Short communication

Thermodynamic extrapolation and martensite-start temperature of substitutionally alloyed steels

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The martensite-start temperature M_s of any steel can, in principle, be calculated by balancing the driving force for nucleation $\Delta F_{M_s}^{\gamma\to\alpha'}$ against the available chemical free energy change accompanying the transformation from austenite to martensite. Calculation of the latter quantity involves the extrapolation of the free energy surfaces of austenite and ferrite into temperature regimes where they are not in thermodynamic equilibrium; several methods are available for this purpose.[1,2] An advanced method of this kind is based on the Lacher[3] and Fowler and Guggenheim[4] formalisms, and was first applied to steels by Aaronson *et al.*[5] This was subsequently corrected by Shiflet *et al.*,[6] and was recently modified by Bhadeshia[2] in order better to represent martensitic transformations.

An advantage of the above method is that it can be readily adapted to account for the influence of substitutional alloying elements Y_i on transformation thermodynamics.[7,8] In essence, the presence of substitutional alloying elements is acknowledged by allowing for their effects on the magnetic and non-magnetic components of the free energy change accompanying the γ–α transformation in pure iron. Additionally, the C–Y interaction is taken into account by suitably modifying the pairwise C–C interaction energy.

The above approach amounts to ignoring the existence of separate Fe and Y atoms; the lattice is treated as an assembly of averaged, hypothetical 'superelement' atoms. This procedure seems to work reasonably well in the equilibrium region of the phase diagram,[9] although its validity has never been satisfactorily assessed in domains where the phases are not in thermodynamic equilibrium. Hence, the purpose of the present work was twofold; it was not only intended to appraise the superelement technique by considering martensitic transformations in low-alloy steels, but it was additionally hoped to account thermodynamically for the M_s temperatures of such steels.

METHOD

Modifying the equation of Ref. 2 to allow for substitutional element effects (according to Ref. 7), we get, at the M_s temperature,

$$\begin{aligned}\Delta F_{M_s}^{\gamma\to\alpha'} = {} & 2xRT\ln x + x|\Delta\bar{H}_\alpha - \Delta\bar{H}_\gamma - (\Delta S_\alpha - \Delta S_\gamma)T \\ & + 4\omega_\alpha - 6\bar{\omega}_\gamma| \\ & - 4RT(1-x)\ln(1-x) + 5RT(1-2x)\ln(1-2x)\end{aligned}$$

$$\begin{aligned} & -6RTx\ln\left|\frac{\delta_\gamma - 1 + 3x}{\delta_\gamma + 1 - 3x}\right| \\ & -6RT(1-x)\ln\left|\frac{1-2J_\gamma + (4J_\gamma - 1)x - \delta_\gamma}{2J_\gamma(2x-1)}\right| \\ & +3RTx\ln(3-4x) + 4RTx\ln\left|\frac{\delta_\alpha - 3 + 5x}{\delta_\alpha + 3 - 5x}\right| \\ & +(1-x)\Big|141\sum_i Y_i(\Delta T_{\mathrm{mag}_i} - \Delta T_{\mathrm{NM}_i}) \\ & +\Delta F_{\mathrm{Fe}}^{\gamma\to\alpha}\{T - 100\sum_i Y_i\Delta T_{\mathrm{mag}_i}\}\Big| + \Delta f^* \quad \ldots\ldots \quad (1)\end{aligned}$$

where

$\delta_\alpha = |9 - 6x(2J_\alpha + 3) + (9 + 16J_\alpha)x^2|^{1/2}$
$\delta_\gamma = |1 - 2(1 + 2J_\gamma)x + (1 + 8J_\gamma)x^2|^{1/2}$
$J_\alpha = 1 - \exp(-\omega_\alpha/RT)$
$J_\gamma = 1 - \exp(-\bar{\omega}_\gamma/RT)$.

In equation (1), T refers to the M_s temperature (in absolute degrees) and is the term to be evaluated, R is the gas constant, x is the mole fraction of carbon, and Y_i is the atom fraction of the ith substitutional alloying element when the presence of carbon is disregarded. $\Delta T_{\mathrm{mag}_i}$ and ΔT_{NM_i} refer to the displacement in the temperature at which the free energy change accompanying the $\gamma\to\alpha$ transformation in pure iron (i.e. $\Delta F_{\mathrm{Fe}}^{\gamma\to\alpha}$) is evaluated in order to allow for the changes (per at.-%) due to alloying element effects on the magnetic and non-magnetic components of $\Delta F_{\mathrm{Fe}}^{\gamma\to\alpha}$, respectively. These terms were obtained from Refs. 8 and 10 and values for $\Delta F_{\mathrm{Fe}}^{\gamma\to\alpha}$ from Ref. 11. The other parameters are as follows:

(i) the partial molar heat of solution of carbon in ferrite = $\Delta\bar{H}_\alpha = 111\,918$ J mol^{-1} (Ref. 12) and similarly
$\Delta\bar{H}_\gamma = 35\,129 + 169\,105x$ J mol^{-1} (Ref. 13)
(ii) the excess partial molar non-configurational entropy of solution of carbon in ferrite = $\Delta S_\alpha = 51{\cdot}44$ J mol^{-1} K^{-1} (Ref. 12) and similarly
$\Delta S_\gamma = 7.639 + 120{\cdot}4x$ J mol^{-1} K^{-1} (Ref. 13).

ω_α, the carbon–carbon interaction energy in ferrite was taken to be 48 570 J mol^{-1}, based on the average of the results of Ref. 14. ω_γ (the corresponding C–C interaction energy in austenite) values were derived, as a function of the concentrations of various alloying elements, using the procedure of Refs. 6 and 7) and the optimized activity data of Uhrenius.[15] These results are plotted in Fig. 1, and allowed the calculation of the averaged interaction $\bar{\omega}_\gamma$ by the

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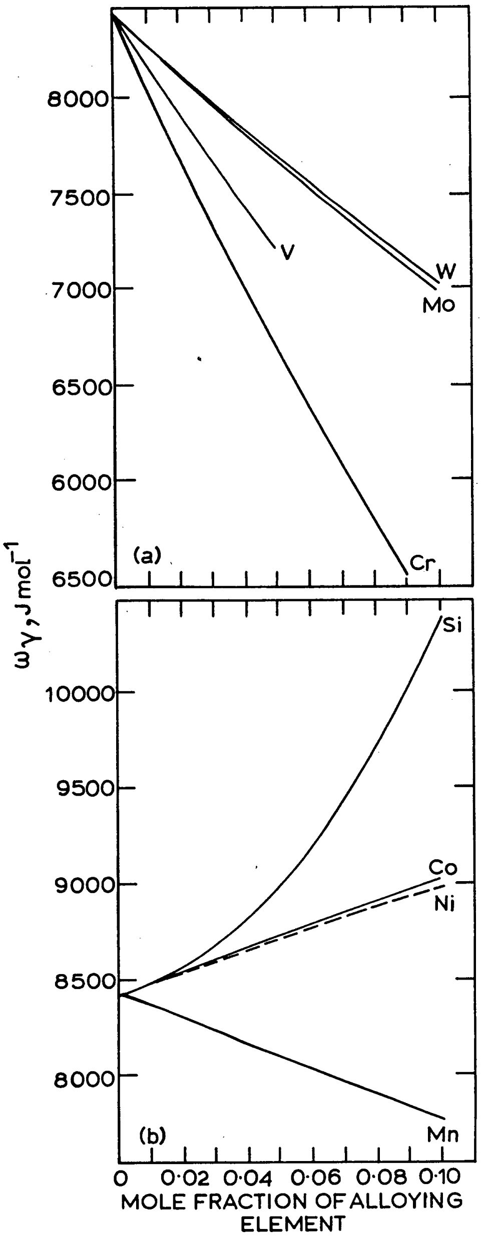
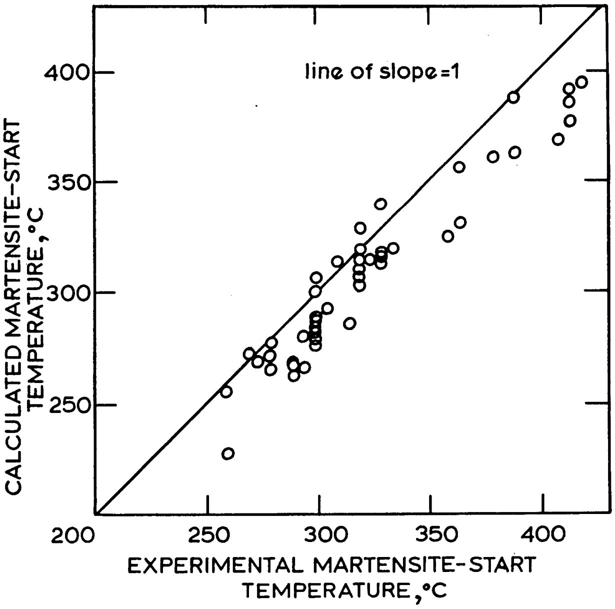


1 Variation of carbon–carbon interaction energy in austenite as function of concentrations of various alloying elements

method of Kinsman and Aaronson.[7] Δf^*, the Zener ordering term, was evaluated as by Fisher.[16] The remaining term $\Delta F_{M_s}^{\gamma\to\alpha'}$ was taken to be equivalent to that evaluated by Bhadeshia[2] for plain carbon steels, as a function of the carbon content of the martensite. This obviously involves the assumption that $\Delta F_{M_s}^{\gamma\to\alpha'}$ is identical for Fe–C and Fe–C–Y steels, and is only a function of the carbon content. The assumption is considered to be reasonable since the present analysis was conducted on the data of Steven and Haynes;[17] the relatively low concentrations of alloying elements of their steels are not expected to modify the crystallography or substructure of the martensite, especially since the effect of carbon was taken into account through the data of Ref. 2. Carbon has by far the most significant influence on the crystallography and substructure of martensite.



2 Comparison between computed and experimental M_s temperatures of various low-alloy steels: experimental data due to Steven and Haynes[17]

Having assembled all the necessary parameters, the M_s temperature was calculated by iteratively solving equation (1), until the two sides of the equation balanced with a residual error of < 0·01%. The analysis was carried out for almost the whole range of steels tabulated by Steven and Haynes; the reason for excluding a few steels was that some of the steels concerned had practically identical compositions.

RESULTS AND CONCLUSIONS

It is clear from Fig. 2 that the predicted results are in rather good agreement with the experimental data of Steven and Haynes. It does, however, seem that the superelement approach tends to somewhat underestimate the M_s temperatures, although on average the difference between the predicted and experimental results is acceptably small (the order of 10–20 K).

We therefore conclude that the superelement extrapolation technique is justified for low-alloy steels, but note that to a small extent it tends to overcompensate for the presence of substitutional elements, thereby predicting a higher undercooling before the onset of martensitic transformation than is actually the case. This small discrepancy may in part be due to the analytical assumption that the critical driving force necessary before the onset of martensite formation is only a function of the carbon content.

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