Determination of Martensite Start Temperature for Engineering Steels
Part II. Correlation between Critical Driving Force and Ms Temperature

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Various physical models are discussed based on different correlations established between the Ms temperature, the critical driving force, and the steel chemistry. These correlations were derived for a group of Fe-(0.2-0.5)C-(0.5-2)Mn-(0.5-2)Si-(0.5-2)Cr-(0.1-0.7)Mo test alloys, which serve as a good representative for most low alloy engineering steels. The chemical driving force was calculated by thermodynamic software and the Ms temperature was predicted by a validated artificial neural network model. Two basic physical models are discussed: the Ms-dependent model and the chemistry-dependent model. In the Ms-dependent model, the critical chemical driving force is linearly related to the Ms temperature: the effect of the steel chemistry is indirect. The standard error of the simple Ms-dependent model is 51.9 J/mol when the spontaneous Zener ordering of carbon atoms is taken into account. The chemistry-dependent model is based on the hypothesis that the critical driving force can be fully represented in terms of the steel chemistry. The critical driving force has been estimated using either linear, exponential, Pythagorean or mixed superposition laws. Comparisons of the critical driving force predicted by these addition methods with the thermodynamic result indicate that an exponential addition method, with the optimum exponent index value of 2.07 (approximately square) gives the best predictive result. The quality of the linear relation between the critical driving force and the Ms temperature is improved slightly if the critical driving force is corrected for the elastic strain energy, estimated by assuming that the elastic modulus, lattice constants, and molar volumes of ferrite and austenite are both temperature- and chemistry-dependent, is removed from the critical driving force. Analysis indicates that the simple Ms-dependent model will be improved after considering the extra minor effect of steel chemistry. In contrast, the error of the chemistry-dependent model can be hardly related to the Ms temperature. Based on the above analysis, an accurate mixed Ms-dependent plus chemistry-influence model, in which the elastic strain energy is considered, is developed, and which yields for the chemical driving force $-\Delta G^* = 3247 - 4.8446 \cdot Ms$ (°C), with a standard error of only 40.7 J/mol.

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1. Introduction

As discussed in the previous article,\textsuperscript{1} a statistical model can describe the dependency of the Ms temperature on the steel chemistry with high accuracy. However, it fails to predict the influences of heat treatment procedures, the initial microstructure of the austenite, external stress, internal strain, pre-martensite transformation, and transformation strain, on the Ms temperature. In contrast to the statistical models, physical models for determining the Ms temperature are based on the current understanding of martensitic transformation mechanism and thermodynamic properties. Martensitic transformation may be regarded as a spontaneous plastic deformation driven by the chemical driving force,\textsuperscript{2} which mainly consists of the Gibbs energy difference between the parent and product phases and depends upon both chemistry and temperature.

According to the classical nucleation theory,\textsuperscript{3} the minimum energy required to overcome the nucleation barrier may include elastic energy, interfacial energy and frictional work and stored defect energy. As examined by Hsu and Chang\textsuperscript{4} for the Fe-C binary system using thermodynamic calculations, and by Raghavan and Antia\textsuperscript{5} for low alloy commercial steels using a statistical analysis, the critical driving force for the martensitic transformation of bcc to fcc in an iron-base alloy is more or less constant at about 1100 J/mol. Cool and Bhadeshia\textsuperscript{6} showed that the critical driving force varies slightly with the carbon concentration. However, in some earlier publications,\textsuperscript{7} the critical driving in binary Fe-C system was calculated to be within 1450 to 3320 J/mol at a temperature range of 750 to 500 K.\textsuperscript{8,9}

Whereas the Ms temperature is of vital engineering importance, the critical driving is of more physical significance since it is directly associated with the transformation mechanism. The great importance of the concept of a critical driving force to determine the martensitic transformation temperature and even the underlying mechanism has led us to devote attention to the dependence of critical driving force on alloying element concentrations and temperature.

2. Test Alloys and Thermodynamic Calculation Method

2.1 Composition of test alloys

The composition range of the chosen test alloys has been described in our previous publications.\textsuperscript{10,11} A class of Fe-C-Si-Mn-Cr-Mo test alloys has been examined with the composition range of 0.2-0.5C, 0.5-2.0Si, 0.5-2.0Mn, 0.5-2.0Cr and 0.1-0.7Mo (mass%). The composition variation steps are 0.1, 0.5, 0.5, 0.5, and 0.2 (mass%) for C, Si, Mn, Cr, and Mo, respectively. Clearly, this relevant composition range covers most of the low alloy engineering steels. The Ms temperatures of all alloys were predicted by an artificial neural network (ANN) model. The standard error for the ANN model, $\sigma^\text{ANN}$, is around 12°C. As a result, all predictions discussed later on in this article will inherit this error, and the total error then amounts to
\[ \sigma_{\text{MS}}^{\text{total}} = \sqrt{(\sigma_{\text{MN}}^{\text{NN}})^2 + (\sigma_{\text{MS}})^2} = \sqrt{144 + (\sigma_{\text{MS}})^2} \quad (\text{°C}). \] (1)

2.2 Thermodynamics

The thermodynamic calculations involved here have been performed using a commercial software package, MTDATA.\(^{[2]}\)

The two sublattice model\(^{[19]}\) was used to express the Gibbs energies of ferrite and austenite phases. The first sublattice is occupied by substitutional atoms and the second is occupied by interstitial atoms (in this study primarily carbon) and vacancies (V). The Gibbs free energies of ferrite (b.c.c.), \(G^f\), (without miscibility) and austenite (f.c.c.), \(G^a\), were calculated separately by allowing only one phase to exist in the system. Then, the molar Gibbs free energy differences, \(\Delta G^\text{r-a} = G^a - G^f\), at different temperatures were obtained. The Gibbs free energies of both phases include unary terms of free energies, mixing entropies, excess free energies describing the deviation from the regular solution model, and magnetic contributions. The temperature step was set to 5°C. Note that the transformation product discussed so far is nothing but a carbon-supersaturated ferrite. As the model concerns martensite formation, the Zener ordering of carbon atoms\(^{[5,9]}\) should be considered. The ordering energy is calculated according to Fisher’s method,\(^{[5]}\) in which, the Zener ordering parameters are related to the ratio of \(T_c/T_c\), where \(T\) is the temperature examined (in this study, \(T = T_c\)), and \(T_c\) is the so-called critical temperature. Note the difference between the critical temperature for Zener ordering and that for martensitic transformation. No Zener ordering takes place when martensite transformation occurs above \(T_c\), i.e., \(M_s/T_c \geq 1\). In such a case, the Zener ordering energy equals zero.

The thermodynamics database selected in this software is based on the SGTE (Scientific Group Thermodata Europe) data, including Solution Database 3.01, Solution Database plus 3.02, Substance Database 6.10, and Unary Database 3.00. The application of this software is restricted to the listed original database. As mentioned above, this paper deals with the Fe-C-Si-Mn-Cr-Mo system. In the thermodynamic database, all 10 unary (the meaning of unary is defined in ref. 12) sub-systems in both the matrix (austenite, A1) and the product (ferrite, A2) have been supplied. Nevertheless, some binary sub-systems and most ternary sub-systems are absent from the database. Care should be taken since the binary sub-systems of Si : (C, Va), (CrMo) : Va, (CrSi) : Va, and Mo : (C, Va) are absent. Note that elements before the colon consist of the substitutional sublattice while those after the colon construct the interstitial sublattice. Va stands for vacancy. Our previous statistical examinations\(^{[5]}\) suggested strong interactions between Si and C, Cr and Mo, Cr and Si, and Mo and C.

3. Results and Discussion

3.1 Procedures for \(M_s\) determination

Figure 1 schematically shows the correlation between the steel chemistry, critical chemical driving force, and \(M_s\) temperature. Two shaded squares represent two basic methods for \(M_s\) prediction: physical and statistical. The \(M_s\) temperature can be estimated directly from the steel composition using various statistical formulas (see route 1 in Fig. 1\(^{[1]}\))

\[ M_s = g(x_i) \] (2)

where \(x_i\) represent the composition of a steel in atomic percentage. One of the disadvantages of this method is that it is difficult to predict \(M_s\) temperature for steel compositions outside the domain from which the statistical model was validated. The physical approach to estimate the \(M_s\) temperature is as accurate as the determination of the critical driving force, \(-\Delta G^*\). The critical driving force for the athermal heterogeneous decomposition of austenite contains at least two separate terms:

\[ -\Delta G^* = -\Delta G^*_{n} + E_f^* \] (3)

where

\[ -\Delta G^*_{n} = -\Delta G^*_{chem} + E_n^* \] (4)

\(-\Delta G^*_{chem}\) is the critical chemical driving force, and \(E_n^*\) is the Zener ordering energy. \(E_f^*\) is the fault energy. At the \(M_s\) temperature, the driving force balances the transformation barrier. That is,

\[ -\Delta G^*_{n} + E_f^* = W_f^* + E_s^* + E_s^* + E_s^* \] (5)

where \(W_f^*\), \(E_s^*\), and \(E_s^*\) are the frictional work, elastic strain energy, stored defect energy in the martensitic nucleus (plate) and ferrite/austenite interfacial energy, respectively.

The critical chemical driving force and the frictional work at the \(M_s\) temperature are the most important factors in determining the martensite transformation behavior.\(^{[19]}\) The critical driving force can be related to either the \(M_s\) temperature or the steel chemistry, \(x_i\), that is,

\[ -\Delta G^* = f_1(M_s) \] (6)

\[ -\Delta G^* = f_1(x_i). \] (7)

If \(E_f^*\) is independent of the \(M_s\) temperature and steel chemistry, then eqs. (6) and (7) can be rewritten in the form

\[ -\Delta G^*_{n} = f_1(M_s) - E_f^* = f_1(M_s) \] (8)

and
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\[-\Delta G^*_\eta = F'_i(x_i) - E'_f = F_1(x_i).\]  (9)

All discussions throughout this article are based on eqs. (8) or (9).

For example, if the critical chemical driving force is known, according to either eqs. (8) or (9), corresponding to either Route 2 or 3 in Fig. 1, the second step for predicting the Ms temperature is to find the correlation between the chemical driving force and the temperature in a certain alloy (see Route 4 in Fig. 1):

\[-\Delta G_\eta = f(T).\]  (10)

Substituting eqs. (8) or (9) into eq. (10) will generate the solution of Ms, as illustrated by Route 5 in Fig. 1. Note that if the standard error of a prediction for the chemical driving force, \(\sigma_{\Delta G}\), is known, then the standard error of the corresponding prediction of an Ms temperature, \(\sigma_{Ms}\), can be determined as

\[\sigma_{Ms} = \frac{\sigma_{\Delta G}}{\left| \frac{\partial \Delta G_{Ch}}{\partial T} \right|_{T=Ms}},\]  (11)

where \(\left| \frac{\partial \Delta G_{Ch}}{\partial T} \right|_{T=Ms}\) is the tangent of the curve at the Ms temperature. Note that because \(\left| \frac{\partial \Delta G_{Ch}}{\partial T} \right|_{T=Ms}\) depends on both the steel chemistry and the Ms temperature, \(\sigma_{Ms}\) corresponding to the same \(\sigma_{\Delta G}\) but for different alloys may be different. In the physical approaches to determine the Ms temperature, only the standard error of the critical driving force will be mentioned.

For a given steel, the chemical driving force for the athermal decomposition of the austenite is the Gibbs free energy difference between austenite and ferrite. The Gibbs free energies of austenite and ferrite can be calculated from a thermodynamic database. Figure 2 shows how the calculation involving both thermodynamic calculation and a regression analysis of Ms data is done for an Fe-0.5C-0.5Si-0.5Mn-0.5Cr-0.5Mo alloy. The difference between the Gibbs free

energy of austenite and ferrite is the temperature dependent chemical driving force (i.e., Route 4 in Fig. 1). The temperature of 603°C (Point A), at which \(-\Delta G_{Ch}^* = 0\), is the critical temperature, \(T_0\), for the athermal decomposition of the austenite. Equation (8), the relation between the critical driving force and Ms, is shown in Fig. 2 by the thin solid line. Details of the derivation of this line are given in Section 3.2. The intercept point B in Fig. 2 or the solution to eqs. (8) and (10) yields the Ms temperature.

3.2 The Ms-dependent models

To be able to determine the Ms temperature, eq. (8) needs to be specified first. By examining 104 engineering steels whose Ms temperatures are all known (they are predicted with an ANN model), the function in eq. (8) can be determined statistically. Figure 3 shows the correlation between the critical chemical driving force calculated by MTData and the Ms temperature. The fact that the critical chemical driving force depends on the Ms temperature as shown in Fig. 3 indicates that there is no unique critical chemical driving force value related to martensitic transformation with different Ms temperatures. The correlation between the critical chemical driving force and the Ms temperature can be approximated by the following equation

\[-\Delta G_{Ch}^* = 2814.5 \left( \frac{1}{\text{mol}} \right) - 2.9991 \left( \frac{1}{\text{mol·°C}} \right) \cdot Ms.\]  (12)

Note that the Zener ordering energy has not yet been taken into account in the above calculation. The critical temperature for the spontaneous ordering of carbon atoms in martensite has been determined by Zener’s eq.\(^9\) The critical temperature is assumed independent of substitutional alloying elements. The decrease of free energy has then been calculated by Fisher’s method.\(^7\) After incorporating the Zener ordering energy thus obtained, the critical driving force at the Ms temperature was calculated again. The correlation between the critical driving force and Ms temperature is then written as

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![Figure 2](image_url)  
**Fig. 2** Example of determining the Ms temperature by calculated the critical driving force. The composition of the example alloy is Fe-0.5C-0.5Si-0.5Mn-0.5Cr-0.5Mo (mass%); A indicates the critical temperature, \(T_0\); B indicates the Ms temperature predicted by eq. (15) (273°C).

![Figure 3](image_url)  
**Fig. 3** Correlation between critical chemical driving force and Ms temperature without consideration of Zener ordering energy.
\[-\Delta G_n^* = 2945.0 \frac{J}{mol} - 3.3414 \frac{J}{mol \cdot ^\circ C} \cdot Ms. \quad (13)\]

Showing a slight increase in the dependence of critical driving force on $Ms$. The standard errors of $-\Delta G_n^*$, $\sigma_{\Delta G}$, is 51.9 J/mol. Although the standard error is not reduced after taking the Zener ordering effect into account, the incorporation of the ordering effect is mandatory from a physical point of view.

Equation (13) is actually the first order approximation of eq. (8). Its general form is

\[-\Delta G_n^* = A \left( \frac{J}{mol} \right) + B \left( \frac{J}{mol \cdot ^\circ C} \right) \cdot Ms. \quad (14)\]

In the case of the example alloy involved in Fig. 2, the intercept point $B$ yields 273$^\circ$C as the estimate for $Ms$. The $Ms$ value predicted by the ANN is 287$^\circ$C. Taking into account the accuracy of the ANN, the agreement is excellent.

A similar relation between the critical driving force and $Ms$ temperature in low alloy steels has been suggested by Raghavan and Antia$^5$ using the equation

\[-\Delta G_{Ch}^* = 1975 \left( \frac{J}{mol} \right) - 1.234 \left( \frac{J}{mol \cdot ^\circ C} \right) \cdot Ms_{KR}. \quad (15)\]

They have used 1152 systematically generated test compositions, and their $Ms$ temperatures were calculated by Kung and Rayment’s equation.$^{15}$ For the current database, the error for eq. (15), $\sigma_{\Delta G}$, is as high as 280 J/mol, so their equation does not apply here.

There is also another check of the validity of eqs. (12), (13), and (15). The maximum $Ms$ values, $Ms^*$, calculated from the above three equations by setting $-\Delta G_{Ms}^* = 0$, are 938, 881, and 1600$^\circ$C, respectively. It is apparent that the result from eq. (13) is more reasonable since it is less than 910$^\circ$C, the equilibrium temperature of austenite and ferrite. Meanwhile, if the $Ms$ of pure iron is taken as 545$^\circ$C, as obtained in our previous publication,$^1$ the corresponding critical chemical driving forces, $-\Delta G_{545}$, calculated from the three equations are 938, 1124, and 1302 J/mol, respectively. The critical driving force for martensite formation in very dilute iron alloys was assumed to be a constant value of 1100 J/mol, or to vary slightly with the carbon concentration, between 900 and 1400 J/mol in Fe-C system with C mass percentages between 0.22 and 1.35.$^6,16$ Again, the prediction of eq. (13) is quite satisfactory, and more reasonable than those of eqs. (15) and (12).

In addition, Imai et al.$^{17}$ have also found that the critical chemical driving force for martensite formation is proportional to the C content, and thus to the $Ms$ temperature in Fe-C binary alloys. This was supported by Bell and Owen’s$^{18}$ results. Bhadeshia$^{16,19}$ applied similar criteria to alloyed steels and obtained a good prediction of the $Ms$ temperature. In other publications from Bhadeshia’s group,$^{20,22}$ they have derived some similar equations in the form of eq. (14), which they call universal displaceable nucleation function; however, they chose various pairs of parameters for $B$ and $A$: 2.8 and 2444,$^{20}$ 3.637 and 1537,$^{21,22}$ and 5.96 and 5204.$^{22}$ The large differences in parameter values in eq. (14) is attributed to the different test alloy databases used. The variation means at least that there is not a universal equation for Widmanstätten ferrite, bainite, and martensite. The results listed in Table 1 show clearly that neither of their universal equations works on the current database. Note that their parameters were derived to describe the thermal displaceable nucleation of either bainitic or Widmanstätten ferrite, where the redistribution of carbon atoms is allowed. This further implies that the nucleation mechanism of bainitic and Widmanstätten ferrite is different from that of martensite. The small error of 51.9 J/mol and the good linear relationship after taking the Zener ordering energy into account indicate that it is safe to use eq. (13) in predicting the $Ms$ temperature within the relevant composition range.

### 3.3 The chemistry-dependent models

#### 3.3.1 General description

An alternate way to determine $\Delta G^*$ is the use of eq. (9) instead of (8). This is also straightforward since $Ms$ mainly depends on the steel chemistry and $\Delta G_n^*$ is a function of the $Ms$ (eq. (14)). For the present study, the carbon concentrations of all alloys range from 0.2 and 0.5 mass%. Disregarding the influence of substitutional alloying elements, the corresponding critical chemical driving force was reported to vary between 1200 and 1400 J/mol.$^{45}$ However, Fig. 3 indicates that the critical driving force required varies between 1500 and 2200 J/mol. This indicates the critical driving force depends not only on carbon concentration but also on the substitutional alloying element concentrations. The chemistry dependence of the critical chemical driving force can be described (see also eq. (9)) as follows

\[-\Delta G_{Ch}^* = F(x_i). \quad (16)\]

<table>
<thead>
<tr>
<th>Methods</th>
<th>$A$</th>
<th>$B$</th>
<th>$R$</th>
<th>$\sigma_{\Delta G}$</th>
<th>$Ms^*$</th>
<th>$-\Delta G_{545}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raghavan-Antia$^5$</td>
<td>1975</td>
<td>-1.234</td>
<td>280.0</td>
<td>1600</td>
<td>1302</td>
<td></td>
</tr>
<tr>
<td>Universal displaceable nucleation function$^{20}$</td>
<td>2444</td>
<td>-2.8</td>
<td>2664.5</td>
<td>873</td>
<td>918</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1537</td>
<td>-3.637</td>
<td>1866.5</td>
<td>423</td>
<td>445</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5204</td>
<td>-5.96</td>
<td>166.7</td>
<td>873</td>
<td>1956</td>
<td></td>
</tr>
<tr>
<td>Present model: $E_n^*$ is considered</td>
<td>2945</td>
<td>-3.3414</td>
<td>0.9621</td>
<td>51.9</td>
<td>883</td>
<td>1125</td>
</tr>
<tr>
<td>Present model: $E_n^*$ is neglected</td>
<td>2815</td>
<td>-2.9991</td>
<td>0.9538</td>
<td>51.6</td>
<td>939</td>
<td>1180</td>
</tr>
<tr>
<td>Present model: $E_n^*$ is considered</td>
<td>3272</td>
<td>-4.9183</td>
<td>0.9859</td>
<td>46.9</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Present model: Mixed method</td>
<td>3247</td>
<td>-4.8446</td>
<td>0.9891</td>
<td>40.7</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
If the compositions and the \( M_s \) temperatures of a class of steels are known, eq. (16) can be obtained by determining the correlation between the critical chemical driving force and the \( M_s \) temperature, as shown by Route 3 in Fig. 1, as well as in Fig. 2. The solution to eqs. (10) and (16) is then the \( M_s \) temperature for any new alloying composition.

### 3.3.2 Mixed superposition rule

Employing a heterogeneous athermal nucleation model, incorporating the theory of solid solution strengthening and disregarding the effect of other obstacles, Ghosh and Olson (GO)\(^{23}\) described the composition dependence of the athermal fractional work for martensitic interface motion, which governs the kinetics of barrierless heterogeneous nucleation. They assume that the martensitic formation is of the same form as that for slip deformation, using a mixed superposition rule to represent the role of different alloying elements. Note that, in their work, the elastic strain energy accompanying martensitic reaction is supposed to be independent of chemical composition and temperature. Using both linear and Pythagorean addition methods,\(^{24}\) the critical chemical driving force is expressed in terms of athermal strengths of alloying elements\(^{23}\)

\[
-\Delta G_{\text{GO}}^* = 1010 + 4009\sqrt{x_C} + \sqrt{(1879\sqrt{x_{\text{Si}}})^2 + (1980\sqrt{x_{\text{Mo}}})^2 + (1868\sqrt{x_{\text{Cr}}})^2 + (1418\sqrt{x_{\text{Mo}}})^2}, \quad \text{J mol}^{-1}. \tag{17}
\]

In Fig. 4(a), the critical driving forces predicted by eq. (17) are plotted versus those calculated using MTData. As the data are not scattered around the diagonal in Fig. 4(a), it is clear that the Ghosh-Olson driving force is different from the critical chemical driving force calculated by MTData; the line drawn in Fig. 4(a) is a least square fit that relates the two critical driving forces:

\[
-\Delta G_{\text{GO}}^* = -0.3973 \cdot \Delta G_\eta^* \left( \frac{J}{\text{mol}} \right) + 1120.2 \left( \frac{J}{\text{mol}} \right). \tag{18}
\]

The standard error of eq. (18) for \( -\Delta G_{\text{GO}}^* \) is 70.7 J/mol. Similarly, the Ghosh-Olson driving force calculated by eq. (17) can be related directly to the \( M_s \) temperature predicted by the ANN model. The data points are scattered around a line of

\[
-\Delta G_{\text{GO}}^* = 2326 - 1.4344^* M_s \quad (\text{C}), \quad (\text{J mol}^{-1}). \tag{19}
\]

This indicates that an \( M_s \) temperature can be calculated directly from eqs. (17) and (19) without any knowledge of thermodynamics and disregarding the physical meaning of the Ghosh-Olson driving force. If the standard error of eq. (17) is also taken into account, the prediction error for the critical driving force is 87.7 J/mol. Although we can use eqs. (17) and (19) to determine the \( M_s \) temperature of a steel, it should be pointed out again that \( -\Delta G_{\text{GO}}^* \) is different from the chemical driving force, as shown in Fig. 4(a).

### 3.3.3 Exponential superposition rule

Cool and Bhadeshia (CB)\(^{25}\) have also examined the relation between critical driving force and steel chemistry by leaving all the coefficients in eq. (17) unchanged but using a linear square root superposition law. They obtained an equation:

\[
\Delta G_{\text{CB}}^* = 683 + 4009\sqrt{x_C}^{0.5} + 1879\sqrt{x_{\text{Si}}}^{0.5} + 1980\sqrt{x_{\text{Mo}}}^{0.5} + 1868\sqrt{x_{\text{Cr}}}^{0.5} + 1418\sqrt{x_{\text{Mo}}}^{0.5}, \quad \text{J mol}^{-1}. \tag{20}
\]

The offset factor of 683 J/mol was fitted to give the optimum agreement based on the linear square root superposition. The offset factor again includes the combined effects of the interfacial and strain energy terms. The lower value of the parameter indicates a lower elastic energy or larger size of nucleus. The results following eq. (20) are plotted versus the critical chemical driving force determined by MTData in Fig. 4(b). It is more difficult to relate this chemical driving force to that predicted by MTData. The predictions from eq. (20), \( -\Delta G_{\text{CB}}^* \), are roughly related to \( M_s \) by the equation.

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**Fig. 4** Determination of the critical driving force by different methods. (a) Ghosh-Olson\(^{23}\) driving force; (b) Cool-Bhadeshia\(^{25}\) driving force.
\[-\Delta G^*_\text{CB} = 2312.3 - 1.5102 \cdot M_s.\] (21)

The degree of scatter in Fig. 4(b) is larger than that in Figs. 3 or 4(a). Note that Cool and Bhadasia\(^{(5)}\) suggested the change of the offset parameter of eq. (17) from 1010 to 683 J/mol. Since eqs. (17) and (20) use different superposition laws, it is unclear why only the offset parameters should change. The statistical regression parameters are summarised in Table 2.

Employing eq. (20), the regression yields an offset parameter of 698.3 J/mol for all test alloys involved in this paper when the influence coefficients of all alloying elements remain the same as those in eq. (17). Since changing the offset parameter in eq. (20) does not significantly improve the predicting accuracy, a more reasonable re-regression based on the simple linear square root superposition rule, called \(n = \frac{1}{2}\) rule, is necessary to determine the correlation between the critical driving force and chemical composition. The new correlation is then expressed in the form:

\[
\Delta G^*_{n=0.5} = 405 + 8450x_C^{0.5} + 970x_Si^{0.5} + 1999x_Mn^{0.5} + 2549x_C^{0.5} - 3666x_Mn^{0.5}, \quad \text{J/mol}^{-1}. (22)
\]

The total standard deviation of this method has been reduced to 81.6 J/mol, which is indeed significantly improved (see Table 2), but still rather high.

3.3.4 Optimum exponent superposition rules

Friedrichs and Haasen\(^{(5)}\) suggested an exponential superposition rule for calculating the critical chemical driving force, using an exponent index of 3/2. Employing this rule, the standard error is calculated to be 80.7 J/mol. Meanwhile, based on the Pythagorean addition rule,\(^{(24)}\) the total error is estimated to be 69.0 J/mol. It is clear in Table 2 that the magnitude of the standard error depends on the value of the exponent index, \(n\). It is then worthwhile to find the optimum value of \(n\), which corresponds to the minimum standard error. The general form of the exponential expression is

\[
\Delta G^*_{n} = k_0 + \sum k_i x_i^n. \quad (23)
\]

Figure 5(a) shows the changes in the standard error and the statistical correlation coefficient with the increase of the exponent index. An optimum value is obtained at an exponent index of around 2 (mathematically, \(n = 2.07\)). The corresponding total standard error reduces to 69.0 J/mol.

Figure 5(b) shows the correlation between the critical driving force calculated by eq. (23) with an exponent \(n = 2.07\) and that calculated by MTData. They are related by the equation

\[
\Delta G^*_{2.07} = 0.9344 \Delta G^*_{0.9} - 119 \quad (J/mol) \quad (24)
\]

![Fig. 5 Calculation of the critical chemical driving force by employing the exponential superposition law. (a) Dependencies of standard error and correlation coefficient on the exponent index: An optimum value of \(n = 2.07\) is obtained, at which the standard error has the minimum while the correlation coefficient reaches its maximum. (b) Determination of the critical chemical driving force by taking an exponent index of 2.07.](image-url)
with a correlation coefficient of $R = 0.9667$. From Table 2, where all correlation coefficients are listed, we know that the regression is clearly improved at the optimum exponent index value, albeit the physical meaning of this optimum value is not very clear yet.

3.3.5 Influence of binary interactions on critical driving force

Similar to the statistical analysis of the influence of alloying elements on the $M_s$ temperature, all binary interactions can be incorporated into the statistical regression. If the exponent index is taken as 2, the total standard error of the binary interaction expression is $60.1$ J/mol, using an equation form of

$$
\Delta G^*_n = k_0 + \sum_{i,j} k_{ij} x_i x_j.
$$

As shown in Fig. 6, the binary interaction model gives a good prediction of critical driving force.

By setting all composition variables to zero, $x_i = 0$, we can estimate the various critical driving forces for the martensitic transformations in pure iron predicted by different methods. The results are given in Table 2. From our best regression of $n = 2.07$ and the binary method with $n = 2$, we obtained a value around 1425 J/mol. This is notably different from our previous value of 1100 J/mol. It seems that if we extrapolate the equations derived from engineering database, we tend to obtain a critical driving force of around 1100 J/mol. On the other hand, if we start our analysis from the thermodynamic database, the critical driving force for martensite for pure Fe is even higher than 1400 J/mol. So far we have not found a proper explanation for this difference; a similar result has also been reported in previous publications.

Similarly, if the chemical critical driving force for the “pure” Fe is set as 1125 J/mol, the $M_s$ temperatures of “pure” iron can be calculated by different methods described above. The results are again listed in Table 2. Surprisingly, a temperature of 547°C is obtained from the binary method, which is almost the same as the $M_s$ temperature of “pure” Fe, 545°C, which has been reported in our previous article.

3.4 Consideration of the elastic strain energy

As mentioned above, eq. (17) assumes that the elastic strain energy is independent of the temperature and steel chemistry. This assumption is examined here by introducing a linear dependency of both elastic modulus and lattice constants (molar volumes) of ferrite and austenite upon either temperature or chemical composition. The lattice constants and elastic moduli of both austenite and ferrite have been related to the temperature and steel chemistry by regressing 168 systematic data. The hydrostatic elastic strain (the dilatational component) was then calculated according to Olson and Cohen’s simple model. The remaining component of the critical chemical driving force calculated from MTData is obtained by correcting for the elastic strain energy

$$
-\Delta G^*_e = -\Delta G^*_n - E^*_e.
$$

The correlation between the remaining part of the critical chemical driving force and the $M_s$ temperature is shown with an equation of

$$
-\Delta G^*_e = 3272 \left( \frac{J}{mol} \right) - 4.9183 \left( \frac{J}{mol \cdot ^\circ C} \right) \cdot M_s.
$$

The scattering of the data points is surprisingly reduced compared with that in Fig. 3. The standard error is reduced to 46.9 J/mol.

3.5 Improvement of the $M_s$-dependent model

Finally, let us check if the error in eq. (13) arises from the variation in steel chemistry

$$
-\Delta G^*_n = f(M_s) + Error(x_i)
$$

or, in another way, if the error of eq. (16) arises from the variation of the $M_s$ temperature

$$
-\Delta G^*_n = F(x_i) + Error(M_s).
$$

Figure 7 shows how the difference between the critical chemical driving force calculated by MTData and that predicted by binary interaction model by setting $n = 2$, $Error(M_s)$, changes against the $M_s$ temperature. The errors are randomly scattered over the whole $M_s$ temperature range. Therefore, the prediction of eq. (29) can not be improved by introducing an $M_s$ related function.

In the case of chemistry-dependent model, it is not possible to make a similar plot, as chemistry has in this case 5 parameters. However, if we fit a linear equation, we find

$$
Error(x_i) = 9.1 - 1279.9 x_C + 2064.6 x_A + 2608.6 x_Mn + 4877.1 x_Cr - 22269.9 x_Mo
$$

which reduces the standard error from 51.9 to 33.3 J/mol. It is indeed a significant improvement.

Finally, when corrected for the elastic strain energy, and taking kinds of possible correction factors introduced in this article, the $M_s$-dependent component of the critical driving force is calculated. The best fitting relation between the critical chemical driving force and the $M_s$ temperature is given

![Fig. 6 Binary interaction model for predicting the critical chemical driving force by setting the exponent index value to 2.](image-url)
by

\[ \Delta G_f^* = 3247 \left( \frac{J}{\text{mol}} \right) - 4.8446 \left( \frac{J}{\text{mol} \cdot \text{K}^\circ} \right) \cdot M_s. \]  \hspace{1cm} (31)

The standard error of this regression is as low as 40.7 J/mol.

4. Conclusions

By examining the correlation between the critical chemical driving force (calculated by a commercial thermodynamic program), the steel chemistry and the \( M_s \) temperature (predicted by a validated artificial neural network model) for a database system of engineering steels: Fe-(0.2–0.5)C-(0.5–2.0)Mn-(0.5–2.0)Si-(0.5–2.0)Cr-(0.1–0.7)Mo, it is concluded that

1. The \( M_s \) temperature of a steel can be physically calculated by either an \( M_s \)-dependent or a chemistry-dependent physical model.

2. In the \( M_s \)-dependent model, the critical chemical driving force is linearly related to the \( M_s \) temperature disregarding the effect of the chemistry. A good linearity is obtained by taking the spontaneous Zener ordering of carbon atoms into account. The standard error of the simple \( M_s \)-dependent model is 51.9 J/mol.

3. In the chemistry-dependent model, the critical driving force has been calculated with various superposition laws. After comparing the critical driving force predicted by these superposition laws with the thermodynamic result, it is concluded that an exponential superposition method gives better prediction result. The efficiency of this method depends further on the exponent index. Systematic analysis indicates that the best prediction can be achieved by taking an exponent index value of 2.

4. The dilatation component of the elastic strain energy has been calculated by assuming that the elastic moduli, the lattice constants, and the molar volumes of ferrite and austenite be both temperature- and chemistry-dependent. By taking into account the elastic strain energy, the combination of the critical driving force calculated from the simple \( M_s \)-dependent models, the linear dependency of the critical driving force on the \( M_s \) temperature is improved.

5. Analysis indicates that the error of the simple \( M_s \)-dependent model can be reduced by considering minor effect of steel chemistry. However, the error of the chemistry-dependent model can hardly be related to the \( M_s \) temperature.

6. Based on the above analysis, an extended \( M_s \)-dependent plus chemistry-influence model is developed, in which the elastic strain energy has also been considered. The relation between the effective \( M_s \)-dependent part of the critical driving force and the \( M_s \) temperature is expressed linearly by \(-\Delta G_f^* = 3247 - 4.8446 \cdot M_s (\text{K}^\circ)\). The standard error of this prediction is as low as 40.7 J/mol.

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