Driving force for martensitic transformation in steels

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The free energy change accompanying martensite formation at the $M_s$ temperature of steels $\Delta F_{M_s}^{e*}$ is evaluated using various thermodynamic methods together with relatively accurate and recent thermodynamic data. $\Delta F_{M_s}^{e*}$ has been found to be rather less than was originally believed, and varies between $-900$ and $-1400$ J mol$^{-1}$ as a function of the carbon content; however, the variation is not monotonic.

An estimate of the magnitude of the driving force $\Delta F_{M_s}^{e*}$ available at the martensite-start temperature $M_s$ of steels is an important prerequisite for a detailed understanding of the nucleation and growth characteristics of ferrous martensites.

Early investigations of Fe–C alloys$^{1,2}$ indicated that $\Delta F_{M_s}^{e*}$ is essentially independent of the $M_s$ temperature (and hence of the carbon content). However, Imai$^3$ et al. used statistical thermodynamics to demonstrate that $|\Delta F_{M_s}^{e*}|$ monotonically increases with carbon content. Bell and Owen$^4$ subsequently confirmed this conclusion using Fisher’s method$^5$ for extrapolating the free energy curves of ferrite and austenite. Table 1, which contains some of the information of Refs. 3 and 4, not only illustrates the sensitivity of $\Delta F_{M_s}^{e*}$ to the carbon content, but also shows that $\Delta F_{M_s}^{e*}$ for steels can be rather high compared with, for example, carbon-free Fe–Ni martensites.

Since the above pioneering investigations, substantial new and relatively accurate thermodynamic data have become available; the purpose of the present work was to reassess and extend the results of the earlier investigations in the light of the new data.

**RESULTS**

The $M_s$ temperatures utilized in all of the calculations presented below are due to Greninger.$^5$

**Fisher method**

Fisher$^5$ and Bell and Owen$^4$ used the following expression to determine the free energy change accompanying martensite formation

$$\Delta F_{M_s}^{e*} = (1 - x)\Delta F_{Fe}^{e*} + (1 - x)RT\ln \left( \frac{\Gamma_{Fe}}{\Gamma_{Fe}} \right) + xRT\ln \left( \frac{\Gamma_{C}}{\Gamma_{C}} \right) + \Delta f^*$$

(1)

The third term in equation (1) can be expanded as

$$RT\ln \left( \frac{\Gamma_{Fe}}{\Gamma_{Fe}} \right) = \Delta H_{Fe}^{*} - \Delta H_{Fe}^{*} - RT(\Delta S_{Fe}^{*} - \Delta S_{Fe}^{*})$$

(2)

where $\Delta H_{Fe}^{*}$ is partial molar heat of solution of carbon in ferrite and in austenite respectively and $\Delta S_{Fe}^{*}$ is the partial molar non-configurational entropy of solution of carbon in ferrite and in austenite respectively.

Bell and Owen chose $\Delta H_{Fe}^{*} = 40\,133$ J mol$^{-1}$ (from the work of Ellis et al.$^9$) and in agreement with Fisher took $\Delta H_{Fe}^{*} = 85\,834$ J mol$^{-1}$. However, Lobo and Geiger$^{10}$ recently determined $\Delta H_{Fe}^{*}$ to be $111\,918$ J mol$^{-1}$ at temperatures below $1000$ K, and pointed out that their experimental data were free from various 'intercept effects' which had dogged earlier investigations. Similarly, for $T < 1000$ K, they deduced $\Delta S_{Fe}^{*} = 51\,44$ J mol$^{-1}$ K$^{-1}$. There seem to be no data on the variation of $\Delta H_{Fe}^{*}$ or $\Delta S_{Fe}^{*}$ as a function of $x$. However, Lobo and Geiger$^{11}$ found that $\Delta H_{Fe}^{*}$ and $\Delta S_{Fe}^{*}$ do in fact vary with $x$. Furthermore, since the data of Ref. 11 were determined at relatively low temperatures, the relationships the authors deduced should be the most reliable for the present purposes. From Refs. 10 and 11,

$$RT\ln \frac{\Gamma_{Fe}}{\Gamma_{Fe}} = 111\,918 - 51\,44T$$

(3a)

$$RT\ln \frac{\Gamma_{C}}{\Gamma_{C}} = 35\,129 - 7\,639T$$

(3b)

$$RT\ln \frac{\Gamma_{C}}{\Gamma_{C}} = 76\,789 - 43\,8\,T$$

(3c)
1 Variation of free energy change (accompanying martensitic transformation at \(M_s\) temperature) as function of carbon content: curves 1 and 2 correspond to present analysis, using methods indicated, whereas other curves are due to Bell and Owen\(^4\) and Imai et al.\(^5\)

\[
\Delta F^{x\to s} = 2xRT\ln x + x|\Delta \tilde{H}_{c}^{c} - \Delta \tilde{H}_{c}^{s} - (\Delta \tilde{S}_{\phi}^{c} - \Delta \tilde{S}_{\phi}^{s})T + 4\omega_{a} - 6\omega_{a}| - 4RT(1 - x)\ln (1 - x) + 5RT(1 - 2x)\ln (1 - 2x)
\]
\[
- 6RT\ln \left| \frac{\delta_{z} - 1 + 3x}{\delta_{z} + 1 - 3x} \right| - 6RT\ln \left| \frac{1 - 2J_{x} + (4J_{y} - 1)x - \delta_{x}}{2J_{x}} \right| + 3RT\ln (3 - 4x)
\]
\[
+ 4RT\ln \left| \frac{\delta_{z} - 3 + 5x}{\delta_{z} + 3 - 5x} \right| + (1 - x)\Delta \tilde{F}_{e}^{x\to s} + \Delta \tilde{F}^{*} \tag{6}
\]

where
\[
\delta_{z} = \left( 9 - 6x(2J_{z} + 3) + 9 + 16J_{x}x^{2} \right)^{1/2}
\]
\[
\delta_{y} = \left( 1 - 2(1 + 2J_{z})x + (1 + 8J_{z})x^{2} \right)^{1/2}
\]
\[
J_{x,y} = 1 - \exp \left( - \omega_{a,y}/RT \right)
\]
\[
\omega_{a} = 8054 \text{ J mol}^{-1} \tag{Ref. 11}
\]

The \(\Delta \tilde{H}\) and \(\Delta \tilde{S}_{\phi}\) values were again represented by the data of Lobo and Geiger.\(^{10,11}\)

The driving force curve calculated using equation (6) is also in Fig. 1.

Imai, Izumiya, and Tsuchiya method

This is essentially a statistical–thermodynamics method, and the final equation is given as

\[
\Delta F^{x\to s} = x(F_{c}^{c} - F_{c}^{s}) + \frac{x}{R} \ln \left( \frac{x}{1 - x} \right) - x \ln \left( \frac{x}{1 - 6x} \right)
\]
\[
+ \left( \frac{x^{2}}{1 - x} \right) \Omega R T \ln \left| \frac{\phi_{c}^{c}(T)}{\phi_{c}^{s}(T) R_{c}^{s}} \right| \tag{7}
\]

where
\[
F_{c}^{c} - F_{c}^{s} = \phi_{c}^{c} - \phi_{c}^{s}, - \phi_{c}^{c} - 2 \ln \left| \frac{\phi_{c}^{c}(T)}{\phi_{c}^{s}(T)} R_{c}^{s} \right| \tag{8}
\]
and
\[
\Omega = 1/4 \left| \left\{ 1 - \exp \left( - \frac{\phi_{c}^{c} - \phi_{c}^{s}}{R T} \right) \right\} \right| + \left\{ 2 - \exp \left( - \frac{\phi_{c}^{c} - \phi_{c}^{s}}{R T} \right) \right\}
\]
\[
- 2 \exp \left( - \frac{\phi_{c}^{c} - \phi_{c}^{s}}{R T} \right) \left| Z \right| \tag{9}
\]

where \(\phi_{c}^{c} - \phi_{c}^{s}\) and \(\phi_{c}^{c} - \phi_{c}^{s}\) represent the iron–carbon pairwise interaction energies in ferrite and austenite. \(R_{c}^{s}\) represents the partition functions concerning the oscillation state of carbon in ferrite and austenite, and \(\phi_{c}^{c}\) represents the partition functions concerning the electronic state of carbon in ferrite and austenite. \(Z\) is the coordination number of the austenite lattice. \(\rho\) is a constant related to the strain energy due to the tetragonality caused by a carbon atom in the ferrite lattice.

Imai et al. used an expression due to Gilbert and Owen\(^{17}\) to represent \(\Delta F_{c}^{x\to s}\). However, comparison with the data of Kaufman et al.\(^ {18}\) shows that this results in a large overestimation of \(\Delta F_{c}^{x\to s}\), and in addition, exaggerates the sensitivity of \(\Delta F_{c}^{x\to s}\) with respect to \(M_s\). For example, at \(x = 0.02\), \(\Delta F_{c}^{x\to s}\) would be overestimated by \(\sim 330 \text{ J mol}^{-1}\) and at \(x = 0.06\) the overestimation would be by \(550 \text{ J mol}^{-1}\).

\* \(\Delta F^{x\to s}\) refers to the free energy change accompanying the transformation of austenite to supersaturated ferrite and may be converted to \(\Delta F^{x\to s}\) by the inclusion of the \(\Delta \tilde{F}^{*}\) term.
Furthermore, the inclusion of the term \(|\rho(x/(1-x))^2|\) in equation (7) is not understood, since this really represents the change in internal energy accompanying the transformation of supersaturated ferrite to tetragonal martensite.\(^8\) Again, this would tend to exaggerate the sensitivity of \(\Delta F_{\text{M}^*}^{*}\) to \(M^*\), and would substantially increase the magnitude of the driving force.

Imai \textit{et al.} take \((\phi_{\text{f}_{\text{M}}} - \phi_{\text{f}_{\text{F}}} - \phi_{\text{F}})\) to be approximately equal to \(\Delta H^*\), i.e. the heat absorbed when one mole of carbon is transferred from the austenite to the ferrite (or in other words, the enthalpy change, referred to as \(-\Delta G_\text{f}\) by Zener\(^9\)). However, they use a value of 23 246 J mol\(^{-1}\) for \(\Delta H^*\), a value which does not agree with that given by Zener (to whom they refer) or with a more recently derived quantity of 39 245 J mol\(^{-1}\) (Ref. 14, p. 756).

In order to deduce the last term \((8)\), Imai \textit{et al.} refer to the Fe-C equilibrium phase diagram, a situation in which the following equations should apply\(^3\)

\[
\frac{\Delta F_{\text{Fe}^*}}{RT} = \ln \left[ \frac{1 - 2x_{\text{Fe}}}{1 - x_{\text{Fe}}} \right] - \ln \left[ \frac{1 - 2x_{\text{Fe}}}{1 - x_{\text{Fe}}} \right] + \frac{x_{\text{Fe}}^2}{(1-x_{\text{Fe}})^2} \quad (10)
\]

and

\[
\frac{F_{\text{Fe}} - F_{\text{C}}}{RT} = \ln \left[ \frac{x_{\text{Fe}}}{1 - 2x_{\text{Fe}}} \right] - \ln \left[ \frac{x_{\text{Fe}}}{3(1-2x_{\text{Fe}})} \right] + \frac{2x_{\text{Fe}}}{1 - x_{\text{Fe}}} \quad (11)
\]

Noting that they quote \(\phi_{\text{C}}\) as 4321 J mol\(^{-1}\) and evaluating \(\Omega\) from equation (9), we find, using equation (10), that at the eutectoid temperature (996 K, \(x_{\text{Fe}} = 0.0361, x_{\text{C}} = 0.000095\), \(\Delta F_{\text{Fe}^*}^{*} = -279\) J mol\(^{-1}\), a value which is clearly incorrect, both in sign and in magnitude.

On the other hand, \(\Omega\) was evaluated using equation (10) and the Gilbert and Owen expression for \(\Delta F_{\text{Fe}^*}^{*}\) (as used in Ref. 3), it was found impossible to obtain a solution for \(\phi_{\text{Fe}^*} - \phi_{\text{C}}\) with equation (9).

In summary, it seems that equations (9)-(11) do not form a self consistent set. This belief was found to hold even when more accurate parameters, i.e. \(\Delta H^*\) = 39 245 J mol\(^{-1}\), \(\Delta F_{\text{Fe}^*}^{*}\) according to Ref. 7) were substituted. It appears that there is some derivation error in the theory of Ref. 3, the nature of which is not clear. Hence, the results of Imai \textit{et al.} are not considered further.

**DISCUSSION AND CONCLUSIONS**

From Fig. 1 it is evident that the curves calculated using the new thermodynamic data differ substantially from those of Refs. 3 and 4. At all carbon levels, and especially at the higher carbon contents, the driving force for martensite formation is lower; \(\Delta F_{\text{Fe}^*}^{*}\) is also less sensitive to variations in the carbon content. The agreement between the calculations using the Fisher method and the Lacher, Fowler, and Guggenheim (LFG) theory is reasonable and it is satisfying that both curves exhibit the same trends. The minima in these curves and the inflexion in the Bell and Owen curve are due to the increasing (with \(x\) reduction in the free energy of martensite relative to austenite by the Zener ordering effect.

It seems difficult to decide which of the two new curves better represents the true situation. For the set of \(M\), temperatures used in the calculations, both the Fisher method and the LFG method are able to account for (at least) the stored energy of an isolated plate of martensite which amounts to \(\sim 700\) J mol\(^{-1}\) (Ref. 19). However, since the \(\Delta F_{\text{Fe}^*}^{*}\) values calculated by the Fisher method tend to approach the magnitude of the stored energy at the higher carbon levels, sufficient driving force would not be available for transformation should there exist an appreciable barrier to the nucleation of martensite. Although the \(M^*\) temperatures for even higher carbon steels do not seem to be well established, if we take the \(M^*_1\) of 1.95 wt.\%C steel to be \(\sim 350^\circ C\), the Fisher analysis would predict \(\Delta F_{\text{Fe}^*}^{*} = -890\) J mol\(^{-1}\) while the LFG treatment gives \(\Delta F_{\text{Fe}^*}^{*} = -1450\) J mol\(^{-1}\). This implies that there is a maximum in the LFG curve 2; this maximum was estimated to reach \(\Delta F_{\text{Fe}^*}^{*} \approx -1250\) J mol\(^{-1}\). On the other hand, the Fisher curve continues to rise. It therefore seems likely that the LFG calculations are nearer the true situation. Additionally, the LFG method is less empirical and a more systematic method of extrapolation compared with the Fisher technique.

In conclusion, it appears that the free energy change accompanying martensite formation at the \(M\) temperatures of steels is rather less than was originally thought, and varies between 900 and 1400 J mol\(^{-1}\). It is possible that a better estimate is given by the LFG extrapolation, in which case the above range narrows to between 1100 and 1400 J mol\(^{-1}\) for \(x = 0.01-0.06\). In addition, while \(\Delta F_{\text{Fe}^*}^{*}\) does vary with carbon content, the variation is neither monotonic nor very large.

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**REFERENCES**