Thermodynamic Re-assessment of the Mn-C System

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1. Aim of investigations

To provide a thermodynamic description of the Fe-Mn-C system which is as accurate and reliable as possible, especially at low temperatures.

Fe-Mn-C

Fe-C
[Mus1985]

Mn-C
[Hua1990]

Fe-Mn
[Wit2004]

W. Huang, Scand. J. Metall., 19 (1990) 26
2. Previous assessment

An inverse miscibility gap above 4800 K

Incorrect appearance of the Mn$_2$C (hcp) phase at low temperature

Fig. 1. Calculated phase diagram
3. Thermodynamic modeling

a. Solid Solution Phases

The carbon solution in manganese is described by interstitial solution models with one sublattice occupied by manganese atoms and the other one occupied by the both carbon and vacancies.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBCC</td>
<td>(Mn)\textsubscript{1}(C, Va)\textsubscript{1}</td>
</tr>
<tr>
<td>CUB</td>
<td>(Mn)\textsubscript{1}(C, Va)\textsubscript{1}</td>
</tr>
<tr>
<td>FCC</td>
<td>(Mn)\textsubscript{1}(C, Va)\textsubscript{1}</td>
</tr>
<tr>
<td>HCP</td>
<td>(Mn)\textsubscript{1}(C, Va)\textsubscript{0.5}</td>
</tr>
<tr>
<td>BCC</td>
<td>(Mn)\textsubscript{1}(C, Va)\textsubscript{3}</td>
</tr>
</tbody>
</table>
b. Stoichiometric Phases

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

\[ \Delta^\circ G(\text{Mn}_n\text{C}_m, T)=a+bT+\Delta c_p(\text{Mn}_n\text{C}_m, T) \]

\[ \Delta c_p(\text{Mn}_n\text{C}_m, T)=0 \quad (\text{The Neumann-Kopp rule}) \]
Fig. 2. Experimental data on the chemical potential of Mn in various phase equilibria
b. Stoichiometric Phases

Metastable end-members $\text{Mn}_2\text{C}$ (hcp) and $\text{MnC}$ (fcc)

$$\Delta^\circ G(\text{Mn}_n\text{C}_m, T) = a + bT + \Delta c_p(\text{Mn}_n\text{C}_m, T)$$

$$\Delta c_p(\text{Mn}_n\text{C}_m, T) = 0 \quad \text{(The Neumann-Kopp rule)}$$
4. Results

Calculated phase diagram of the Mn-C system

--- Hua1990 
-- this work
Calculated phase diagram of the Mn-C system

-- Hua1990

-- this work
Calculated chemical potential of Mn in various phase equilibria
## Enthalpies of formation of binary manganese carbides

<table>
<thead>
<tr>
<th></th>
<th>Selected experiment values</th>
<th>Ab initio (T=0K)</th>
<th>Previous assessment</th>
<th>Present work</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MnC</strong></td>
<td></td>
<td>27971</td>
<td>251</td>
<td>0</td>
</tr>
<tr>
<td><strong>Mn\textsubscript{2}C</strong></td>
<td></td>
<td>-3858</td>
<td>-11128</td>
<td>-6000</td>
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<tr>
<td><strong>Mn\textsubscript{7}C\textsubscript{3}</strong></td>
<td>-10677\textsuperscript{(1)} -9100\textsuperscript{(2)}</td>
<td>-6944</td>
<td>-11176</td>
<td>-10669</td>
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<tr>
<td><strong>Mn\textsubscript{5}C\textsubscript{2}</strong></td>
<td>-10567\textsuperscript{(1)} -8900\textsuperscript{(2)}</td>
<td>-6476</td>
<td>-10978</td>
<td>-10565</td>
</tr>
<tr>
<td><strong>Mn\textsubscript{3}C</strong></td>
<td>-9918\textsuperscript{(1)}</td>
<td>-6993</td>
<td>-10094</td>
<td>-9911</td>
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<tr>
<td><strong>Mn\textsubscript{23}C\textsubscript{6}</strong></td>
<td>-10716\textsuperscript{(1)} -8465\textsuperscript{(3)}</td>
<td>-8381</td>
<td>-10622</td>
<td>-10706</td>
</tr>
</tbody>
</table>

Calculated chemical potential of Mn in various phase equilibria compared with experimental data

V.N. Eremenko et al., Tugo plavkie Karbidy (Russ.), G.V. Samsonov, ed., "Naukova Dumka", Kiev, Ukr. SSR, 1970, 204

Calculated phase diagram of the Mn-C system compared with experimental data

J. Fenstad et al., Int. J. Mat. Res. 98 (2007) 10
Z. Ma et al., Steel Res. 62 (1991) 481
Activity coefficients of manganese in Mn-C melts

- Hua1990
- this work

1628 K
1673 K
1723 K
1773 K
Activity coefficients of carbon in Mn-C melts

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Hua1990

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this work

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\[
\ln(\gamma_C) = \text{Mole fraction C}
\]

1628 K
1673 K
1723 K
1773 K

5. Conclusion

The thermodynamic description of Mn-C system has been updated in the following ways:

- The Gibbs functions of the stable manganese carbides have been evaluated using recently published data of Zaitsev et al.

- The Gibbs function of the metastable $\text{Mn}_2\text{C}$ has been evaluated using enthalpy of formation obtained by ab initio calculation.

- New experimental data on the position of the liquidus line and the activity of manganese and carbon in the Mn-C melts have been used for optimization of liquid phase.

The reevaluation of the phase equilibria and thermodynamic functions gives a new thermodynamic description without the weaknesses of the previous one.
Acknowledgement

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