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An approximate approach for the calculation of M_s in iron-base alloys

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Having estimated the critical driving force associated with martensitic transformation, $\Delta G^{\alpha\to M}$, as

$$\Delta G^{\alpha\to M} = 2.1\sigma + 900$$

where σ is the yield strength of austenite at M_s, in MN m^{-2}, we can directly deduce the M_s by the following equation:

$$\Delta G^{\gamma\to M}|_{M_s} = \Delta G^{\gamma\to\alpha} + \Delta G^{\alpha\to M} = 0.$$

The calculated M_s are in good agreement with the experimental results in Fe–C, Fe–Ni–C and Fe–Cr–C, and are consistent with part of the data in Fe–Ni, Fe–Cr and Fe–Mn alloys. Some higher "M_s" determined in previous works may be identified as M_a, M_s of surface martensite or bainitic temperature. The M_s of pure iron is about 800 K. The M_s in Fe–C can be approximately expressed as

$$M_s\ (^\circ\mathrm{C}) = 520 - [\%\mathrm{C}] \times 320.$$

In Fe–X, the effect of the alloying element on M_s depends on its effect on T_0 and on the strengthening of austenite. An approach for calculation of $\Delta G^{\gamma\to\alpha}$ in Fe–X–C is suggested. Thus dM_s/dx_c in Fe–X–C is found to increase with the decrease of the activity coefficient of carbon in austenite.

1. Introduction

No satisfactory approach for M_s calculation of fcc→bcc (bct) in iron-base alloys has been well established, owing to the difficulty of estimating the non-chemical free energy (usually considered to be the strain energy) associated with the martensitic transformation. An effort has been made to calculate the strain energy, but no unique available result appears to be shown. Truncating the complexity of the strain energy calculation, the present author suggested a new approximate approach for estimation of the critical driving force, and in turn for M_s calculation for the martensitic transformation of fcc–bcc (bct) in ferrous alloys [1–3] on the basis of some previous discrete works [4–7], and the result seems encouraging [2, 3], although it may be inapplicable to thermoelastic martensites. Hornbogen [6] suggested that the critical driving force (free energy change from T_0 to M_s) may consist of the driving force for nucleation and the shearing energy, i.e. the energy required for onset of the shearing process of transformation. Argent [7] took the stored energy (dislocation strain energy) in martensite as the total critical driving force in his work on Fe–Cr and Fe–Co. His results are in fair agreement with the experimental data, although they are 43 and 23 K higher than the data of Andrew [8] and Steven and Haynes [9], respectively. However, this approach, which does not take account of the strength of the matrix, seems invalid for the alloy systems in which the alloying element markedly strengthens the austenite matrix such as Fe–Si, Fe–W, Fe–Mo and Fe–V. Up to now, most of the works of calculating the critical driving force have been done only by means of the

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known experimental M_s, such as recent works on Fe–C and Fe–X–C [10, 11]. An introduction to an approach for direct deduction of M_s appears to be needed. This paper gives a brief concept of this approach, and also makes a comparison between the result of calculation and the experimental M_s.

2. The basic concept of an approximate approach

In previous works, T_0 was defined as the temperature for $\Delta G^{\gamma\to\alpha} = 0$ in Fe–X, and $\Delta G^{\gamma\to\alpha'} = 0$ in Fe–C, in which $\Delta G^{\gamma\to\alpha'} = \Delta G^{\gamma\to\alpha} + \Delta G^{\alpha\to\alpha'}$. $\Delta G^{\alpha\to\alpha'}$ is the free energy change during the ordering of carbon atoms in martensite. According to the following reasons $\Delta G^{\alpha\to\alpha'}$ may be neglected in alloys with $x_c < 0.06$:

(i) the structure of low-C martensite is cubic where the $\Delta G^{\alpha\to\alpha'}$ is unavailable,

(ii) the carbon atoms are distributed in partial disorder in virgin bct martensite [12, 13],

(iii) the ordering configuration was inherited from that of austenite [14], and

(iv) the partial ordering might be a result of the formation of (1 1 0) twinning [15].

Therefore, in Fe–C ($x_c < 0.06$) T_0 may also be defined as the temperature for $\Delta G^{\gamma\to\alpha} = 0$, and T_0 is the equilibrium temperature between fcc and bcc phases. Let $\Delta G^{\alpha\to \mathrm{M}}$ be the driving force required for transformation, i.e. the free energy change between T_0 and M_s then, at M_s, we have

$$\Delta G^{\gamma\to \mathrm{M}} = \Delta G^{\gamma\to\alpha} + \Delta G^{\alpha\to \mathrm{M}} = 0 \quad (1)$$

and the driving force may be expressed as $\Delta G^{\alpha\to \mathrm{M}}$ or $-\Delta G^{\gamma\to\alpha}$. In fcc → bcc, it seems reasonable to consider there first is formed a bcc micro region as an embryo, whether it is formed by propagation of a dislocation loop as an interface [16] or by a stacking fault bounded by a Shockley imperfect dislocation [17, 18]. Such an embryo will not be stabilized until at T_0, and $\Delta G^{\alpha\to \mathrm{M}}$ is the energy required to form martensite from the propagation of such an embryo.

In Equation 1, the term $\Delta G^{\gamma\to\alpha}$ can be obtained by various models, i.e. Fisher, KRC and LFG [2, 3]. The required critical driving force for transformation is mainly composed of the shearing energy, i.e. the energy required for onset of the shearing process, and stored energy, i.e. the successive energy required for forming martensite; the former may be related to the yield strength of the parent phase, and the latter is concerned in the substructures in the martensite formed and the adjoining deformed austenite. The experimental results by West [19, 20], Ansell [21] and their co-workers revealed the linear relationship between the yield strength of austenite and the M_s temperature. Ishida [22] has suggested the same idea. The shearing energy, U_s, required for the martensitic transformation can be expressed as

$$U_s = \tfrac{1}{2}[V\phi\tau] \quad (2)$$

where V is the total deformed molar volume, i.e. the sum of the molar volume of martensite formed, V_m, and that of austenite deformed (accomodation) V_γ, ϕ the shearing amount and τ is the shear stress. Let σ be the yield strength of austenite at M_s, $\tau = \sigma/m$, in which $m = 2$ to 3. Noting the accomodation of martensite itself and also the deformation hardening of austenite, we may put σ instead of τ in Equation 2, i.e.

$$U_s = \tfrac{1}{2}V\phi\sigma. \quad (3)$$

Taking $V_\gamma \simeq V_m = 0.75\,\mathrm{cm^3\,mol^{-1}}$ [5], $\phi = 0.28$, with the invariant plane strain ~ 0.23 [23] and shape strain $\sim 9^0$ [24], and letting the unit of σ be in $\mathrm{MN\,m^{-2}}$ and substituting them in Equation 3, we have

$$U_s = 2.1\sigma\,\mathrm{J\,mol^{-1}}. \quad (4)$$

The stored energy includes both stored energy in martensite and deformed austenite. The dislocation density in low carbon martensite is $10^{12}\,\mathrm{cm^{-2}}$ in order of magnitude [25]. Then the stored energy in dislocated martensite $= 400\,\mathrm{J\,mol^{-1}}$. The dislocation density of the matrix neighbouring the martensite is in the same order of magnitude as above [24], and the stored energy in deformed austenite is also $400\,\mathrm{J\,mol^{-1}}$. The estimated twin boundary energy in high carbon martensite is about $400\,\mathrm{J\,mol^{-1}}$ (see Appendix). Then the stored energy for any proportion of dislocations and twins in martensite is $400\,\mathrm{J\,mol^{-1}}$ and the total stored energy is $800\,\mathrm{J\,mol^{-1}}$, significantly different from that obtained by Lee *et al.* [26]. Take $100\,\mathrm{J\,mol^{-1}}$ as the miscellaneous required energy, such as dilatational energy ($\sim 70\,\mathrm{J\,mol^{-1}}$ [5]) and surface energy, etc. ($\sim 30\,\mathrm{J\,mol^{-1}}$ [16]). We have the total stored energy $\Sigma\Gamma = 900\,\mathrm{J\,mol^{-1}}$. Suppose $\Sigma\Gamma$ varies insensitively with the composition and temperature and the effect of which on M_s is mainly through the σ of the matrix. Then we can estimate the approximate value of the critical driving force, $\Delta G^{\alpha\to \mathrm{M}}$ or $-\Delta G^{\gamma\to\alpha}$, at M_s:

$$\Delta G^{\alpha\rightarrow M} = 2.1\sigma + 900\,\mathrm{J\,mol^{-1}}. \quad (5)$$

$\Delta G^{\alpha\rightarrow M}$ may also involve the energy associated with an external magnetic field, stress energy and the energy provided by imperfections in the parent phase which may be added to the right side of Equation 5 if necessary.

3. The M_s of pure iron

The M_s of pure iron has not been identified. According to the previous thermodynamics approach in Fe–C [4, 5, 27], it must be 800 K, which is in good agreement with some experimental data in pure iron [28–30] but inconsistent with other data, i.e. 1030 K [31–33]. Extrapolation from the experimental M_s in Fe–C yields the M_s of pure iron as 520° C [34], but from that in Fe–X various values may be obtained, such as 973 [35, 16], 953 [36] and even below 870 K [37]. Even the same author extrapolated the M_s of pure iron with contradictory results from Fe–C [4] and Fe–Ni [35].

The strength of γ-Fe at 1200 K is approximately 55 MN m^{-2}, and at temperatures above 800 K the strength increment resulting from the lowering of temperature is about 18 MN m^{-2} per 100 K. Then the yield strength of pure iron at M_s, σ^0, would be

$$\sigma^0 = 55 + 0.18\,(1200 - M_s^{\mathrm{Fe}}) \quad (6)$$

where M_s^{Fe} is the M_s of pure iron. As the substructure in martensite of pure iron resembles that of low carbon martensite [38], $\Sigma\Gamma = 900$ is also adequate for pure iron. From Equation 5, we have

$$\Delta G^{\alpha\rightarrow M} = 2.1\,[55 + 0.18\,(1200 - M_s^{\mathrm{Fe}})] + 900\,\mathrm{J\,mol^{-1}}. \quad (7)$$

Substituting Equation 7 in equation 1:

$$\Delta G^{\gamma\rightarrow M} = \Delta G_{\mathrm{Fe}}^{\gamma\rightarrow\alpha} + 2.1\,[55 + 0.18\,(1200 - M_s^{\mathrm{Fe}})] + 900 = 0. \quad (8)$$

Taking $\Delta G_{\mathrm{Fe}}^{\gamma\rightarrow\alpha}$ given by Kaufman *et al.* [39] yields M_s^{Fe} as 800 K, in good agreement with the experimental value, 793 K [29, 30, 34], while taking $\Delta G_{\mathrm{Fe}}^{\gamma\rightarrow\alpha}$ by Orr and Chipman [40] yields 835 K. An M_s^{Fe} of 812 K from an empirical formula by Andrew [8] and 834 K by Steven and Haynes [9] is very close to 812 and 800 K, respectively. An M_s^{Fe} of 820 K has been taken as a more probable value by Christian [41].

It is shown that the lower values of M_s in pure iron obtained by experiment with a specimen containing traces of impurity (carbon) are exact M_s, while higher ones with a high purity specimen do readily produce massive ferrite, surface martensite or bainite during quenching. The work of Wayman and Alstetter [42] showed that the quenching product of zone-refining iron, in which surface relief also appeared, only indicated surface martensite since the corresponding inner structure was non-martensitic and suggested that the higher values in experiment of M_s might be those of surface martensite but not the M_s of the bulk specimen [43]. Wilson [44] believed that the transformation temperature of pure iron of 973 K is really bainitic and M_s is 820 ± 10 K.

4. M_s of Fe–C

$\Delta G^{\gamma\rightarrow\alpha}$ in Fe–C can be obtained by applying the following equation:

$$\Delta G_{\mathrm{Fe-C}}^{\gamma\rightarrow\alpha} = (1 - X_c)\Delta G_{\mathrm{Fe}}^{\gamma\rightarrow\alpha} + (1 - X_c)RT\ln(a_{\mathrm{Fe}}^{\alpha}/a_{\mathrm{Fe}}^{\gamma}) + X_cRT\ln(\gamma_c^{\alpha}/\gamma_c^{\gamma}) \quad (9)$$

where $\gamma_c^{\alpha}/\gamma_c^{\gamma}$ can be deduced from the Fisher model [45]. Utilizing the latest Fe–C diagram [46] and taking $\Delta H_c^{\alpha} = 83\,680$ [47] $\Delta H_c^{\gamma} = 44\,630$ [48] J mol^{-1}, thus we have

$$RT\ln(\gamma_c^{\alpha}/\gamma_c^{\gamma}) = 39013 - 11.4T \quad (10)$$

$RT\ln(\gamma_{\mathrm{Fe}}^{\alpha}/\gamma_{\mathrm{Fe}}^{\gamma})$ is found by the geometric model [49] as

$$RT\ln(\gamma_{\mathrm{Fe}}^{\alpha}/\gamma_{\mathrm{Fe}}^{\gamma}) = \frac{RT}{5}\left[3\ln\frac{3-8X}{3(1-X)} - \ln\frac{1-6X}{1-X}\right]$$

Taking $\Delta G_{\mathrm{Fe}}^{\gamma\rightarrow\alpha}$ given by Kaufman *et al.* [39], and substituting these in Equation 9, we get $\Delta G_{\mathrm{Fe-C}}^{\gamma\rightarrow\alpha}$.

Experiment shows that the increment of yield strength of austenite with 1 at% C would be 28 MN m^{-2} and with the lowering of temperature, 20 MN m^{-2} per 100 K [50]. Thus the yield strength of austenite at M_s, σ, with various carbon contents may be shown in the following equation:

$$\sigma = 130 + 2800X_c + 0.2\,(800 - M_s) \quad (11)$$

in which 130 MN m^{-2} is the yield strength and 800 K is the M_s of γ-Fe. The $\Delta G^{\alpha\rightarrow M}$ of Fe–C may be obtained through Equation 5 as

$$\Delta G^{\alpha\rightarrow M} = 2.1\,[130 + 2800X_c + 0.2\,(800 - T)] + 900. \quad (12)$$

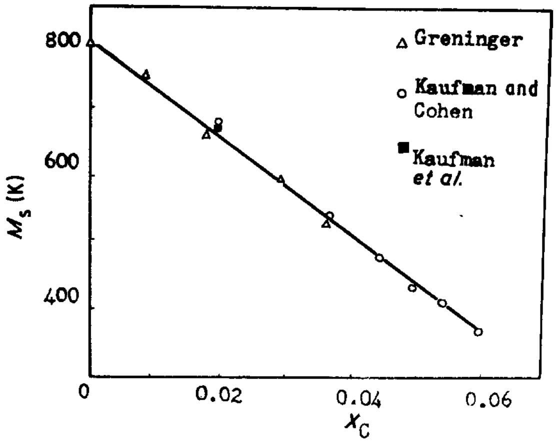

Figure 1 The M_s of Fe–C.

Substituting Equations 9 and 12 into 1, we obtain the M_s of Fe–C alloys with various carbon contents, as shown in Fig. 1, which are in good agreement with typical experimental results [16, 34, 49]. 1 at% C lowers the M_s about 70 K, or the effects of %C on M_s (° C) are as follows:

$$M_s\,(^\circ\mathrm{C}) = 520 - [\%\mathrm{C}] \times 320 \quad (13)$$

There is a linear correlation between M_s and X_c, as shown in Fig. 1, and so is there between M_s and the yield strength of austenite at M_s. It follows that factors affecting the yield strength, such as grain size and dislocation configuration in austenite, will be the function of M_s.

5. M_s in Fe–X

Regarding Fe–X as a regular solution, we can deduce the $\Delta G^{\gamma\to\alpha}$ in Fe–X as

$$\Delta G^{\gamma\to\alpha} = (1-x_i)\Delta G_{\mathrm{Fe}}^{\gamma\to\alpha} + x_i \Delta G_i^{\gamma\to\alpha} + x_i(1-x_i)(B-A) \quad (14)$$

Substituting $\Delta G^{\alpha\to\mathrm{M}}$ obtained through Equation 5 together with Equation 14 into Equation 1 yields the M_s in Fe–X.

5.1. M_s in Fe–Ni

$\Delta G_{\mathrm{Fe-Ni}}^{\gamma\to\alpha}$ in Fe–Ni is obtained by (i) the Kaufman and Cohen (KC) model [35], (ii) the Rao *et al.* (RRW) model [51] and (iii) the $\Delta G_{\mathrm{Ni}}^{\gamma\to\alpha}$ value of Kaufman [52] and the $(B-A)$ value from Breedis and Kaufman [53] – the KBK model, respectively. With reference to the yield strength of quenched austenite in Fe–31 Ni, ~ 250 MN m^{-2} [54], and that at M_s in Fe–29.55 Ni, ~ 245 MN m^{-2} [54], it seems reasonable to take the yield strength of

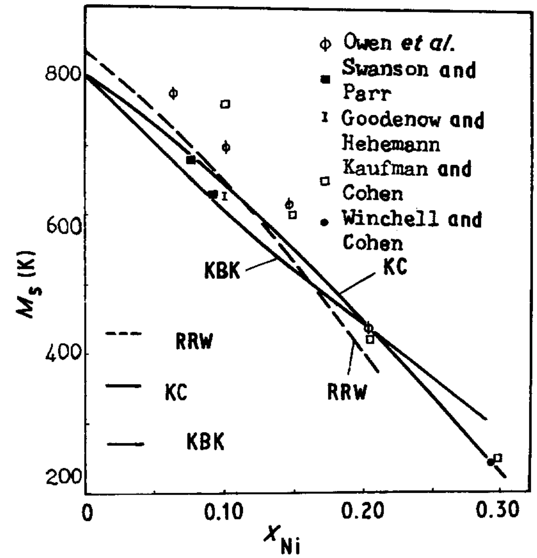

Figure 2 The M_s of Fe–Ni.

austenite at M_s of alloys $X_{\mathrm{Ni}} = 0.1$, 0.2 and 0.3 as 150, 200 and 250 MN m^{-2}, respectively. The M_s calculated by following the KC, RRW and KBK models are shown in Fig. 2. They are consistent with the listed experimental M_s values [35, 56–59], and 1 at% Ni lowers the M_s about 16.5 K from the KC model. There are large divergences among the experimental data of M_s in alloys with < 20 at% Ni in which the higher values seem doubtful. Experiment has shown that the massive transformation [28] or bainite [60] might occur in alloys with 0 to 15 at% Ni after quenching at a rate up to 5500 K sec^{-1}. Following this, it seems convincing that the M_s measured for Fe–Ni (< 20 at%) by KC [35] with a quenching rate of 5 K min^{-1} may be M_a or the bainitic temperature rather than M_s. Even if the quenching rate was as high as 6×10^4 K sec^{-1} and the surface relief of martensite was revealed [36], it is probable that the specimen produced only surface martensite [55]. The irrelevant conclusion that the driving force in low nickel alloys was only several tens J mol^{-1}, which has been widely accepted for as long as 30 years, might be discarded.

5.2. M_s in Fe–Cr

$\Delta G^{\gamma\to\alpha}$ in Fe–Cr is calculated by applying Kaufman's model [61]. Referring to the yield strength of austenite in Cr-steel at 425° C [21], 1 at% Cr will offer strength about 14 MN m^{-2} in Fe–Cr. Taking the yield strength of austenite at M_s in alloys with $X_{\mathrm{Cr}} = 0.05$, 0.1, 0.15 and 0.2 as 140,

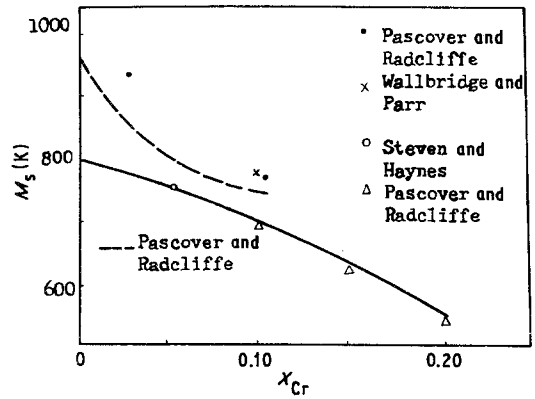

Figure 3 The M_s of Fe–Cr.

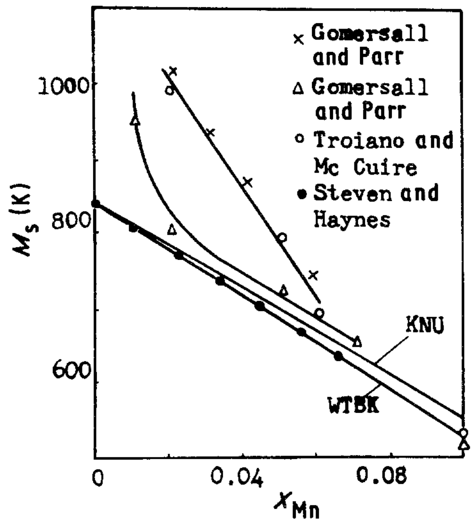

Figure 4 The M_s of Fe–Mn.

160, 180 and 200 MN m^{-2}, yields the M_s in Fe–Cr alloys as shown in Fig. 3, and the experimental M_s [9, 62–64] are also listed in which the M_s measured by Pascover and Radcliffe (PR) [62] are somewhat higher and just fall in a line with the data of an alloy with $X_{Cr} = 0.01$ given by Wallbridge and Parr [64]. Parr pointed out that the surface relief in Fe–Cr was questionable [37] and it was also inferred that specimens of Fe–Cr may form surface martensite [65]. Therefore these three points mentioned above may be M_a or M_s of surface martensite.

The dashed line in Fig. 3 following PR [62] explains the fact that the M_s of pure iron might be 970 K as a result of extrapolation from M_s of Fe–Cr that seems pervertible.

5.3. M_s in Fe–Mn

We have $\Delta G^{\gamma \to \alpha}_{Fe-Mn}$ by applying (i) the model of Kirchner, Nishizana and Uhrenius – the KNU model [66] with $\Delta G^{\gamma \to \alpha}_{Fe}$ of Orr and Chipman [40] and (ii) $\Delta G^{\gamma \to \alpha}_{Mn}$ of Weiss and Tauer [67] and the $(B - A)$ value of Breedis and Kaufman [53] – the WTBK model.

Referring to 200 MN m^{-2} as the yield strength of austenite in Fe–30 Mn–5 Cr [68], we may take 140, 150, 160, 170 and 180 MN m^{-2} as the yield strength of austenite in Fe–Mn with $X_{Mn} = 0.02$, 0.04, 0.06, 0.08 and 0.10, respectively.

Fig. 4 shows the M_s in Fe–Mn as the result of following the KNU and WTBK models and the experimental data measured by various authors [9, 69, 70]. Results from the two models are close to each other and consistent with that of Steven and Haynes [9]. The M_s with a quenching rate of 460 K sec^{-1} [70] and that obtained by Troiano and McCuire [69] has the same trend, so we may put them in the same line. They are much higher and may be a transformation temperature other than M_s when we take the present result as a criterion. We may connect the data with a quenching rate of 10 000° C sec^{-1} in another curve, as shown in Fig. 4, except for $X_{Mn} = 0.1$ [70]. The authors [70] pointed out that although they appeared as surface relief the transformation characteristic was still uncertain because their etched and polished structure resembled that formed by massive transformation. Identified by the present approach, the transformation point of the alloy with 1 at % Mn is not M_s, that with $X_{Mn} = 0.10$ is really M_s and the other data remain uncertain. It has been inferred that alloys with $< 6\%$ Mn do readily undergo massive transformation.

5.4. Acquiring the strength of austenite from known M_s in Fe–Si

Following the result given by Kaufman *et al.* [39], ΔH_i in Fe–Si may be a constant value -2175 J mol^{-1}. Silicon raises T_0 but slightly lowers M_s; consequently, it increases the driving force and in turn greatly raises the yield strength of austenite. Assume that 1 at % of silicon in Fe–Si lowers M_s by 5 K, it will increase by 20 MN m^{-2} the yield strength of austenite at M_s. The strengthening effect of silicon on austenite is significantly greater than that of nickel, chromium and manganese.

The above results imply that in Fe–X, an alloying element greatly lowering the T_0 and strengthening the austenite lowers M_s greatly, e.g. C. An alloying element lowering T_0 but slightly strengthening the austenite, lowers M_s also but lowers dM_s/dx moderately, e.g. manganese, chromium and nickel, while those raising T_0 but strengthening the austenite, have only little effect on M_s, e.g. silicon. Cobalt raises T_0 and M_s as well [37], so it is reasonable to interpret that cobalt strengthens austenite less than silicon does. Molybdenum, tungsten and vanadium raise T_0 but they are well-known elements which considerably strengthen the austenite, and thus lower M_s. All these can be quantitatively deduced through, e.g. Equations 1, 5 and 14.

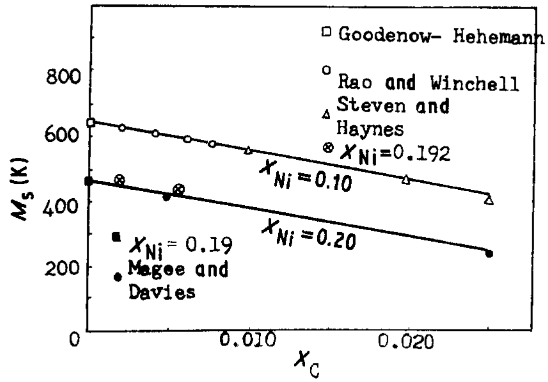

Figure 5 The M_s in Fe–Ni–C.

6. M_s in Fe–X–C

The following formula was suggested for $\Delta G^{\gamma\to\alpha}$ in Fe–X–C as a dilute solution:

$$\Delta G^{\gamma\to\alpha} = x_{Fe}\Delta G_{Fe}^{\gamma\to\alpha} + x_c RT\ln(\gamma_c^\alpha/\gamma_c^\gamma) + x_i \Delta G_i^{\gamma\to\alpha} + x_i(1-x_i)(B-A) \qquad (15)$$

where γ_c^α and γ_c^γ are activity coefficients of carbon in Fe–X–C solid solutions α and γ, respectively; thus, the interaction of carbon and the alloying element has been considered*. The last two items on the right side in Equation 15 involve the effect of the alloying element in Fe–X–C. It is suggested that the activity data ought to be selected from the experiments at the lowest possible temperature. There are a lot of activity data of carbon in Fe–X–C austenite, but in ferrite they are unavailable and we have to take the γ_c^α in Fe–C instead. Assume that the effect of carbon and alloying element on the yield strength of austenite is additive and can be obtained through σ in Fe–C and in Fe–X.

6.1. M_s in Fe–Ni–C

Taking γ_c^γ from Wada *et al.* [71], γ_c^α from Swartz [72], $\Delta G_{Fe}^{\gamma\to\alpha}$ by Kaufman *et al.* [39] and $\Delta G_i^{\alpha\to\gamma}$ and $(B-A)$ value from the KC model for Fe–Ni, and following Equation 15 yields $\Delta G^{\gamma\to\alpha}$ in Fe–Ni–C. M_s is shown in Fig. 5, in good agreement with the observed values [9, 58, 73–75]. Rao *et al.* [51] deduced the following formula for M_s in Fe–Ni–C:

$$M_s(K) = 834 - 7430x_c - 1790x_{Ni}. \qquad (16)$$

The authors mentioned that Equation (16) was valid above 400 K. Equation 16 gives a somewhat higher value than the experimental M_s because of too low a driving force (840 to 1255 J mol^{-1}) estimated. From Equation 5, the driving force of Fe–Ni–C might be at least 1300 J mol^{-1} (i.e. for an alloy with $X_{Ni} = 0.1$ and $X_c = 0.01$).

6.2. Fe–Cr–C

Take γ_c^γ from Wada *et al.* [76], γ_c^α from Swartz [72], and take $\Delta G_{Fe}^{\gamma\to\alpha}$, $\Delta G_{Cr}^{\gamma\to\alpha}$ and the $(B-A)$ value the same as for Fe–Cr. Substituting the results of Equations 5 and 15 in Equation 1, yields M_s in Fe–Cr–C ($X_{Cr} = 0.032$ and 0.06) as shown in Fig. 6, which are consistent with the measured M_s [8, 9, 56, 77].

The values of γ_c^γ in Fe–Ni–C are greater than

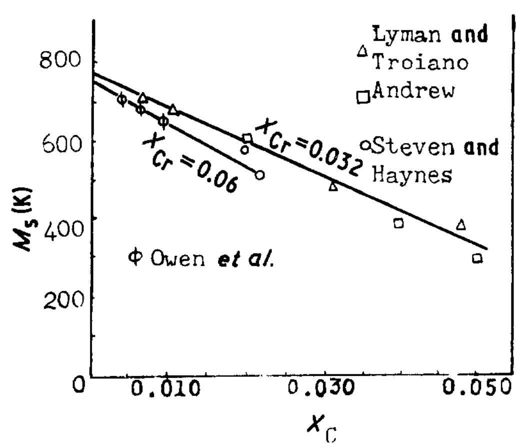

Figure 6 The M_s in Fe–Cr–C.

*Let C and D be the parameters of interaction of carbon and the alloying element in γ and α, respectively. The term $x_i x_c$ $(D-C)$ would be added to Equation 15. However, the product value of x_i and x_c is very small and $(D-C)$ is not so large, so this term might be neglected.

those in Fe–C, while γ_c^γ values in Fe–Cr–C are smaller. At the same time, the values of γ_c^γ in Fe–Ni–C increase with Ni-content, while the values of γ_c^γ in Fe–Cr–C decrease with Cr-content. From Equation 15 it is revealed that carbon lowers T_0 in Fe–Ni–C less than in Fe–Cr–C. In the case of the same contribution of carbon to the strengthening of the austenite in Fe–X–C, the effect of carbon on lowering of M_s in Fe–X–C just depends on the activity (or activity coefficient) of carbon in Fe–X–C austenite. Since it rises in Fe–Ni–C and lowers in Fe–Cr–C, $dM_s/dx_c \simeq 8500$ K in alloys with $X_{Ni} = 0.1$ and $dM_s/dx_c \simeq 10\,500$ for $X_{Cr} = 0.03$. Thus, at the same strength level, Ni-steel often displays a higher M_s than Cr-steel does.

When the effect of carbon on the strengthening of austenite in Fe–X–C is approximately identical, following the activity coefficient data of carbon in austenite in Fe–X–C [76, 78], it is possible to predict the degree of lowering of the M_s by carbon in Fe–X–C in the following order: Fe–Si–C, Fe–Ni–C, Fe–Co–C, Fe–Mn–C, Fe–Cr–C, Fe–Mo–C and Fe–V–C. If there is a large difference of the effect of carbon on the strengthening of austenite in various systems, it is necessary to take the strengthening effect together with activity data into account for prediction of the effect of carbon on M_s.

Owing to the more powerful strengthening effect of carbon on austenite than other alloying elements, carbon acts as the main element controlling the driving force.

7. Conclusion

The study on M_s of the martensitic transformation fcc → bcc (bct) in iron-base alloys may be summed up as follows.

1. The change of free energy associated with martensitic transformation in iron-base alloys may be formulated as the algebraic sum of $\Delta G^{\gamma\to\alpha}$, the energy required for the stabilization of the embryo with bcc structure, and $\Delta G^{\alpha\to M}$, the energy required for the propagation of the bcc embryo to form martensite. The $\Delta G^{\alpha\to M}$ may be estimated as

$$\Delta G^{\alpha\to M} = 2.1\,\sigma + 900\ \mathrm{J\,mol^{-1}}$$

where σ is the yield strength (in $\mathrm{MN\,m^{-2}}$) of austenite at M_s. Estimation of σ yields M_s directly that is in good agreement with the experimental values in Fe–C, Fe–Ni–C and Fe–Cr–C systems, and partly in pure iron, Fe–Ni, Fe–Cr and Fe–Mn in which the previous higher measured values of M_s have been proved to be the starting temperature of massive transformation, M_a, the M_s of surface martensite or bainitic temperature rather than the real M_s of bulk specimen.

2. The M_s of pure iron have been deduced as about 800 K. In Fe–C 1 at% C lowers M_s about 70 K, or

$$M_s(^\circ\mathrm{C}) = 520 - [\%\mathrm{C}] \times 320$$

while in Fe–Ni 1 at% Ni lowers M_s 16.5 K; in Fe–Cr 1 at% Cr lowers $M_s \sim 10$ K and dM_s/dx rises as $X_{Cr} > 0.1$, and in Fe–Mn 1 at% Mn lowers M_s ~ 30 K. The driving force and the yield strength of austenite at M_s may be obtained from the known M_s. In Fe–X, the effect of the alloying element on M_s depends on its effect on T_0 and on the strengthening of austenite. This may be interpreted quantitatively.

3. The following formula for $\Delta G^{\gamma\to\alpha}$ is suggested for Fe–X–C:

$$\Delta G^{\gamma\to\alpha}_{\mathrm{Fe-X-C}} = x_{\mathrm{Fe}}\Delta G^{\gamma\to\alpha}_{\mathrm{Fe}} + x_c RT\ln(\gamma_c^\alpha/\gamma_c^\gamma) + x_i\Delta G_i^{\gamma\to\alpha} + x_i(1-x_i)(B-A)$$

in which γ_c^α and γ_c^γ are activity coefficients of carbon in Fe–C ferrite and in Fe–X–C austenite, respectively.

Through the above equation and the estimated driving force the M_s in Fe–Ni–C ($X = 0.1$ and 0.2) and Fe–Cr–C ($X = 0.032$ and 0.06) are obtained and are found to be consistent with the measured values.

When the effect of carbon on the strengthening of austenite in Fe–X–C is nearly identical, the dM_s/dx_c in Fe–X–C depends on γ_c^γ. It may be predicted that dM_s/dx_c increases in the following order: Fe–Si–C, Fe–Ni–C, Fe–Co–C, Fe–Mn–C, Fe–Cr–C, Fe–Mo–C and Fe–V–C. In Fe–X–C, dM_s/dx increases with the amount of carbon and alloying elements, and carbon acts more markedly, because of its powerful effect on the driving force.

Appendix

The stored energy in dislocation martensite is estimated as

$$U_m = Gb^2\rho V_m \qquad \text{(A1)}$$

where G, the strain energy induced by the formation of unit length of dislocation $= 8 \times 10^4$ MN $\mathrm{m^{-2}}$, b, the Burgers vector of dislocation $= 2.6 \times 10^{-8}$ cm, ρ, the density of dislocations $= 10^{12}$

cm^{-2} and V_m, the molar volume of martensite = 7.5 cm^3 mol^{-1}. Then, U_m = 400 J mol.

The stored energy in deformed austenite is

$$U_\gamma \simeq Gb^2 \rho V_\gamma. \tag{A2}$$

Assume $V_\gamma \approx V_m$, then U_b = 400 J mol^{-1}.

The stored energy in twinned martensite is mainly the twin boundary energy in martensite. Let $\bar{l}$ be the average length of a martensite plate, $\bar{V}$ the average volume of each plate, ΔX the distance between the internal twins in martensite, t the minimum thickness of the plate, ΔF the twin boundary energy and take $\bar{l} = 5 \times 10^{-2}$ cm, $\Delta X = 5 \times 10\,cm^{-7}$ [79], $\bar{V} = 10^{-8}\,cm^3$ [80], $t = 5 \times 10^{-5}$ cm [16], $V_m = 7.5\,cm^3\,mol^{-1}$ [5], $\Delta F = 24 \times 10^{-7}\,J\,mol^{-1}$ [16]. The stored energy in twinned martensite U_t may be expressed as

$$U_t = \varphi \left(\frac{V_M}{V} \cdot \frac{\bar{l}}{\Delta X} \cdot l \cdot t\,\Delta F \right) = 450 \varphi\,J\,mol^{-1} \tag{A3}$$

in which φ is the shape factor of a martensite plate. As the cross-section of the martensite plate is rectangular in shape, $\varphi = 1$, while that in an ellipsoid, $\varphi = \pi/4$. We take $\varphi = 0.90$. So the average stored energy in twinned martensite is also 400 J mol^{-1}.

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