On thermodynamic calculation of M_s and on driving force for martensitic transformations in Fe–C

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The calculation of the driving force, T_0, and the free energy change associated with the martensitic transformation, $\Delta G^{\gamma\rightarrow\alpha}$, in Fe–C given by Hsu is used to obtain M_s (temperature at which $\Delta G^{\gamma\rightarrow M} = 0$) values by combining various expressions for $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$ with evaluations of $\Delta G^{\gamma\rightarrow\alpha}$ from Fisher, Kaufman, Guggenhiem and others. A combination of the Lobo–Fisher–Guggenhiem model with $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$ values from Mogutnov, and of the Hsu model (A) with $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$ values from Kaufman and co-workers are in good agreement with experimental values of M_s. Hsu's model, however, is much simpler. Experimental M_s values for Fe–C are well represented and the M_s temperature with $X_c = 0.06$ determined by Greninger, seem too high. The calculated driving force not only depends on the model adopted for $\Delta G^{\gamma\rightarrow\alpha}$ evaluation but also mainly on the values of $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$ and M_s. It is probable that values of driving force increase continuously with carbon content.

1. Introduction

The free energy change associated with the martensitic transformation in Fe–C may be expressed by

$$\Delta G^{\gamma\rightarrow M} = \Delta G^{\gamma\rightarrow\alpha(\alpha')} + \Delta G^{\alpha(\alpha')\rightarrow M} \quad (1)$$

M_s may be defined as the temperature at which $\Delta G^{\gamma\rightarrow M} = 0$. Traditionally, T_0 in Fe–C is defined as the equilibrium temperature of α' phase and austenite, i.e. the temperature at which $\Delta G^{\gamma\rightarrow\alpha'} = \Delta G^{\gamma\rightarrow\alpha} + \Delta G^{\alpha\rightarrow\alpha'} = 0$, in which $\Delta G^{\alpha\rightarrow\alpha'}$ (sometimes designated as ΔG^*) is the free energy change accompanying the ordering of carbon atoms in the α phase. In line with present ideas about partial ordering in virgin martensite, Hsu [1] has defined T_0 as the temperature at which $\Delta G^{\gamma\rightarrow\alpha} = 0$ and neglected ΔG^*. There exist various values of $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$ [2–5] and models for evaluation of $\Delta G^{\gamma\rightarrow\alpha}$; for example those of Fisher [6], Bhadeshia [7], Kaufman *et al.* [8], Lacher [9], Fowler and Guggenhiem [10] and Hsu [1]. In previous work the driving force at M_s, $\Delta G^{\alpha(\alpha')\rightarrow M}$ or $-\Delta G^{\gamma\rightarrow\alpha(\alpha')}$, can only be determined from experimental M_s values, whereas Hsu has calculated M_s directly by thermodynamic methods:

$$\Delta G^{\alpha\rightarrow M} = 5\sigma_{M_s}^{\gamma} + 217\,\mathrm{cal\,mol^{-1}} \quad (2)$$

$$\sigma_{M_s}^{\gamma} = 13 + 280X_c + 0.02(M_s - T) \quad (3)$$

where $\sigma_{M_s}^{\gamma}$ (in $\mathrm{kg\,mm^{-2}}$) is the yield stress of austenite at M_s. ΔG is in units of $\mathrm{cal\,mol^{-1}}$ and can be converted to $\mathrm{J\,mol^{-1}}$ by multiplying by 4.19. Many expressions are currently available for the free energy accompanying the transformation in pure iron (Equations 8 to 11). This paper compares the M_s values obtained by various combinations of models for evaluating $\Delta G^{\gamma\rightarrow\alpha}$ with expressions for $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$, and compares the results with experimental values. Additionally, new accurate values of M_s for Fe–C alloys are also presented and the driving force for the martensitic transformation in Fe–C is discussed.

2. Formulation of $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$

In the '60's and '70's, Kaufman *et al.* [2], Orr and Chipman [3], Mogutnov *et al.* [4] and Agren [5] revised the earlier values of $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$ as follows below.

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Let the change in heat capacity at constant pressure, $\Delta C_p^{\gamma\to\alpha}$, of pure iron be $\Delta C_p = c + 2dT + 6eT^2$ where T is the temperature. Then c, d and e are constants and we have

$$\begin{aligned}\Delta G_{Fe}^{\gamma\to\alpha} &= \int \Delta C_p^{\gamma\to\alpha}\, dT - T\int (\Delta C_p^{\gamma\to\alpha}/T)\, dT \\ &= \Delta H_{Fe}^0 - T\Delta S_{Fe}^0 + cT - cT \\ &\quad \times \ln T - dT^2 - eT^3 \qquad (4)\end{aligned}$$

where ΔH_{Fe}^0 and ΔS_{Fe}^0 are ΔH and ΔS for the transformation $\gamma \to \alpha$ of pure iron at 0 K respectively. Since $\Delta S \to 0$ as $T \to 0$ K, c may become zero and at low temperatures we have

$$\Delta G_{Fe}^{\gamma\to\alpha} = \Delta H_{Fe}^0 - dT^2 - eT^3 \qquad (5)$$

Various authors have expressed $\Delta G_{Fe}^{\gamma\to\alpha}$; Equations 8 to 10, for which the data below 500 K are unavailable. We need to extend $\Delta C_p^{\gamma\to\alpha}$ to lower temperatures and obtain $\Delta H_{Fe}^{\gamma\to\alpha}$ by integration.

$$\begin{aligned}\Delta H_{Fe}^{\gamma\to\alpha} &= \int \Delta C_p^{\gamma\to\alpha}\, dT = I_1 - 1.43T \\ &\quad + 0.0018T^2 \qquad (6)\end{aligned}$$

When $T = 500$ K, $\Delta H_{Fe}^{\gamma\to\alpha} = -1855$ cal mol^{-1} [3] and we obtain $I_1 = -1590$. From

$$\begin{aligned}\Delta G_{Fe}^{\gamma\to\alpha} &= -T\int \frac{\Delta H_{Fe}^{\gamma\to\alpha}}{T^2}\, dT \\ &= I_2 T - 0.0018T^2 - 1590 + 1.43T\ln T \qquad (7)\end{aligned}$$

and $\Delta G_{Fe}^{\gamma\to\alpha} = -870$ cal mol^{-1} at $T = 500$ K [3], we obtain $I_2 = -6.55$ cal mol^{-1}. So $\Delta G_{Fe}^{\gamma\to\alpha}(T)$ can be obtained at $200 < T < 500$ K. $\Delta G_{Fe}^{\gamma\to\alpha}$ from Kaufman *et al.* [2] is given by

$$\begin{aligned}\Delta G_{Fe}^{\gamma\to\alpha} &= -1303 - 17.778\times 10^{-4}T^2 \\ &\quad + 28.667\times 10^{-6}T^3 - 4.889\times 10^{-8}T^4 \\ &\qquad T \leqslant 300 \\ \Delta G_{Fe}^{\gamma\to\alpha} &= 684.58 - 7993.65\times 10^{-2}T \\ &\quad - 290.818\times 10^{-4}T^2 + 9.449 \\ &\quad \times 10^{-6}T^3 + 14.361T\ln T \\ &\qquad 300 < T < 700 \\ \Delta G_{Fe}^{\gamma\to\alpha} &= 4887.74 - 11184.235\times 10^{-2}T \\ &\quad - 116.526\times 10^{-4}T^2 + 17.1592T\ln T \\ &\qquad 700 < T < 1000 \qquad (8)\end{aligned}$$

$\Delta G_{Fe}^{\gamma\to\alpha}$ from Orr and Chipman [3] is given by

$$\begin{aligned}\Delta G_{Fe}^{\gamma\to\alpha} &= -1590 - 6.55T - 0.0018T^2 \\ &\quad + 1.43T\ln T \qquad 200 \leqslant T < 500 \\ \Delta G_{Fe}^{\gamma\to\alpha} &= -1661.59 - 530.8\times 10^{-2}T \\ &\quad - 16.92\times 10^{-4}T^2 + 1.245T\ln T \\ &\qquad 500 \leqslant T \leqslant 800 \\ \Delta G_{Fe}^{\gamma\to\alpha} &= 4983.576 - 11146.1\times 10^{-2}T \\ &\quad - 110.665\times 10^{-4}T^2 + 17.0045T\ln T \\ &\qquad 800 < T \leqslant 1100 \qquad (9)\end{aligned}$$

$\Delta G_{Fe}^{\gamma\to\alpha}$ from Mogutnov *et al.* [4] is given by

$$\begin{aligned}\Delta G_{Fe}^{\gamma\to\alpha} &= -1413 + 2.69\times 10^{-4}T^2 \\ &\quad + 19.59\times 10^{-6}T^3 - 3.78\times 10^{-8}T^4 \\ &\qquad T \leqslant 300 \\ \Delta G_{Fe}^{\gamma\to\alpha} &= 1462.27 - 106.988T - 0.0364T^2 \\ &\quad + 11.213\times 10^{-6}T^3 + 18.957T\ln T \\ &\qquad 300 < T < 700 \\ \Delta G_{Fe}^{\gamma\to\alpha} &= -2640.74 + 8.455T - 9.52\times 10^{-4}T^2 \\ &\quad - 0.715T\ln T \qquad 700 \leqslant T \leqslant 1100 \qquad (10)\end{aligned}$$

The data from Agren [5] is close to that of Orr and Chipman [3]. The results from Equations 8 to 10 as a function of temperature are shown in Fig. 1, and are nearly equal to the data published from the other authors which are also shown. Fig. 1 shows that at temperatures below 600 K, values of $\Delta G_{Fe}^{\gamma\to\alpha}$ from the various authors became more divergent with the lowering of temperature.

3. Calculation of M_s

Fisher's [6] initial model in which the change in the chemical potential of carbon in $\gamma \to \alpha$, $\Delta\mu_C^{\gamma\to\alpha}$, is the only function of temperature was revised by Bhadeshia [7] using the activity data of carbon from Lobo and Geiger's [11, 12] experiment at 848 to 682° C. In the modified Fisher model, $\Delta\mu_C^{\gamma\to\alpha}$ not only depends on temperature but also on the atomic fraction of carbon, X_C, and may be expressed in cal mol^{-1} (1 cal = 4.19 J mol^{-1}) as

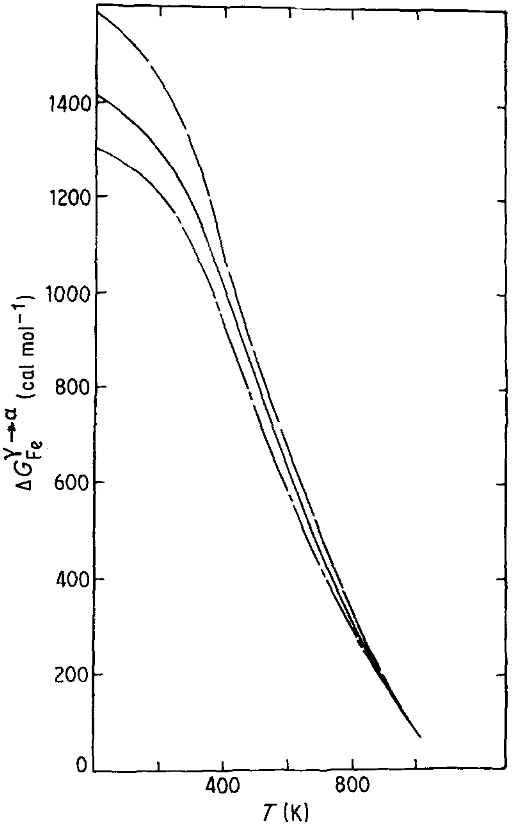

Figure 1 $\Delta G_{Fe}^{\gamma\rightarrow\alpha}(T)$ from various authors. --- Kaufman *et al.* [2]; -- Orr and Chipman [3], — Mogutnov *et al.* [4].

$$\Delta\mu_{C}^{\gamma\rightarrow\alpha} = RT\ln(\gamma_{C}^{\alpha}/\gamma_{C}^{\gamma})$$
$$= 18404 - 10.46T - (40418 - 28.77T)X_C \qquad (11)$$

where γ_{C}^{α} and γ_{C}^{γ} are the activity coefficients of carbon in ferrite and austenite respectively. In the Fisher model, T_0 is defined as the temperature at which

$$\Delta G^{\gamma\rightarrow\alpha'} = \Delta G^{\gamma\rightarrow\alpha} + \Delta G^{*} = 0 \qquad (12)$$

and

$$\Delta G^{\gamma\rightarrow\alpha} = X_C\Delta\mu_{C}^{\gamma\rightarrow\alpha} + (1 - X_C)\Delta\mu_{Fe}^{\gamma\rightarrow\alpha}$$

where $\Delta\mu_{Fe}^{\gamma\rightarrow\alpha}$ is taken from the geometric model:

$$\Delta\mu_{Fe}^{\gamma\rightarrow\alpha} = \frac{RT}{5}\left[3\ln\frac{3 - 8X_C}{3(1 - X_C)} - \ln\frac{1 - 6X_C}{1 - X_C}\right] \qquad (13)$$

and ΔG^{*} is the Zener ordering term taken from Fisher's [6] initial work. Substituting Equations 11 and 13 into Equation 12 yields $\Delta G^{\gamma\rightarrow\alpha}$. Noting that

$$\Delta G^{\gamma\rightarrow\alpha'} = \Delta G^{\gamma\rightarrow\alpha} + \Delta G^{*} \qquad (14)$$

and making Equation 14 = 0, we obtain T_0. Substituting Equations 2, 3 and 14 into Equation 1 and making Equation 1 = 0, we obtain M_s as a function of X_C for different values of $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$, as shown in Fig. 2, in which the experimental values of M_s of Greninger [13], Kaufman *et al.* (KRC) [8] and the present work are also shown.

Fig. 2 shows that if the Fisher model is applied to evaluate $\Delta G^{\gamma\rightarrow\alpha}$, it is necessary to take $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$ from Orr and Chipman [3] in calculations of M_s.

In the KRC model [8], T_0 is defined by the Fisher model and $\Delta G^{\gamma\rightarrow\alpha}$ is defined by Shiflet *et al.* (SBA) [14] may be expressed in cal mol⁻¹ by

$$\Delta G^{\gamma\rightarrow\alpha} = \frac{RT}{13 - 12\exp(-1405/RT)} \times \left\{ [14 - 12\exp(-1405/RT)] \right.$$

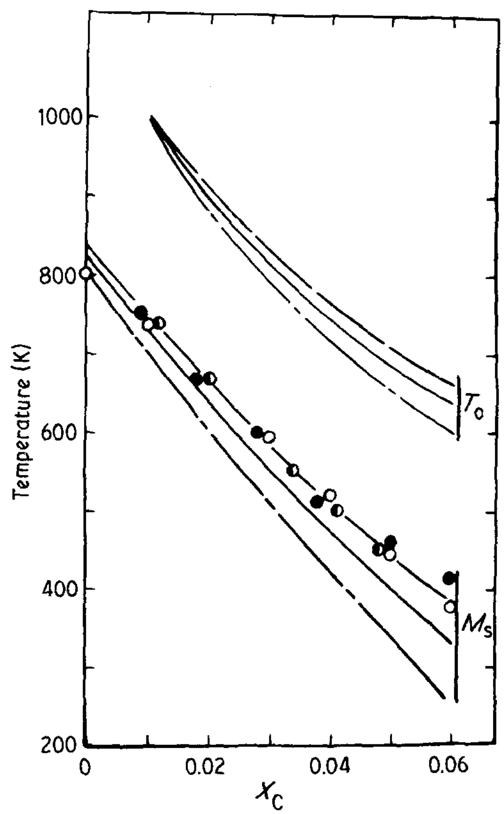

Figure 2 Calculated values of M_s using the Fisher model. --- Kaufman *et al.* [2]; -- Orr and Chipman [3]; — Mogutnov *et al.* [4]; ○, Kaufman *et al.* [8]; ●, Greninger [13]; ◐, present work.

$$\times (1-X_C)\ln(1-X_C) - \{1-[14-12 \times \exp(-1405/RT)]X_C\}\ln\{1-[14 - 12\exp(-1405/RT)]X_C\}\Big) + X_C[18404-10.46T-(40418 - 28.77T)X_C] + (1-X_C)\Delta G_{Fe}^{\gamma\rightarrow\alpha} \quad (15)$$

If we make Equation 15 = 0, we obtain T_0. By application of Equations 1, 2, 3 and 15, M_s is obtained as shown in Fig. 3, revealing that as the KRC model is applied to evaluate $\Delta G^{\gamma\rightarrow\alpha'}$, it is better to take Orr and Chipman's $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$.

The thermodynamic formalisms of Lacher [9] and Fowler and Guggenheim [10] (referred to as LFG) were revised and first applied to steel by Aaronson and co-workers: SBA [14] and ADP [15]. Bhadeshia [16] recently found the interaction energy of C–C to be 48570 J mol^{-1} (11608.51 cal mol^{-1}) instead of the negative value in the SBA model, and derived an explicit but very complex expression for $\Delta G^{\gamma\rightarrow\alpha}$. In this modified LFG model, ΔG^* is also applied. The result of calculating M_s with the LFG model and various values of $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$ is shown in Fig. 4, revealing that Mogutnov's values of $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$ fit the LFG model very well.

Hsu [1] has suggested that ΔG^* may be neglected and has taken

$$RT\ln(\gamma_C^{\alpha}/\gamma_C^{\gamma}) = 9320-2.71T \quad (16)$$

and $\Delta\mu_{Fe}^{\gamma\rightarrow\alpha}$ as defined by Equation 13 (Hsu model (A)). Substituting Equations 13 and 16 into Equation 12 yields $\Delta G^{\gamma\rightarrow\alpha}$. M_s is obtained by application of Equations 1, 2, 3 and 8 as shown in Fig. 5. It is clear that $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$ values of Kaufman *et al.* [8] give the best fit for the Hsu model (A). In the Hsu (B) model (modified Fisher–Bhadeshia model), $\Delta\mu_C^{\gamma\rightarrow\alpha}$ is taken from Equation 11 and ΔG^* is also neglected. The calculated values of M_s with the various models and the experimental values of M_s are within the range of predictions of the Hsu (A) and Hsu (B) models, as shown in

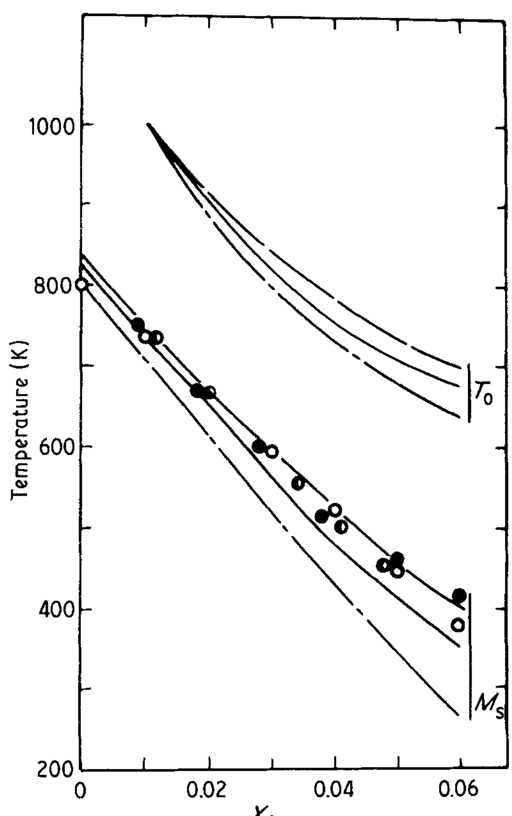

Figure 3 Calculated values of M_s using the KRC model. For key to symbols see Fig. 2 caption.

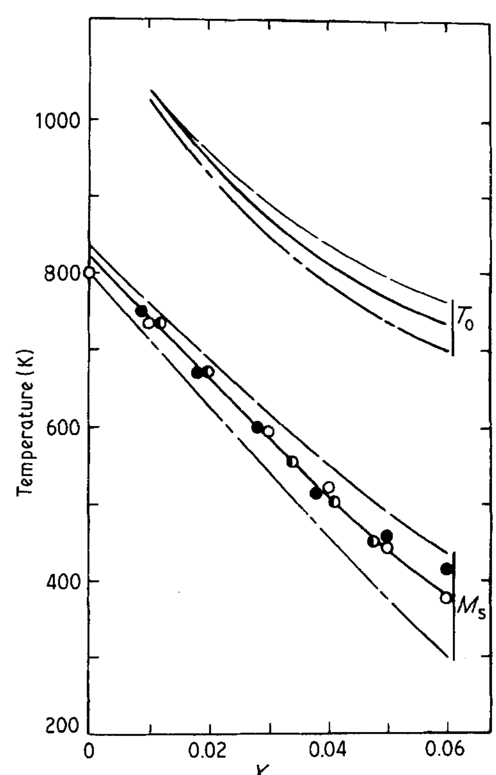

Figure 4 Calculated values of M_s using the LFG model. For key to symbols see Fig. 2 caption.

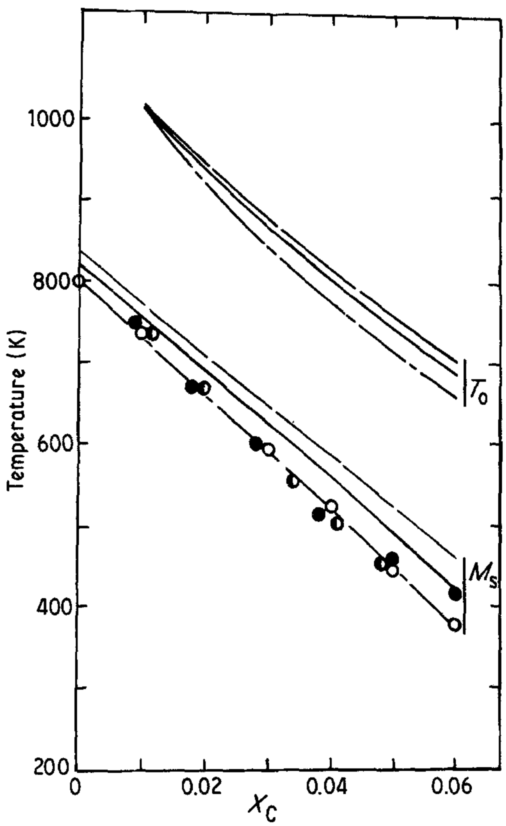

Figure 5 Calculated values of M_s using the Hsu (A) model. For key to symbols see Fig. 2 caption.

Fig. 6, in which $\Delta G_{Fe}^{\gamma\to\alpha}$ values from Mogutnov *et al.* [4] are used. Analogous results will also be obtained as other $\Delta G_{Fe}^{\gamma\to\alpha}$ are applied.

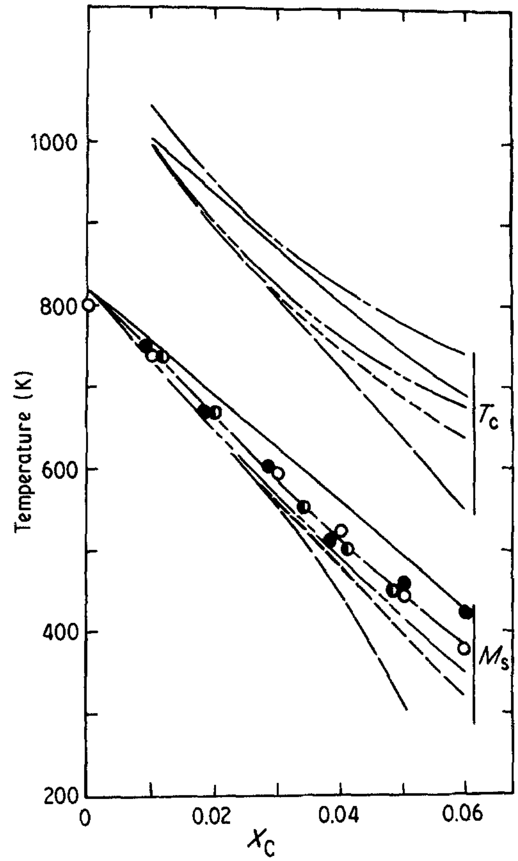

Figure 6 Calculated values of M_s using the various models with $\Delta G_{Fe}^{\gamma\to\alpha}$ values from Mogutnov *et al.* [4]. — Hsu (A)–Hsu model; –·– LFG–Hsu model; –··– KRC–Hsu model; ···· Fischer–Hsu model; – – Hsu (B)–Hsu model; ○, Kaufman *et al.* [8]; •, Greninger [13]; ◐, present work.

4. Experimental values of M_s

M_s in Fe–C alloy with $X_C = 0.0115, 0.02, 0.034, 0.041$ and 0.049 were determined by means of thermal analysis in the present work. Pure iron was used and the content of impurities was less than 0.02 (wt%) and silicon less than 0.03 wt%. Due attention was paid so as to keep constant austenite grain size of ASTM no. 5, and minimize the precipitation of proeutectoid product. The cooling from the austenitizing temperature was conducted by hydrogen blasting. The experimental M_s values obtained in the present work are shown in Fig. 7. These are in good agreement with those detected by Kaufman *et al.* [8] who did not state their experimental procedure in detail. The M_s value of the alloy with $X_C = 0.06$, as extrapolated from this work, is approximately 378 K, being 37 K lower than that of Greninger [13]. The M_s value of the alloy with $X_C = 0.06$ from Greninger seems too high, probably owing to too low a cooling rate with helium, which may have led to the precipitation of some cementite.

5. Driving force

Using calculations of the driving force at M_s of Fe–C with $\Delta G^{\gamma\to\alpha}$ from various models, $\Delta G_{Fe}^{\gamma\to\alpha}$ from Kaufman *et al.* [2] and experimental M_s values from Greninger [13], Bhadeshia [7] recently concluded that at higher carbon contents ($X_C >$ 0.04), the driving force decreases, and for $X_C <$ 0.04, the driving force is less sensitive to variations in the carbon content. In his work, the results from both Fisher's and the LFG model exhibit the same trends, but a minimum in the driving force is obtained in the LFG treatment. The author believed that the results of the LFG model are more reasonable than the results of the Fisher treatment in which the driving force decreases con-

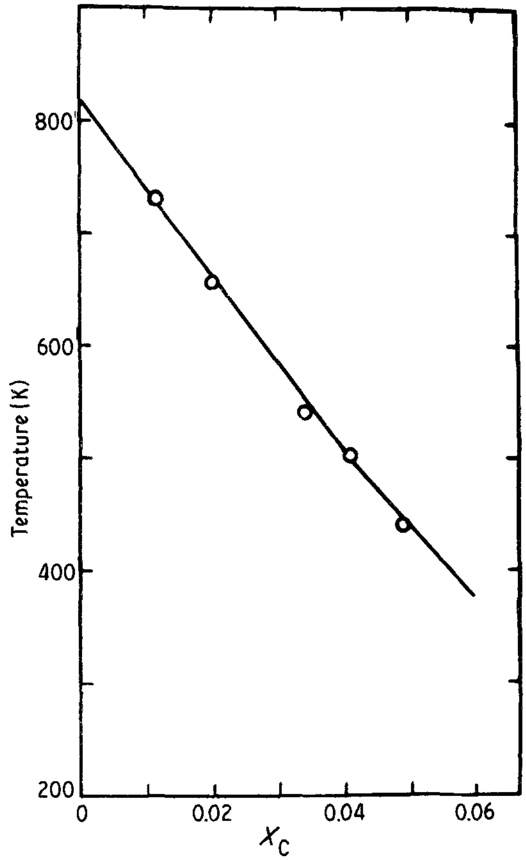

Figure 7 Experimental values of M_s obtained in the present work.

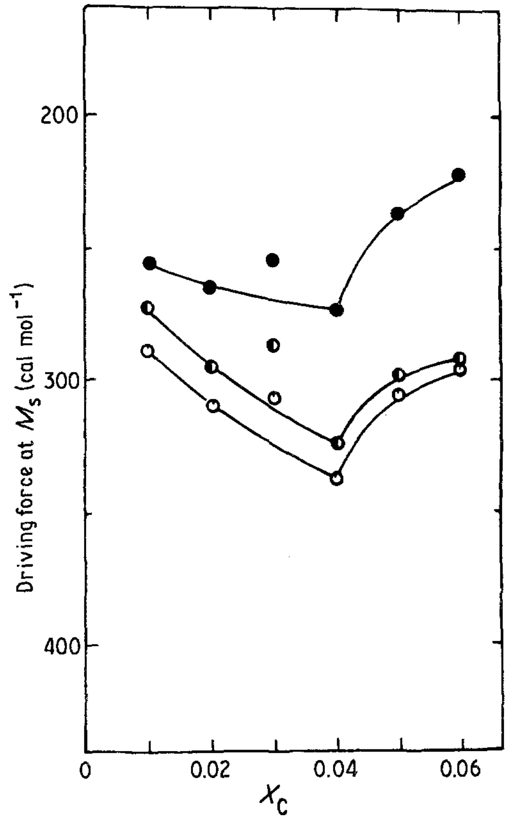

Figure 8 Calculated values of driving force using M_s values of Greninger [13]. •, the Fisher model with $\Delta G_{Fe}^{\gamma \rightarrow \alpha}$ values from Kaufman *et al.* [2]; ◐, the LFG model with $\Delta G_{Fe}^{\gamma \rightarrow \alpha}$ values from Kaufman *et al.* [2]; ○, the Fisher model with $\Delta G_{Fe}^{\gamma \rightarrow \alpha}$ values from Mogutnov *et al.* [4].

tinuously with the increase in carbon content when X_C is above 0.04.

The present work repeated the calculation of driving force with known M_s values and the results obtained are shown in Figs. 8 and 9. In Fig. 8, the Fisher–Kaufman and LFG–Kaufman treatments are analogous to that of Bhadeshia but the Fisher–Mogutnov curve is considerably different from the Fisher–Kaufman curve. Fig. 9 shows the results of combining the LFG treatment with $\Delta G_{Fe}^{\gamma \rightarrow \alpha}$ values from Kaufman and M_s values from Greninger [13], $\Delta G_{Fe}^{\gamma \rightarrow \alpha}$ values from Mogutnov with M_s values from Kaufman *et al.* [8] and M_s from this work. The latter two curves show quite different trends from Bhadeshia. For X_C values greater than 0.04, the M_s values of Greninger seem too high, as stated above, and lead to a maximum driving force at $X_C = 0.04$. The LFG–Mogutnov–Kaufman *et al.* curve shows the same trend as the LFG–Mogutnov–present work curve (Fig. 9) showing an increase in driving force with carbon content which is consistent with the results of predictions given by Hsu [1]. The calculated driving force thus not only depends on the model used to evaluate $\Delta G^{\gamma \rightarrow \alpha}$ but also on the $\Delta G_{Fe}^{\gamma \rightarrow \alpha}$ and M_s values adopted.

6. Conclusion

Combination of the LFG treatment with $\Delta G_{Fe}^{\gamma \rightarrow \alpha}$ values from Mogutnov and the combination of Hsu's model (A) with $\Delta G_{Fe}^{\gamma \rightarrow \alpha}$ values from Kaufman *et al.* [2] give good agreement with the experimental M_s values. Although the LFG treatment represents a more rigorous approach and $\Delta G_{Fe}^{\gamma \rightarrow \alpha}$ values from Mogutnov were obtained by a refined derivation, the LFG formula seems unnecessarily complex. The Hsu model (A) is much simpler and more convenient for M_s calculation. It is likely that the driving force increases with the increase in carbon content, contrary to some recent suggestions made by Bhadeshia [7].

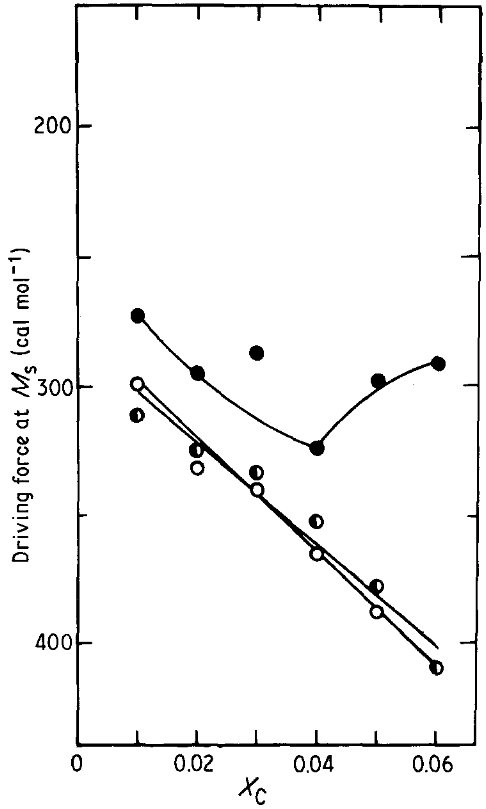

Figure 9 Calculated values of driving force using the LFG model with M_s values from various authors. •, $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$ values from Kaufman *et al.* [2] and M_s values from Greninger [13]; , $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$ values from Mogutnov *et al.* [4] and M_s values from Kaufman *et al.* [8]; ○, $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$ values from Mogutnov *et al.* [4] and M_s values from the present work.

References

1. XU ZUYAO (T. Y. HSU), *Acta Metall. Sinica* **15** (1979) 329.
2. L. KAUFMAN, E. V. CLOUGHERTY and R. J. WEISS, *Acta Metall.* **11** (1963) 323.
3. R. L. ORR and J. CHIPMAN, *Trans. TMS–AIME* **239** (1967) 630.
4. B. M. MOGUTNOV, I. A. TOMILIN and L. A. CHVARCMAN, "Thermodynamics of Fe–C Alloys" (Metallurgy Press, Moscow, 1972) p. 110.
5. J. AGREN, *Met. Trans.* **10A** (1979) 1847.
6. J. C. FISHER, *Trans. AIME.* **185** (1949) 688.
7. H. K. D. H. BHADESHIA, *Met. Sci.* **15** (1981) 175.
8. L. KAUFMAN, S. V. RADCLIFFE and M. COHEN, in "Decomposition of Austensite by Diffusional Processes", edited by V. F. Zackay and H. I. Aaronson (Interscience Publishers, New York, London, 1962) p. 313.
9. J. R. LACHER, *Proc. Cambridge Phil. Soc.* **33** (1937) 518.
10. R. H. FOWLER and E. A. GUGGENHIEM, "Statistical Thermodynamics" (Cambridge University Press, New York, 1939).
11. J. A. LOBO and G. H. GEIGER, *Met. Trans.* 7A (1976) 1347.
12. *Idem, ibid.* 7A (1976) 1359.
13. A. B. GRENINGER, *Trans. ASM* **30** (1942) 1.
14. G. J. SHIFLET, J. R. BRADLEY and H. I. AARONSON, *Met. Trans.* 9A (1978) 999.
15. H. I. AARONSON, H. A. DOMAIN and G. M. POUND, *Trans. TMS–AIME* **236** (1966) 753.
16. H. K. D. H. BHADESHIA, *Met. Sci.* **14** (1980) 230.

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