KINETICS OF F.C.C. → B.C.C. HETEROGENEOUS MARTENSITIC NUCLEATION—I. THE CRITICAL DRIVING FORCE FOR AETHERMAL NUCLEATION

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Abstract—Employing available experimental data for athermal f.c.c. → b.c.c. martensitic transformation in binary, ternary and multicomponent Fe-base alloys, a model is developed and tested for the critical driving force at the \( M_s \) temperature. Incorporating the theory of solid solution hardening, we describe the composition dependence of the athermal frictional work for martensitic interface motion governing the kinetics of barrierless heterogeneous nucleation. The available data suggests that the composition dependence of the athermal frictional work is of the same form as that for slip deformation. We have evaluated the athermal strengths of 14 alloying elements Al, C, Co, Cr, Cu, Mn, Mo, Nb, Ni, Si, Ti, V and W from the experimental data. Except for Al, Ni and Co, the athermal strengths of the common substitutional alloying elements are similar in magnitude, while the interstitial solutes C and N exert a stronger influence. Previously proposed superposition laws are used to account for the presence of multiple solutes having different athermal strengths. With an improved assessment of the magnetic parameters of alloy systems, the model predicts \( M_s \) temperatures within \( \pm 40 \) K for \( M_s > 300 \) K where thermal contributions to the frictional work can be neglected.

I. INTRODUCTION

Martensitic transformation can be regarded as a form of spontaneous plastic deformation driven by chemical forces [1]. The extension of the kinetic theory of slip deformation to the three-dimensional glissile motion of a martensitic interface has been established in both theory [2] and experiment [3]. Numerous microstructural elements can act as obstacles to the martensitic interface and hence affect the martensitic interface mobility and transformation kinetics. As summarized in Table 1, these obstacles can be conveniently classified according to their dimensionality [4], while their size scale may differ by several orders of magnitude. Besides the microstructural elements such as the spatial arrangement of such elements can also be an important factor in controlling the martensitic transformation kinetics. In engineering materials it is quite likely that all these obstacles will be present simultaneously. However, to make a quantitative study of the influence of each type of obstacle it is necessary to select a particular class of material where the effect of other obstacles can be minimized or eliminated. Solid solution strengthened alloys are the most suitable candidate in this context. Here the solute atoms can be treated as point sources and the theory of solid solution strengthening can be applied in understanding and analyzing the kinetic parameters. In precipitation strengthened alloys additional complexity arises due to the dependence of inter-particle distance on average particle size, the finite size of the precipitates, and the possibility of coherency effects. As precipitation-strengthened systems will inevitably include solution strengthening effects, a quantitative treatment of solution hardening is an important first step towards such systems.

Beyond its scientific interest, f.c.c. (face centered cubic) → b.c.c. (body centered cubic) martensitic transformation plays an integral role in the design of ultrahigh-strength martensitic alloys [5] particularly in applications of dispersed-phase transformation toughening [6]. In the latter case, considerable enhancement of the fracture toughness is achieved through the crack-tip martensitic transformation of small austenite particles (20–50 nm) precipitated in the b.c.c. matrix. In either case, the relative stability of the austenite phase is very important in order to induce martensitic transformation at a desired temperature or stress level. It has also been demonstrated that the austenite strength influences the kinetics of martensitic transformation and martensite morphology [7–9]. The stability of austenite is controlled by the amount and the type of alloying element [10], and hence these are very important in determining the critical driving force for martensitic nucleation.

Most of the alloys for commercial applications are multicomponent in nature. Various empirical formulae for the composition dependence of the martensite start temperature \( (M_s) \) for low alloy steels [11] or for highly alloyed steels [12] have been published.
However, these empirical relationships have limited application as they do not apply to a wide range of composition (concentration and the type of alloying element), and they lack a mechanistic basis. The energetics of heterogeneous nucleation of f.c.c. $\rightarrow$ b.c.c. martensitic transformation has been well established for both bulk materials and small particles [1, 13, 14]. The purpose of this investigation is to develop a model to calculate the critical driving force for athermal martensite nucleation in multi-component alloys. This is done within the framework of heterogeneous martensite nucleation theory incorporating the existing literature data on the athermal martensitic transformation in Fe-base alloys. The need for such a model was recognized during the course of ongoing research to design advanced ultrahigh-strength steels in composition ranges previously unexplored [5].

2. ENERGETICS OF HETEROGENEOUS MARTENSITIC NUCLEATION

Olson and Cohen [13] developed a model for heterogeneous martensitic nucleation that obviates the need for pre-existing embryo with a martensitic structure, but requires a suitable nucleating defect in the austenite as depicted in Fig. 1(a). A dislocation model allows the prediction of various interfacial properties, such as the interfacial stress fields, energy, stability and interfacial mobility [1]. In their general description of interphase boundaries, Olson and Cohen [15–17] described the semi-coherent f.c.c./b.c.c. martensitic interface in terms of coherency dislocations accomplishing transformation strain as depicted in Fig. 1(b) and anticoherency dislocations reducing the strain energy as depicted in Fig. 1(c). Interactions of microstructural elements with the martensitic interface long-range stress field give rise to an athermal resisting force while interactions with the interfacial core give rise to short-range contributions that can be overcome by thermal activation. Depending on the microstructural elements, these interactions can be point-line, point-surface, line-line, line-surface and surface-surface types. A general model for the mobility of martensitic interfaces controlled by point particles in which the strain and the elastic modulus are homogeneous has been developed [2]. It has been shown that under normal experimental conditions it is unlikely that in typical metallic alloys the motion of a martensitic interface is controlled by the crystal periodic resisting force or the Peierls barrier. However, in strongly directionally bonded crystals, such as ZrO$_2$ ceramics [18] and possibly actinide alloys [19], it is likely that the Peierls barrier is the source of interfacial friction. Direct measurement of interfacial mobility of thermoelastic martensite in Cu–Al–Ni alloys is found to be consistent with the concept of thermally activated interfacial motion [3]. Various obstacles interacting with the martensitic interface during growth were identified to be particles of $\gamma$- and 2H-phases giving rise to athermal frictional stress, and fine-scale lattice displacements in the solid solution giving rise to thermal frictional stress. For ferrous alloys, we will demonstrate here and in Part II [20] that f.c.c. $\rightarrow$ b.c.c. heterogeneous martensite nucleation kinetics is also obstacle controlled where barrierless nucleation is governed by the interfacial mobility. In this study, we will evaluate the long-range contributions due to a three-dimensional random distribution of different solute atoms in iron. In Part II [20] we will evaluate the short-range thermal contributions due to different

![Fig. 1. Dislocation model of heterogeneous semi-coherent nucleation. (a) Initial defect modelled as group of dislocations in an interface. (b) Martensitic interfacial coherency dislocations bounding embryo derived from “disassociation” of initial defect. (c) Additional interfacial dislocation structure generated to maintain semi-coherent state [13].](image-url)
solute atoms and the long-range contributions due to forest dislocations.

Following Olson and Cohen [13], the total energy describing the heterogeneous semicoherent nucleation process in Fig. 1 is given by the sum of a defect dislocation energy and a fault energy. At sufficient driving force (obtained by cooling or an applied field), the fault energy becomes negative and gives rise to a barrierless condition where a nucleus can grow spontaneously, at a rate controlled by the interfacial mobility. The critical condition for semicoherent nucleation is then given by a balance between the negative fault energy and the interfacial frical work, i.e.

$$\Delta G_{\text{cr}} + \sigma^d + \frac{2\sigma}{md} = -(w_p + w_a),$$

where $n$ is the number of close-packed planes comprising the nucleus thickness (defined by the defect size), $d$ is the spacing between close-packed planes, $\Delta G_{\text{cr}}$ is the volume Gibbs energy difference between the f.c.c. and b.c.c. phases, $\sigma^d$ is a volume strain energy, $\sigma$ is the semicoherent interfacial energy, $w_p$ and $w_a$ are the athermal (only composition dependent) and thermal (both composition and temperature dependent) components of the interfacial frical work, respectively. Assuming a fixed defect potancy, and adopting molar quantities represented in upper case (e.g. $\Delta G = V_m \Delta g$), the critical driving force ($\Delta G_{\text{cr}}$) is given by

$$\Delta G_{\text{cr}} = K_i + W_0(K_p, X_t) \begin{cases} + W_0(K_p, X_t, T, T), \end{cases}$$

where $K_i$ is a constant that includes strain and interfacial energies and the defect size. The temperature dependencies of both strain and interfacial energies are expected to scale with the temperature dependence of the shear modulus. At sufficiently high temperature, i.e. $T > T_s$, (the temperature above which the thermal component of frictional work is negligible) $W_0(K_p, X_t, T, T) = 0$. The $K_p$'s are presented in Section 4 and the $K_s$'s will be discussed in Part II [20]. Assuming rather weak composition ($X_t$) and temperature ($T$) dependencies in the shear modulus, we then have for nucleation in the athermal regime

$$\Delta G_{\text{cr}} = K_i + W_0(K_p, X_t).$$

### 3. THERMODYNAMICS OF F.C.C. → B.C.C. TRANSFORMATION

Quantification of the thermodynamic driving force is essential for controlling the kinetics of martensitic transformation. For a diffusionless phase transformation, the chemical driving force ($\Delta G_{\text{chem}}$) at a constant temperature is given by the difference in molar Gibbs energies, i.e.

$$\Delta G_{\text{chem}} = G^ \gamma - G^ x.$$  

We have used a two sublattice model [21] to express the Gibbs energies of h.c.c. ($\alpha$) and f.c.c. ($\gamma$) phases. In this model, the first sublattice is occupied by the substitutional elements and the second sublattice is occupied by the interstitial elements (C, N) and vacancies (Va). Then the homogeneity range of any phase is represented by $(M)_p(C, N, Va)_q$, where $M = Al, Co, Cr, Cu, Fe, Mn, Mo, Nb, Ni, Si, Ti, V$ and $p$ and $q$ are the number of sites on the first and second sublattice, respectively. For the f.c.c. phase $p = 1$ and $q = 3$, and for the f.c.c. phases $p = q = 1$. For one formula unit of $(M)_p(C, N, Va)_q$ the Gibbs energy is expressed as

$$G^\gamma = G^\text{ref} + G^\text{mix} + G^\text{inter} + G^\text{mag}.$$  

The term $G^\text{ref}$ is the Gibbs energy of the reference state and is expressed by

$$G^\text{ref} = \sum_M Y_M Y_C G^\text{ref}_{MC} + \sum_M Y_M G^\text{ref}_{MN} + \sum_M Y_M Y_{Va} G^\text{ref}_{V_Na},$$

where $Y_i$ denotes the site fraction of component $i$ on the sublattice it occupies. The parameters $G^\text{ref}_{MC}$ and $G^\text{ref}_{MN}$ represent the Gibbs energy of a hypothetical state where all interstitial sites are filled with C and N, respectively. The parameter $G^\text{ref}_{V_Na}$ represents the Gibbs energy of pure component M in a hypothetical non-magnetic state. These parameters ($G^\text{ref}_{MC}$, $G^\text{ref}_{MN}$ and $G^\text{ref}_{V_Na}$) are taken from the SSOL database of the THERMO-CALC software system [22]. The site fractions are related to the ordinary mole fractions

$$Y_M \frac{X_M}{1 - X_C - X_N} \quad (7a)$$

$$Y_{C,N} \frac{X_{C,N}}{1 - X_C - X_N} \quad (7b)$$

$$\sum_M Y_M = Y_C + Y_N + Y_{Va} = 1. \quad (7c)$$

The term $G^\text{mix} = RT \left[ p \left( \sum_M Y_M \ln Y_M \right) + q \left( Y_C \ln Y_C + Y_N \ln Y_N + Y_{Va} \ln Y_{Va} \right) \right].$  

The non-magnetic excess Gibbs energy ($G^\text{inter}G^\text{mag}$) is expressed by a Redlich–Kister polynomial. As an example, the excess Gibbs energies of the Fe–Ni and Fe–Ni–C systems can be expressed as

$$G^\text{inter}G^\text{mag} = Y_{Fe} Y_{Ni} \left[ L_0^{Fe-N} + (Y_{Fe} - Y_{Ni}) L_1^{Fe-N} + (Y_{Fe} - Y_{Ni})^2 L_2^{Fe-N} + \ldots \right]$$

$$G^\text{inter}G^\text{mag} = Y_{Fe} Y_{Ni} \left[ Y_C L_{FeNi-C} + Y_{Va} L_{FeNi-Va} \right] + Y_C Y_{Va} L_{FeNi-C} + Y_N L_{FeNi-C} + Y_{Va} L_{FeNi-Va}. \quad (9b)$$

In the present investigation, the $L$-parameters of the relevant binary and ternary systems were reevaluated.
such that they are consistent with data for the high-temperature equilibrium phase boundaries as well as the low-temperature $T_0 = 0.5(M_1 + A_1)$, where $M_1$ is the martensite start temperature on cooling and $A_1$ is the austenite start temperature on heating.

The Gibbs energy contribution due to the magnetic ordering, $G^{mag}$, is evaluated with respect to the paramagnetic state of the phase where magnetic moments are completely disordered. $G^{mag}$ is expressed as

$$G^{mag} = RT \ln(\beta + 1)/\tau,$$

where $\beta$ is the composition dependent average magnetic moment, $\tau = T/T_c$ with $T_c$ being the composition dependent critical (Curie or Néel) temperature for magnetic ordering. The function $f(\tau)$ is different above and below $T_c$, and expressed by truncated polynomials [24]. The composition dependence of the Curie temperature and average magnetic moment of a solid solution can also be expressed by a Redlich–Kister polynomial. For example, the $T_c$ and $\beta$ of the Fe–Ni system is given by

$$T_c^{Fe-Ni} = (1-X)T_c^{Fe} + XT_c^{Ni} + X(1-X)(T_c^{Fe} - T_c^{Ni}) + X(1-X)(T_c^{Fe} - T_c^{Ni}) + X(1-X)(T_c^{Fe} - T_c^{Ni}) + X(1-X)(T_c^{Fe} - T_c^{Ni}) + X(1-X)(T_c^{Fe} - T_c^{Ni}) + X(1-X)(T_c^{Fe} - T_c^{Ni}) + X(1-X)(T_c^{Fe} - T_c^{Ni}) + X(1-X)(T_c^{Fe} - T_c^{Ni})$$

where $X$ is the mole fraction of Ni. In order to predict the Curie temperatures and magnetic moments of multicomponent alloys with good accuracy, the model parameters (such as $T_c^{Fe-Ni}$, $T_c^{Ni}$, $T_c^{Fe}$ and $\beta^{Fe-Ni}$, $\beta^{Fe}$, $\beta^{Ni}$) of the relevant binary and ternary systems were evaluated in fitting the available magnetic data. Figure 2(a, b) show the composition dependence of the Curie temperature [25–31] and average magnetic moment [27, 32–33] of b.c.c. Fe–Cr alloys. In the case of Fe–Cr alloys, both $T_c$ and $\beta$ vary in a non-linear and monotonic fashion. Figure 3(a, b) show the composition dependence of the Curie temperature [34–39] and average magnetic moment [32, 35, 38–43] of f.c.c. Fe–Ni alloys. Here, the composition dependences are nonlinear and non-monotonic. In all cases fairly good agreement between the literature experimental data and the model fit was obtained.

4. COMPOSITION DEPENDENCE OF ATERMAL FRICTIONAL WORK

Our approach to solution hardening builds on the established analogy between martensitic transformation and slip deformation [2, 3]. Over the last few decades considerable work has addressed the composition dependence of the frictional force for slip deformation. Various types of concentration depen-

dencies have been proposed, both theoretically and experimentally (see for review Refs [44, 45]). Very recently, Arsenault et al. [46] have carried out comprehensive computer simulations of solid solution hardening, predicting an $X_2^{3.5}$ dependence of the frictional stress for dislocation motion in both dilute and concentrated regimes assuming a random solution structure. They also concluded that the size mismatch is the major factor in solid solution strengthening. However, these theoretical calculations are performed at absolute zero, and truly speaking the composition dependence of the athermal frictional stress arising from very long-range interaction forces is not considered. Therefore, the true athermal behavior has to be established using existing experimental data. Figure 4 shows the composition dependence of the athermal stress for slip deformation of f.c.c. (Cu–Mn) [47] and b.c.c. (Nb–Mo) [48] alloys from experiments on single crystals. It can be noted that the available data can be very well described by the functional form $\tau_2^{3.5}$.
Analogous to the slip deformation behavior of Fig. 4, Fig. 5(a) shows a plot of critical driving force at $M_s$ vs C-concentration in binary Fe-C alloys, in which the data were fitted with the function

$$-\Delta G_{M_s} = K_0 + K_C^{C_{M_s}} C^{n_C},$$

(12)

and a reasonably good fit is obtained. The composition dependence of $M_s$ temperatures in Fe-C alloys were taken from Refs [49–52]. In the C-concentration range considered in Fig. 5(a), the $M_s$ temperatures varied from 450 to 753 K, and it is assumed that the interfacial frictional work is only athermal in nature at these temperatures. The above fit yielded $K_0 = 1010$ J/mol that corresponds to $G^d \approx 450$ J/mol and a defect size of $n = 18$. Both these numbers are in good agreement with earlier estimates [13]. Similarly, Fig. 5(b) shows the effect of Cr [10, 53–55] and Nb [10, 53] on the critical driving force at $M_s$. Once again it can be seen that the composition dependence of the critical driving force can be very well described by equation (12). The coefficients $K_0$ were derived from the effect of Al [10, C [49–52], Co[10, Cr [10, 53–55], Cu [10], Mn [56], Mo [53], Ni [57], Nb [10, 53], Ni [10, 53], Si [10], Ti [53], V [10, 53], W [10] on the $M_s$ temperatures, and they are listed in Table 2. The effect of Al on $M_s$ was found to be very erratic. Using only Yeoc’s data [53] which were obtained after quenching the alloys from 1089 K, we find $K^d_{Al} = 2200$ J/mol. On the other hand, using Ishida and Nishizawa’s data [10] which were obtained after quenching the alloys from 1173 K, we find $K^d_{Al} = 277$ J/mol for $X_{Al} < 0.02$, but $K^d_{Al}$ is found to be negative at higher Al contents. The greater hardening effect with lower solution treatment temperature may reflect on ordering effect for which the random solution models assumed here would be inappropriate.

The corresponding solution hardening coefficients for slip deformation in both b.c.c. and f.c.c. Fe-based alloys are also listed in Table 2. Apart from the stronger effect of interstitial vs substitutional solutes, there is not a very clear correspondence between the effect of a solute on interfacial mobility and its solution hardening in either crystal.

4.1. The superposition laws in multicomponent alloys

So far we have considered only binary alloys. To estimate the athermal frictional work in multicomponent alloys containing different kinds of solute atoms of different strengths, it is necessary to apply a superposition law. A statistical treatment of the athermal frictional stress has not been undertaken in terms of the theory of solid solution hardening. However, Gypen and Deruyttere [58] provided an empirical treatment of both athermal and thermal frictional stresses in multicomponent alloys. Other authors [59–66] have proposed several relationships to account for the critical resolved shear stress in alloys having distinct obstacles of two or more
strengths. The most common expressions for a system containing two different obstacles \( c_1 \) and \( c_2 \) are:

\[
\begin{align*}
\Delta \tau_{\text{alloy}} &= \Delta \tau_{c_1} + \Delta \tau_{c_2} \\
\Delta \tau_{\text{alloy}}^3 &= \Delta \tau_{c_1}^3 + \Delta \tau_{c_2}^3 \\
\Delta \tau_{\text{alloy}}^W &= \Delta \tau_{c_1}^W + \Delta \tau_{c_2}^W \\
\Delta \tau_{\text{alloy}} &= \Delta \tau_{c_1} f_1^{q_1} + \Delta \tau_{c_2} f_2^{q_2},
\end{align*}
\]

where \( \Delta \tau_{c_1} \) and \( \Delta \tau_{c_2} \) are the increments in strength due to the obstacles \( c_1 \) and \( c_2 \), respectively, \( f_1 \) and \( f_2 \) are the relative fractions of the obstacles with \( f_1 + f_2 = 1 \). Equation 13(a) represents linear superposition. Equation 13(b) is the Pythagorean addition rule first proposed by Koppenaal and Kuhmann-Wilsdorf [59]. Equation 13(c) is a generalized version of equation 13(b) [64]. Labusch [65] and Friedrichs and Haasen [66] suggested the exponent \( m \) to be 3/2. Equation 13(d) is a law of mixtures. Other superposition laws have been summarized by Gypen and Deruyttere [58]. It has been proposed that the superposition law not only depends on the relative strengths of the obstacles but also on their relative concentrations [58]. A general trend is that solutes of comparable strength can be combined by the Pythagorean-type laws, while linear superposition better describes the combination of solutes of very different strength.

Based on these models and the demonstrated \( X^{0.5} \) behavior for martensitic transformations, we consider the following superposition law for the athermal fractional work for a martensitic interface in multicomponent alloys

\[
W_p = \sqrt{\sum_i (K_p^i X_i^{q_5})^2} + \sqrt{\sum_j (K_p^j X_j^{q_5})^2} + \sum_k (K_p^k X_k^{q_5})^2 + K_p^C X_C^{q_5},
\]

where \( i = C, N; j = Cr, Mn, Mo, Nb, Si, Ti, V \) and \( k = Al, Cu, Ni, W \). Based on the evaluated \( K_p^i \)s of Table 2 we have divided the components into three distinct categories of relative obstacle strength. A superposition law analogous to equation (13b) within each category and a linear superposition between the categories were assumed. The effect of Co is added separately since it has the tendency to reduce the interfacial frictional work. The latter may be associated with a reduction in shear modulus [67] the explicit composition dependence of which is neglected in the current analysis.

5. COMPARISON BETWEEN THE CALCULATED AND EXPERIMENTAL RESULTS

Based on the above superposition law [equation (14)], the temperatures at which the critical driving force for martensitic nucleation is achieved were calculated for various multicomponent alloys. Figure 6(a) compares the calculated and experimental [11, 68, 69] \( M_c \) temperatures of multicomponent Fe-Ni-C-Mn-Si-Cr-Mo-V dilute (total alloying elements <5 at.% and medium concentrated (total alloying elements 5-10 at.%) alloys. Figure 6(b) shows the comparison between the calculated and experimental \( M_c \) temperatures of concentrated ternary Fe-Ni-C [70-72], Fe-Cr-C [73-74], and multicomponent [68, 75-76] alloys. In the alloys considered in Fig. 6(b), Ni-content varies from 1.17 to 4.29 at.\% [70], 14.5 to 19.2 at.\% [71] and 8.53 to 18.47 at.\% [72], and the C-content varies from 4.53 to 5.87 at.\% [70], 0.134 to 0.635 at.\% [71] and 0.47 to 1.79 at.\% [72]. In the ternary Fe-Cr-C alloys, the Cr-content varies from 3 to 6 at.\% and C-content varies from 0.4 to 4.3 at.\%. In the Fe-Cr-Mn-C-N alloys [76], Cr-content is from 8.5 to 12.5 at.\%, Mn-content is from 0.1 to 5 at.\%, C-content is from 0.005 to 0.07 at.\% and N-content is from 1 to 1.8 at.\%.

In this study \( M_c \) temperatures were also determined for several highly concentrated multicomponent alloys prepared as alloy design prototypes. The com-
positions of these alloys and related commercial alloys are listed in Table 3. All these alloys were fully solution treated at 1473 K for 30 min and $M_1$ temperatures were determined during cooling in an MMC Quenching Dlamometer. Figure 6(c) shows the comparison between the calculated and experimental $M_1$ temperatures. As seen in Fig. 6(a–c), in general the agreement between the calculated $M_1$ and the experimental $M_1$ is good. For the sake of visual comparison, the temperature interval in Fig. 6(a–c) has been kept constant. It may be noted that the extent of scatter is very similar in all groups of alloys. The earlier empirical formulas for $M_1$ proposed by Steven and Haynes [11] and that by Eichelman and Hull [12] were quite different in order to account for different concentration regimes. The present model coupled with our thermodynamic database is found to be capable of predicting $M_1$ within reasonable accuracy over the full range of assessed compositions. The $2\sigma$ (95.5%) confidence interval for the full set of data in Fig. 6(a–c) is $\pm 40$ K.

While equation (14) was found to be applicable to a large number of multicomponent alloys, it was observed that the $M_1$ temperatures of ternary Fe–Cr–C alloys [74–76] for which equation (14) employs linear superposition of Cr and C could be better described by the Pythagorean-type superposition law of the form

$$W_p = \sqrt{(K_p c_1^2 + K_p c_2^2)^2 + (K_p c_1^2 + K_p c_2^2)^2}. \quad (15)$$

The $M_1$ temperatures of these Fe–Cr–C alloys calculated using equation (15) were found to be higher by 40–50°C compared to equation (14) and gave better agreement with experiment.

6. DISCUSSION

Theoretical models underlying the functional forms adopted in the present analysis are based on a number of assumptions which define its expected limitations.

(i) Elastic continuum interaction between the advancing interface (dislocation array) and the solute atoms which are fixed at discrete lattice sites. It is assumed that no diffusional relaxation process takes place.

(ii) Compositively homogeneous and random solid solution, i.e. there is no short-range ordering or clustering which may otherwise change the concentration dependence and provide additional hardening.

(iii) The absence of magnetic friction. While this may be true for paramagnetic austenite, magnetic friction may not always be negligible in ferromagnetic austenite. Magnetic friction could arise from an
interaction between the hydrostatic component of the interfacial stress field with the pressure dependence of the magnetization.

(iv) The size effect is the major source for the interfacial friction, i.e., modulus, chemical and electrical interactions are negligible. Even though these effects were not considered explicitly, their contributions may have been incorporated in the empirical $K_p$ coefficients.

(v) The absence of precipitates (coherent or incoherent) in the austenite. As mentioned earlier a system containing precipitates is further complicated due to the effects of volume fraction of the precipitates, size dependence of the inter-particle distance between the precipitates at a fixed volume fraction, shape and finite size of the precipitates, and possible coherency effects. Based on the dislocation model of martensitic interfacial mobility [16] all these factors will have an influence on the obstacle-dislocation interaction profile and hence will determine the magnitude of the force resisting the interfacial motion.

(vi) Well annealed crystal, i.e., there is no dislocation forest or work hardened substructure. Introduction of dislocation forests is expected to provide a back stress to the martensitic interface. This problem will be discussed further in Part II [20].

(vii) The athermal strength of the solvent matrix is negligible.

The heterogeneous nucleation model [13] employed in this analysis also carries a number of approximations. The temperature and composition dependencies of the interfacial and strain energies are not considered. One primary scaling factor influencing these two terms is the shear modulus. Unfortunately, at this time there is insufficient theoretical basis to predict the composition and temperature dependence of the shear modulus in these multicomponent alloys. Furthermore, while calculating the $M_s$ temperatures in various alloys we have assumed a constant characteristic defect size [$n$ in equation (1)]. The dependence of the effective $n$ on grain size and specimen size is treated elsewhere [14].

Although martensite kinetic data in binary alloys is found to fit an $X^{0.5}$ dependence of athermal frictional work, such a behavior may not be universal. Experimental solid solution hardening data of f.c.c. alloys do not universally exhibit $X^{0.5}$ dependence, and hence several compositional dependencies have been proposed theoretically and experimentally [44]. Limited single crystal data of b.c.c. Fe-base alloys [77] suggest a linear composition dependence of the critical resolved shear stress and this was in fact assumed [78] in defining the slip hardening coefficients listed in Table 2. The motion of a martensitic interface involves interactions with both the parent and product phase crystals. An expected dominance of attractive vs repulsive interactions in solution hardening [44] would favor interaction with the b.c.c. product. This is supported somewhat by the comparative strengths of C and N, and the relatively high strengths of Mn and Si among the substitutional solutes for interfacial hardening (Table 2), which correlate better with the
relative roles of these solutes in b.c.c. vs f.c.c. crystal hardening.

Over the decades several papers have been published regarding the f.c.c.→b.c.c. martensitic transformation temperature of pure Fe and the critical driving force for such a transformation. From the experimental point of view it is very difficult to prove the martensitic nature of the transformation in pure Fe due to the occurrence of other non-martensitic transformations. The reported values of $M_s$ in pure Fe are 834 [12], 823 [55], 793 [79], 1023 [80], 818 [81], 953 [82] and 1013 K [83]. These values are either based on the extrapolation from different binary systems or from actual experiments performed on spectroscopically pure Fe. Due to the non-linear composition dependence the extrapolations of substitutional solid solutions Fe-X (X = Co, Cr, Mn, Ni) or interstitial solid solutions Fe-C or Fe-N yield different values of $M_s$. A wide scatter in the literature data can also be attributed to the fact that the experimental $M_s$ of pure Fe will depend on the content of impurities, such as C and N. Bilby and Parr [84] noted that the apparent $M_s$ temperature decreases sharply from 1023 to 813 K as the non-metallic impurity content increases from 0.0017 mass% to 0.005-0.01 mass%. Based on the present thermodynamic and kinetic analysis we obtain the $M_s$ temperature of pure Fe to be 857 K and the corresponding driving force at $M_s$ is $-1010$ J/mol. This calculated value differs from earlier calculations of 800 [85] and 973 K [86].

7. CONCLUSIONS

The critical driving force for f.c.c.→b.c.c. heterogeneous martensitic nucleation in multicomponent alloys is modelled as the sum of a strain energy term, a defect-size dependent interfacial energy term and a composition dependent interfacial work term. The athermal strengths of 14 alloying elements Al, C, Co, Cr, Cu, Mn, Mo, N, Nb, Ni, Si, Ti, V and W have been evaluated from the experimental data. Except for Al, Co and Ni, the athermal strengths of the commonly used substitutional alloying elements are similar in magnitude. The interstitial solutes C and N have a stronger influence. It has been demonstrated that the composition dependence of $M_s$ temperatures in multicomponent alloys can be satisfactorily described with an accuracy of ±40 K using an appropriate superposition law.

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