Thermodynamics of Fe-Mn-C TRIP/TWIP steels

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1. Introduction

The stacking fault energy (SFE)

- Planar slip together with carbides - SBIP steels (SFE 40-50 mJ/m²)
- Twinning and slip - TWIP steels (SFE 20-40 mJ/m²)
- Martensite formation and slip - TRIP steels (SFE < 20 mJ/m²)

\[ \text{SFE} = f(\Delta G_{\gamma \rightarrow \epsilon}) \]
Thermodynamic models
(Regular solutions, Sublattice model,...)

Experimental techniques
(Calorimetry, electromotive forces,...)

Theory
(Quantum mechanics, Statistical thermodynamics,...)

Model equations for \( \Delta G_\phi(T,x) \)

Crystal structure data

Thermodynamic and phase equilibrium data

Thermodynamic optimization
(Least square method)

\( \Delta G_\phi(T,x) \)

Thermodynamic properties

Phase diagrams

Applications

CALPHAD-type software tools ThermoCalc

MATERIALS CHEMISTRY
2. Binary Systems

Fe-C


Fe-Mn


Mn-C

D. Djurovic and B. Hallstedt 2008

\[
\begin{align*}
\text{Fe}_{23}\text{C}_6 & \quad \Delta G(\text{Fe}_n\text{C}_m,T) - \Delta G(\text{Cementite},T) - \Delta G(\text{Graphite},T) = a \\
\text{Fe}_5\text{C}_2 & \quad \Delta G(\text{Fe}_n\text{C}_m,T) - \Delta G(\text{Cementite},T) - \Delta G(\text{Graphite},T) = a \\
\text{Fe}_7\text{C}_3 & \quad \Delta G(\text{Fe}_n\text{C}_m,T) - \Delta G(\text{Cementite},T) - \Delta G(\text{Graphite},T) = a
\end{align*}
\]
3. Results

Heat capacity of a) Fe$_3$C b) α-Fe c) Graphite

Temperature, K

Heat capacity, J mol$^{-1}$ K$^{-1}$

Enthalpies of formation of metastable iron carbides

\[ \Delta H^\circ_{f} \] 

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta H^\circ_{f} ) @ 298K, J/mol of atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe}_3\text{C} )</td>
<td>3858 5889 6303</td>
</tr>
<tr>
<td>( \text{Fe}_{23}\text{C}_6 )</td>
<td>3891 5889 8973</td>
</tr>
<tr>
<td>( \text{Fe}_5\text{C}_2 )</td>
<td>3996 5997 14371</td>
</tr>
<tr>
<td>( \text{Fe}_7\text{C}_3 )</td>
<td>4437 6488 13905</td>
</tr>
</tbody>
</table>

\[ \text{Fe}_{23}\text{C}_6, \text{Fe}_5\text{C}_2, \text{Fe}_7\text{C}_3 \]

Diagram showing phase transitions and mole fraction of C.
The room-temperature entropy of iron carbides

The Debye-model entropy and predicted Debye temperature

- Based on integration of the experimental heat capacity data of Fe$_3$C
- Previous assessment
- This work
Comparison of (a) the experimental isothermal section of Benz et al. with the calculated isothermal section using TDB from (b) Huang and (c) this work at 873 K.
The calculated Mn distribution ratio between
the α phase and $M_3C$ in comparison
with experimental data.

— Hua1990
— this work
The calculated T-zero line in comparison with experimental data for Fe-17wt%Mn-C alloys.

\[ T_0 \approx \frac{\text{Ms} + \text{As}}{2} \]

\[ T_0 \approx \text{T-zero line in comparison with experimental data for Fe-17wt%Mn-C alloys.} \]

Comparison of (a) the experimental isothermal section of Benz et al. with the calculated isothermal section using TDB from (b) Huang and (c) this work at 1373 K.
The calculated isocarbon activity lines in the $\gamma$ phase at 1420 K and 1273 K in comparison with experimental data.
The calculated Mn distribution ratio between the γ phase and $M_3C$ in comparison with experimental data.

The calculated graphite solubility in the liquid phase in comparison with experimental data.
Comparison between the calculated and experimental liquidus projections in the direction of u(C).

- Schürmann and Geissler’s data extrapolated to the Fe-Mn side give liquidus temperature about 10 to 30 K higher than accepted values.

- The liquidus by Schürmann and Geissler is not in agreement with accepted data on the graphite solubility in the liquid.
6. Summary

The CALPHAD description of Fe-Mn-C system is updated with a modified description of Fe₃C phase by the present authors, recently published reassessment of the Fe-Mn system by Witusiewicz et al. and the reassessment of the Mn-C system by the present authors. A consistent thermodynamic description of the entire Fe-Mn-C system has been obtained by considering ab initio calculated enthalpies of formation of metastable carbides together with critically assessed literature data by Huang. The reevaluation of the phase equilibria and thermodynamic functions leads to better fits to the available experimental data at lower temperatures.
Acknowledgement

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