Der Einsatz von DICTRA in der Werkstoffentwicklung

Thermo-Calc Anwendertreffen
9. - 10. September 2010
Fundamental concepts of DICTRA

Treatment of growth in different geometries

Linear geometry

Spherical geometry

Cylindrical geometry

Ellipsoïdal geometry
Coupling between cells:
equilibrium at the surface $\Leftrightarrow$ equal chemical potentials

value of chem. potentials given by the condition:
flux leaving cell 1 = flux entering cell 2

$$J_i^1 = -J_i^2$$
Local equilibrium (LE) at moving interfaces

\[ \text{LE} \Rightarrow \mu_C^{\alpha} = \mu_C^{\gamma} \quad \mu_X^{\alpha} = \mu_X^{\gamma} \]

**Binary system**

**Ternary system**

Fe-Ni-C, T=1000 K

\( \alpha \rightarrow \gamma \rightarrow \alpha \)
Fundamental concepts of DICTRA

True thermodynamic driving forces have to be used in order to treat diffusion. Consequently, mobilities are the kinetic parameters, not diffusivities.
Interfacial layer at phase boundaries
between martensite and austenite in a maraging TRIP steel
Fe-12.2Mn-1.9Ni-0.6Mo-1.2Ti-0.1Si-0.3Al-0.05C (at%)
### Composition in wt%

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Ni</th>
<th>Co</th>
<th>Mo</th>
<th>Ti</th>
<th>Al</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Maraging</strong></td>
<td>0.01</td>
<td>18</td>
<td>12</td>
<td>4</td>
<td>1.6</td>
<td>0.15</td>
<td>0.05</td>
<td>Balance</td>
</tr>
<tr>
<td><strong>12Mn PH</strong></td>
<td>0.01</td>
<td>2</td>
<td>-</td>
<td>1</td>
<td>1.0</td>
<td>0.15</td>
<td>12</td>
<td>Balance</td>
</tr>
</tbody>
</table>

- **Low carbon: ductile martensite**
- **Precipitation Hardenable**
- **Mn (+Ni): austenite (TRIP)**
Tensile tests

Maraging
(X3NiCoMoTi18-12-4)

12MnPH

Engineering Stress (MPa)

Engineering Strain (%)

aged (450°C/48h)

quenched

Tensile tests (X3NiCoMoTi18-12-4)
Atom probe tomography of a 20nm thick slice

Average composition (at%)
- 10.7% Mn
- 0.6% Mo
- 1.66% Ni
- 0.15% Si
- 1.1% Ti

Average composition (at%)
- 12.2% Mn
- 0.6% Mo
- 2.0% Ni
- 0.15% Si
- 1.17% Ti

Local composition analysis
Local composition analysis

Atom probe tomography of a 20nm thick slice

Quantitative chemical analysis
Local composition analysis

![Graph showing local composition analysis with phase boundaries and chemical content profiles for Mn layer 2: Boundary profile (Martensite to Austenite), nm.](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Mean content in the layer</th>
<th>Total content (APT)</th>
<th>Enrichment within the layer, times</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>26.5 ± 1.5</td>
<td>12.34</td>
<td>2.1</td>
</tr>
<tr>
<td>Ni</td>
<td>2.6 ± 0.3</td>
<td>2.26</td>
<td>1.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Mean content in the layer</th>
<th>Total content (APT)</th>
<th>Depletion within the layer, times</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>70.4 ± 0.3</td>
<td>83.21</td>
<td>1.2</td>
</tr>
<tr>
<td>Ti</td>
<td>0.16 ± 0.02</td>
<td>1.10</td>
<td>6.9</td>
</tr>
<tr>
<td>Mo</td>
<td>0.30 ± 0.05</td>
<td>0.60</td>
<td>2.0</td>
</tr>
<tr>
<td>Al</td>
<td>0.05 ± 0.01</td>
<td>0.33</td>
<td>6.6</td>
</tr>
<tr>
<td>Si</td>
<td>0.04 ± 0.01</td>
<td>0.16</td>
<td>4</td>
</tr>
</tbody>
</table>
Linear cell

DICTRA simulation

<table>
<thead>
<tr>
<th>Element</th>
<th>Ferrite</th>
<th>Austenite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>85.79</td>
<td>83.88</td>
</tr>
<tr>
<td>Mn</td>
<td>10.7</td>
<td>12.2</td>
</tr>
<tr>
<td>Mo</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Ni</td>
<td>1.66</td>
<td>2.0</td>
</tr>
<tr>
<td>Si</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Ti</td>
<td>1.1</td>
<td>1.17</td>
</tr>
</tbody>
</table>
Fe-Mn-Ni, T = 723 K

DATABASE: TCFE6

DICTRA simulation: local equilibrium
Conclusions: 1. agreement with respect to the boundary condition

2. the Mn-enriched zone is too small

3. the Mn diffusion profile in ferrite is too narrow

Mobility of Mn in martensite must be higher than it is in ferrite
How to modify the mobility?

At first a check of the diffusivity matrix

DIC> check-diffusivity-matrix
OUTPUT TO SCREEN OR FILE /SCREEN/:
PHASE NAME : bcc
DEPENDENT COMPONENT ? /Ni/: fe
CONCENTRATION OF Mn IN U-FRACTION /1/: .11
CONCENTRATION OF Mo IN U-FRACTION /.89/: .006
CONCENTRATION OF Ni IN U-FRACTION /.884/: .02
Pressure /100000/:
Temperature /298.15/: 723
OPTION ( dlpbmx0ez or * ) /D/:

Dkj (reduced n=FE)
k / j     MN     MO     NI
Mn       +1.5103E-22 -3.01852E-24 -3.06304E-22
Ni       -2.02661E-23 -1.45054E-23 +1.02522E-22
### How to modify the mobility?

<table>
<thead>
<tr>
<th></th>
<th>k / j</th>
<th>MN</th>
<th>MO</th>
<th>NI</th>
</tr>
</thead>
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<tr>
<td>MN</td>
<td>+1.5103E-22</td>
<td>-3.01852E-24</td>
<td>-3.06304E-22</td>
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<tr>
<td>NI</td>
<td>-2.02661E-23</td>
<td>-1.45054E-23</td>
<td>+1.02522E-22</td>
<td></td>
</tr>
</tbody>
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#### Modification of the mobility

DIC>`amend-mobility-data`

**PARAMETER:** mq(bcc_a2&mn,fe:va;0)

MQ(BCC_A2&MN,FE:VA;0) = -193000

DO YOU WANT TO CHANGE THE NUMBER OF RANGES /NO/: y

I AM SORRY BUT YOU MUST THEN REENTER ALL RANGES

MQ(BCC_A2&MN,FE:VA;0) =

LOW TEMPERATURE LIMIT /298.15/:

FUNCTION: -171310;

HIGH TEMPERATURE LIMIT /6000/:

ANY MORE RANGES /N/:

<table>
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<tr>
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<th>k / j</th>
<th>MN</th>
<th>MO</th>
<th>NI</th>
</tr>
</thead>
<tbody>
<tr>
<td>MN</td>
<td>+6.75788E-21</td>
<td>+2.77233E-21</td>
<td>-1.33319E-20</td>
<td></td>
</tr>
<tr>
<td>MO</td>
<td>-3.48871E-23</td>
<td>+5.94665E-22</td>
<td>+9.18589E-23</td>
<td></td>
</tr>
<tr>
<td>NI</td>
<td>-1.68735E-22</td>
<td>-7.68727E-23</td>
<td>+3.95232E-22</td>
<td></td>
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</tbody>
</table>
Variation of mobility in martensite

**Graph 1:**
- **T = 450°C, Time = 50h**
- **Position relative to initial phase boundary (nm)**
  - Ferrite
  - Austenite
  - Interfacial austenite layer

**Graph 2:**
- Iso-line at 18 at.%

**Graph 3:**
- Mobility in martensite increased by a factor of 12

**Graph 4:**
- Mobility in martensite increased by a factor of 45
DICTRA results with modified mobility

T=450°C, Time=50h
mobility in martensite increased by a factor of 45
Conclusions:

1. Atomic mobility in martensite is definitely higher than in ferrite.

2. The formation of aging-induced austenite at the martensite / $\gamma$ interface is associated with a drastic change in composition.

3. The layer of aging-induced austenite is likely to be responsible for the increase in ductility after annealing.
Influence of Hard Particle Addition and Chemical Interdiffusion on the Properties of Hot Extruded Tool Steel Compounds

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\(^2\) Institut für Werkstoffe, Ruhr-Universität Bochum
\(^3\) Helmholtz-Zentrum Berlin

Materials Science and Engineering A 516 (2009) 193-200

HIP-Cladding is a powder metallurgical process for the production of thick coatings on metallic substrates. A forged or cast basal body (i.e. the substrate) gets wrapped in a capsule. The gap between capsule and substrate is filled with high alloyed tool steel powder and hard phases. After powder filling the capsule is evacuated and sealed. Hot isostatic pressing (HIP) with pressure up to 100 MPa leads to plastic deformation and increased sinter activity. This way a thick metal matrix composite (MMC) is produced as coating.
Since 1987 HPGR have been successfully taken up in the diamond industry in South Africa. Controlled micro-cracking is the main focus in this application. Today HPGR is almost standard in every new diamond plant project.

In the iron ore industry HPGRs were first applied in 1994. More than 7 HPGRs run in pellett plants in Sweden, Brasil, India and Russia.
**Microstructure**

**Substrate:**

1.2714: Fe-0.56%C-1.15%Cr-0.46%Mo-0.08%V-0.75%Mn-0.29%Si-0.11%Cu-1.74Ni

**Coating:**

1.2344: Fe-0.4%C-5%Cr-1.34%Mo-0.97%V-0.3%Mn-0.19%Si-0.1Ni

1.2380: Fe-2.39%C-12.6%Cr-1.1%Mo-3.7%V-0.37%Mn-0.55%Si-0.3Ni
M₆C: “diffusion-none“ phase

DICTRA simulation

substrate

coating

interface

16 mm

FCC matrix

M₆C

W₂C

hard particle

FCC matrix

spheroidal M₆C

FCC matrix

W₂C

hard particle
DICTRA simulation

Dissolution of W₂C

1.2344 : Fe-0.4%C-5%Cr-1.34%Mo-0.97%V (wt%)

T=1150°C

coating matrix 1.2344

mole fraction M₆C

distance / µm

2 h
10 h
300 s
Composition profiles between $W_2C$ and coating.

Graphs showing mole fraction of Cr, Mo, C, and W as functions of distance (µm) for different times (0, 300, 7200, 36000 s) at a temperature of $1150^\circ C$. The compositions are presented in weight percent for Fe-0.4%C-5%Cr-1.34%M-0.97%V.
Composition profiles between coating and substrate

**Substrate:** Fe-0.56%C-1.15%Cr-0.46%Mo-0.08%V-0.75%Mn-0.29%Si-0.11%Cu-1.74Ni

**Coating:** Fe-0.4%C-5%Cr-1.34%Mo-0.97%V-0.3%Mn-0.19%Si-0.1Ni

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**W DICTRA**  
**W EPMA**

**Cr [wt.%]**

**Distance [µm]**

-100 -50 0 50 100

**Coating**  
**Substrate**

**V [wt.%]**

**Distance [µm]**

-100 -50 0 50 100

**Coating**  
**Substrate**

**Ni [wt.%]**

**Distance [µm]**

-100 -50 0 50 100

**Coating**  
**Substrate**

**Fe [wt.%]**

**Distance [µm]**

-100 -50 0 50 100

**Coating**  
**Substrate**
Ferrite precipitation from austenite

**Ck45: Fe-0.49C-0.18Cr-0.22Cu-0.71Mn-0.19Ni-0.31Si**

Exp.: G. Pariser, Thesis RWTH-Aachen 2004

**Metallographic analysis:**

Area density of nuclei \( N_A = 77 / \text{mm}^2 \)

Linear geometry

\[
d = \frac{1}{2} \sqrt{N_A^{-1}}
\]

Spherical geometry

\[
r = \sqrt[3]{\frac{3}{4\pi \cdot N_A^{3/2}}}
\]

\( N_A = 77 / \text{mm}^2 \Rightarrow d = 57 \mu m \)

\( N_A = 77 / \text{mm}^2 \Rightarrow r = 71 \mu m \)
\[ r = \frac{1}{2} \sqrt{N_A^{-1}} \]

\( N_A = 77 / \text{mm}^2 \implies d = 57 \mu \text{m} \)

\text{Exp.: Pariser, Thesis RWTH-Aachen 2004}

\text{Ck45: Fe-0.49C-0.18Cr-0.22Cu-0.71Mn-0.19Ni-0.31Si}
\text{\( T_A = 1200^\circ\text{C}, T = 725^\circ\text{C} \)}
\text{lin. geom., cell size 57\mu m}
Mesostructural aspects

\[ r = \sqrt{\frac{3}{4\pi \cdot N_a^{3/2}}} \]

\[ N_A = 77 \text{ / mm}^2 \implies r = 71 \text{ \(\mu\)m} \]

Ck45: Fe-0.49C-0.18Cr-0.22Cu-0.71Mn-0.19Ni-0.31Si
spher. geom, \(r=71\,\mu\text{m}\), growth from centre
\(T_A=1200^\circ\text{C}\), \(T=725^\circ\text{C}\)
- Austenitization at 1200°C
- Isothermal holding at 725°C for 200h

Exp.: Pariser, Thesis RWTH-Aachen 2004

Microstructural aspects

Pearlite
Ferrite
Bainite
Martensite
Exp.: Pariser, RWTH-Aachen 2004

Fe-0.49C-0.22Cu-0.71Mn-0.19Ni-0.31Si

\[ r = \sqrt[3]{\frac{3}{4\pi \cdot N_A^{3/2}}} \]

\( N_A = 77 \text{ / mm}^2 \quad \Rightarrow \quad r = 71 \text{ \(\mu m\)} \)

Micostructural aspects

Fe-0.49C-0.22Cu-0.71Mn-0.19Ni-0.31Si
spher. geom., 2 cells with \( r = 71 \text{\(\mu m\)} \)
ferrite growth in 2nd cell from periphery

![Graph showing ferrite fraction vs. time](image)