[[\mu_i]] \quad \rightarrow \quad [[\mu_1]] = [[\mu_2]] = \ldots = [[\mu_s]] \]

Contact conditions at the sharp interface

\[
\dot{G}_\text{int} = - \sum_{i=1}^{N} \frac{v}{\Omega} \cdot x_i^1[[\mu_i]]
\]

\[
x_i^1 = x_i^0 - \frac{j_i^0}{v}\Omega
\]

\[
\dot{G}_\text{int} = \sum_{i=1}^{N} j_i^0[[\mu_i]] - \sum_{i=1}^{N} \frac{x_i^0}{\Omega} v[[\mu_i]]
\]

\[
Q_{\text{int}} = \frac{v^2}{M}
\]

**Fluxes of the substitutional components** \((i = 1, \ldots, s)\)

\[
\frac{\partial}{\partial j_i^0} \left[ \dot{G}_\text{int} + \frac{Q_{\text{int}}}{2} + \kappa \left( \sum_{k=1}^{s} j_k \right) \right] = 0 \quad \Rightarrow \quad \kappa = -[[\mu_i]]
\]

\[
[[\mu_1]] = [[\mu_2]] = \ldots = [[\mu_s]]
\]

Contact conditions at the sharp interface

\[
\dot{G}_{\text{int}} = \sum_{i=1}^{N} j_{i}^{o}[[\mu_{i}]] - \sum_{i=1}^{N} \frac{x_{i}^{o}}{\Omega} v[[\mu_{i}]]
\]

\[Q_{\text{int}} = \frac{v^{2}}{M}\]

Fluxes (interstitial components \(i=s+1, \ldots, N\))

\[
\frac{\partial}{\partial j_{i}^{o}} \left[ \dot{G}_{\text{int}} + \frac{Q_{\text{int}}}{2} \right] = 0 \quad \rightarrow \quad [[\mu_{s+1}]] = [[\mu_{s+2}]] = \ldots = [[\mu_{N}]] = 0
\]
Contact conditions at the sharp interface

\[ \dot{G}_{\text{int}} = \sum_{i=1}^{N} j_i^0[[\mu_i]] - \sum_{i=1}^{N} \frac{x_i^0}{\Omega} v[[\mu_i]] \]

\[ Q_{\text{int}} = \frac{v^2}{M} \]

Interface velocity \( v \)

\[ \frac{\partial}{\partial v} \left[ \dot{G}_{\text{int}} + \frac{Q_{\text{int}}}{2} \right] = 0 \quad \rightarrow \quad v = \frac{M}{\Omega} \sum_{i=1}^{N} x_i^0[[\mu_i]] = M \Delta f \]
Sharp-interface and Quasi-sharp interface

Grain growth in a polycrystalline material

Grain boundary motion → decrease the total energy of grain boundaries in the system.

https://www.youtube.com/watch?v=J_2FdkRqmCAh

\[ G = \frac{1}{2} \gamma_b \sum_{k=1}^{n} 4\pi r_k^2 \]
\[ Q = \frac{1}{2M_b} \sum_{k=1}^{n} 4\pi r_k^2 \dot{r}_k^2 \]
\[ V = \sum_{k=1}^{n} \frac{4\pi r_k^3}{3} = \text{const.} \]

Constraints:
\[ \dot{G} = -Q \]
\[ \dot{V} = \sum_{k=1}^{n} 4\pi r_k^2 \dot{r}_k = 0 \]

Lagrange:
\[ \frac{\partial}{\partial \dot{r}_k} \left[ Q + \eta \left( \dot{G} + Q \right) + \xi \sum_{i=1}^{n} \pi r_i^2 \dot{r}_i \right] = 0 \; (k = 1,\ldots,n) \]

\[ \dot{r}_k = -2M_b \frac{1}{r_k} \left[ \frac{1}{r_k} - \frac{1}{r_{\text{crit}}} \right] = 0, \; (k = 1,\ldots,n) \]

Chemisches Potential $\mu$ in small systems

\[ U_{\text{surf.}} = 4r^2 \pi \gamma \]
\[ U_{\text{vol.}} = \frac{4r^3 \pi U_{m}}{3V_{m}} \quad \rightarrow \quad \frac{U_{\text{surf.}}}{U_{\text{vol.}}} = \frac{3\gamma V_{m}}{U_{m}} \cdot \frac{1}{r} \]

\[ dU = TdS - pdV + \mu dn = TdS - pdV + \mu_{\infty} dn + \gamma d\Sigma \]
\[ dU = TdS - pdV + \mu_{\infty} dn + \frac{2\gamma V_{m}}{r} dn \]

\[ \mu = \mu_{\infty} + \frac{2\gamma V_{m}}{r} \]
Ostwald-ripening
A process driven by diffusion
Materials at high temperatures

- Stable microstructure.
- Grain coarsening should be a very slow process.

\[ \bar{R}^3 - \bar{R}_0^3 = \frac{8D(T)\gamma V_m^{\beta} x_{\infty}^{\alpha}}{9RT} t \]

\( D, \gamma, x_{\infty}^{\alpha} \) (as small as possible)

Example 1: \( Y_2O_3 \)-precipitates in steels.

Beispiel 2: Automotive and aerospace industry:

Welding connections close to hot parts.
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  ➢ Dilatometry,
  ➢ In-situ high temperature X-ray diffraction.

• **Conclusions**
HT-LSCM
High temperature laser scanning confocal microscopy

Temperatures up to 1650°C, heating rates up to 50 K/s, 15 frames per second ⇒ dynamic processes.
Dilatometry
Migrating austenite / ferrite interface (LSCM and dilatometry)
Mass fractions in %:
0.06C, 1.7Mn, 0.034Nb, 0.012Ti, 0.24Mo.

Microstructures at 1250°C after different times c) $t = 110s$ and d) $t = 610s$. 
Grain growth by HTLSCM I

$t = 185s$
$\vartheta = 1006^\circ C$

Mean grain size = 9.5$\mu$m,
SD = 6.0$\mu$m
Grain growth by HTLSCM II

476s, 1251°C

Mean grain size = 35.9μm, SD = 25μm
Modeling the kinetics of a triple junction


\[
\gamma_k \sin(\alpha_k - \alpha_i) + \gamma_i \sin(\alpha_i - \alpha_k) = \frac{M_i}{M_T} \kappa \gamma_i
\]

\[i, j, k \ldots = 1, 2, 3 \text{ and } i \neq k, i \neq l, k < l\]

\[
v_{T,x} = -M_T \sum_{i=1}^{3} \gamma_i \cos \alpha_i
\]

\[
v_{T,y} = -M_T \sum_{i=1}^{3} \gamma_i \sin \alpha_i
\]
Motion of grain boundaries at triple junctions I

Triple junction motion at $\vartheta = 1205^\circ\text{C}$ within $\Delta t = 8\text{s}$:

$M_1 = 2, M_2 = 0.267, M_3 = 2.67, M_T = 0.067$.

Motion of grain boundaries at triple junctions II

Triple junction motion within $\Delta t = 8s$:

$$M_1 = 0.33, \ M_2 = 6.7 \cdot 10^{-5}, \ M_3 = 0.267, \ M_T = 0.033.$$  

Future project I

Experimental and theoretical grain growth investigations with different amounts of alloying elements (e.g. Nb).

- **Grain size distribution** as a function of $T$ and composition.
- **Motion of triple junctions** as a function of $T$ and composition.
- **Motion of whole structures** as a function of $T$ and composition.
In situ high temperature XRD

- **Motivation**
  - Mechanical properties: What are the underlying microstructural changes during processing?

- **In-situ X-ray diffraction**
  - Experimental setup
  - X-ray diffractograms and their numerical analysis
  - Microstructural changes in martensitic stainless steel
  - Microstructural changes in high speed steel

- **Noisy diffractograms**
  - Levenberg Marquardt versus Bayes-Theorem
  - Microstructural changes by means of global optimization

- **Comparison of the numerical results**

- **Conclusions**
Mechanical Properties:
What are the underlying microstructural changes during processing?

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>0.40</td>
<td>0.40</td>
<td>15.4</td>
<td>0.9</td>
<td>5.30</td>
</tr>
</tbody>
</table>

Martensitic stainless steel
Experimental setup
In situ high temperature X-ray diffraction (HT-XRD)

X-ray tube with a Göbel mirror to select Cr Kα_1 and Kα_2, parallel beam optic.

Position sensitive detector

Oven (Anton Paar)
Analysis of X-ray diffractograms I
(e.g. powder-metallurgically processed high speed steel)

Diffractogram
Peak areas → Phase fractions

Peak positions → Lattice parameters

Width of Peaks →
→ Crystallite size & lattice strain

Rietveld method combined with a

Fundamental Parameter model
(instrumental influence on the diffractogram)

Double Voigt-model
(crystallite size and lattice strain due to dislocations)

- Measurement
- Model
- Difference
Dislocation density from microstrain $e$:

$$
\rho_0 = \frac{6(1+v)}{b^2(1+2v^2)} = \frac{6(1+v)}{(Ca)^2(1+2v^2)}
$$

$$
d\rho_0 = \left(\frac{\partial \rho_0}{\partial \nu} \rho_0 \right) d\nu + \left(\frac{\partial \rho_0}{\partial a} \rho_0 \right) da
$$

$$
\frac{\partial \rho_0}{\partial \nu} = \frac{1-2v^2-4v}{(1+v)(1+2v^2)} \quad \frac{\partial \rho_0}{\partial a} = -\frac{2}{a}
$$

Analysis of X-ray diffractograms
Mass fraction of carbon

Diffractogram
C in austenite (relative shift lattice parameter)
thermal expansion has to be corrected.

$$\Delta a = 9.5 \cdot 10^{-4} z C \cdot 100 \text{ (nm)}$$

C in martensite (tetragonality)
Temperature independent

$$\frac{c}{a} = 1 + 0.045(w C \cdot 100)$$


Mass fraction of austenite & dislocation density I

Mass fraction of austenite & dislocation density III

Impact strength versus mass fraction of austenite and dislocation density

Diffractograms and their numerical analysis

Low signal-to-noise ratio: Numerical solutions?
Global optimization: Bayesian Statistics applied to the Rietveld Method

\[
L(D|\theta) = \text{const} \cdot \prod_{i=1}^{n} \frac{1}{\sqrt{2\pi\sigma_i^2}} \exp\left(-\frac{[D_i - D_{\text{calc},i}(\alpha_i)]^2}{2\sigma_i^2}\right)
\]

\[
p(\alpha_i, D) = \frac{L(D|\alpha_i) \cdot p(\alpha_i | H)}{p(D | H)}
\]

Likelihood

PRIOR distribution of the model parameters \(\alpha_i\)

EVIDENCE Normalization factor

POSTERIOR distribution of the model parameters \(\alpha_i\)
Local optimization versus global optimization
Residual sum of squares

- $\sum \chi^2 / \text{counts}^2$
- microstrain Lorentz (IB)
Austenite fraction after tempering before cooling
Austenite fraction during tempering
Dislocation density martensite at 25°C (before tempering) and after tempering (650°C) before cooling
Dislocation density of martensite (tempering process 650°C)
Dislocation density austenite complete tempering process
Heat treatment

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>W</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>0.44</td>
<td>0.27</td>
<td>3.7</td>
<td>2.4</td>
<td>5.1</td>
<td>14.1</td>
<td>11.0</td>
</tr>
</tbody>
</table>
Lattice parameter $a$ in austenite & Change of mass fraction of carbon in austenite
Tetragonality $c/a$ & Mass fraction of carbon in martensite
Change of the mass fraction of carbon in austenite & Mass fraction of carbon in martensite
Lattice parameter in austenite, dislocation density in martensite & Hardness (HRC)
Conclusions and Outlook

HT-XRD for in-situ evaluation of process conditions:

- Relations between evolving microstructure and mechanical properties.
- Treatment of noisy diffractograms by global optimization.

Results:

- Microstructural evolution from high quality diffractograms (LM)
- Microstructural evolution from noisy diffractograms (MCMC)

Future goal:

- Evaluation of diffractograms obtained during faster in-situ processes.
Future project II

Heat treatment:

a) Co-reduced HSS?

b) Cr-reduced MSS?

- Material e.g. from Boehler Company.
- Mechanical tests for different steel grades.
- High temperature X-ray diffraction and evaluation.
Thank you for your attention!
Solutions for Critical Raw Materials Under Extreme Conditions (CRM-EXTREME)

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