KINETICS OF F.C.C.→B.C.C. HETEROGENEOUS MARTENSITIC NUCLEATION—II. THERMAL ACTIVATION

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Abstract—A critical analysis of the experimental data for the activation energy for f.c.c.→b.c.c. martensitic nucleation in Fe–Ni, Fe–Ni–C, Fe–Ni–Cr and Fe–Ni–Mn alloys has been performed employing the theory of dislocation discrete-obstacle interaction. It is shown that the normalized activation energy $Q(T)/\mu(T)$ vs normalized driving force $\Delta g/\Delta g$ for isothermal martensitic nucleation follows the general form proposed by Kocks, Argon and Ashby [in Thermodynamics and Kinetics of Slip, Progress in Materials Science, Vol. 19, Pergamon Press, Oxford (1975)] for the kinetics of conventional slip deformation in solid solution strengthened alloys. Curve of the $Q(\Delta g)$ function defines a temperature dependent activation volume for isothermal martensitic nucleation. The analysis is consistent with rate control by the interaction of solute atoms with the thermally-assisted motion of the martensitic interface. The contribution of a solute to the thermal component of interfacial friction is found to scale with its athermal contribution. The analysis incorporates kinetic data for the effects of applied elastic stress and plastic pre-strain, providing a quantitative estimate of the interfacial friction from dislocation forest hardening.

1. INTRODUCTION

It is well established that the martensitic transformation in Fe-base alloys exhibit two distinct kinetic modes: (i) athermal, in which the transformation starts at a well defined temperature ($M_s$), and (ii) isothermal, in which the transformation proceeds at a function of time at a constant temperature. The basic features and kinetic similarities between various modes of transformation have been reviewed recently by Raghavan [1]. The isothermal kinetic mode offers a unique opportunity both from theoretical and experimental point of view because the transformation can be studied as a function of temperature, superimposed stress, magnetic field, and prior plastic deformation, and activation energies can be experimentally measured. This experimental information is very useful for developing and testing a thermally activated kinetic model.

As in our previous treatment of athermal kinetic behavior [2], we consider martensitic transformation in solid solution strengthened alloys. This paper extends analysis to the kinetics of isothermal martensitic transformation at sub-zero temperatures. The objective here is to obtain the basic kinetic parameters needed to predict interfacial frictional work for low temperature f.c.c.→b.c.c. martensitic transformation as functions of alloy composition and temperature. Since martensitic transformation is regarded as a form of spontaneous plastic deformation, we will first analyze the kinetics of conventional slip deformation in Fe-base f.c.c. alloys over a wide temperature range.

2. KINETICS OF SLIP DEFORMATION

The theory of solid solution strengthening primarily deals with the critical resolved shear stress (CRSS) at absolute zero and several statistical treatments have been given [3, 4]. A comprehensive review of the theory of solution hardening has been provided by Nabarro [5] and Neuhäuser and Schwink [6]. Very recently, computer simulation of solution strengthening has been performed by Arsenault and co-workers [7, 8]. They concluded that the size effect was the major factor and that the modulus effect has only a smaller influence in solid solution strengthening. However, to assess the modulus effect a synergistic simulation of combined size and modulus terms is necessary [7]. The plastic deformation at $T > 0$ is usually described by the concept of thermally activated motion of dislocations over individual obstacles. The shear strain rate $\dot{\gamma}(\tau_n, T)$ is then given by a simple Arrhenius relationship

$$\dot{\gamma}(\tau_n, T) = \dot{\gamma}_0 \exp \left( - \frac{Q(\tau_n, T)}{kT} \right),$$

where $\tau_n$ is the effective stress. Kocks et al. [9] have proposed a universal form of the stress dependence of activation energy $Q$ for rigid barriers of an average height $Q_0$ given by

$$Q(\tau_0, T) = Q_0(T) \left[ 1 - \left( \frac{\tau_n}{\tau_0} \right)^p \right].$$

The temperature dependence of $Q_0(T)$ is usually given via scaling with the shear modulus $\mu(T)$, and
is generally weak. In equation (2) exponents \( p \) and \( q \) describe the dislocation–obstacle interaction profile, and in general \( 0 \leq p \leq 1 \) and \( 1 \leq q \leq 2 \). The thermal component \( \tau_{th} \) of the applied shear stress \( \tau_{applied} \) necessary to overcome the short-range obstacles is given by

\[
\tau_{th}(T) = \frac{\mu(0)}{\mu(T)} \tau_{applied}(T) - \tau_n,
\]

(3)

where \( \tau_n \) is the athermal resisting stress arising from long-range interactions. Equation (2) together with equations (1) and (3) yields the temperature dependence of the CRSS

\[
\tau_{applied}(T) = \frac{\mu(T)}{\mu(0)} \tau_{th} \left[ 1 - \left( \frac{T}{T_p} \right)^{1/q} \right]^{1/p} + \frac{\mu(T)}{\mu(0)} \tau_n,
\]

(4)

with \( T_p = \frac{Q_0}{k \ln(\gamma_0/\gamma_j)} \). With equation (3) it can be shown that

\[
\tau_{th}(T) = \tau_{th0} \left[ 1 - \left( \frac{T}{T_p} \right)^{1/q} \right]^{1/p}.
\]

(5)

In considering functional forms for martensitic kinetic behavior it is instructive to consider the kinetics of slip in austenitic alloys. The temperature dependence of the CRSS of an Fe–17.19 at.% Cr–23.79 at.% Ni austenitic alloy, as reported by Bredie and Robertson [10] can be fit to equation (4). The resulting fit with \( p = 0.5 \) and \( q = 1.5 \) is shown in Fig. 1. This data can also be fit with \( p = 0.5 \) and \( q = 2 \), resulting in different values of \( \tau_n \) and \( \tau_{th0} \), but is not well described by the \( p = 1 \) and \( q = 1.5 \) form recently proposed by Arsenault and Li [8].

The presence of an athermal frictional stress can also be seen in Fig. 1. In our previous analysis [2], we have discussed the corresponding frictional work \( W_f \) for motion of a f.c.c./b.c.c. martensitic interface in multicomponent alloys. In the next sections we will discuss the thermal component of friction \( W_{th} \) for a f.c.c./b.c.c. martensitic interface in multicomponent alloys and test the kinetic parameters. In the case of slip deformation, the quantitative nature of obstacles and rate controlling steps of the process is determined by analyzing the temperature dependence of CRSS as a function of temperature and composition. We will follow an analogous procedure in order to determine some of the fundamental parameters for f.c.c. → b.c.c. martensitic nucleation by analyzing the activation energy data for such a process.

### 3. KINETICS OF ISOTHERMAL MARTENSITIC TRANSFORMATION

The activation energies for isothermal martensitic nucleation have been measured in several

<table>
<thead>
<tr>
<th>Table 1. Experimental investigation of the kinetics of f.c.c. → b.c.c. isothermal martensitic transformation in Fe-base alloys</th>
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<tbody>
<tr>
<td>Reference</td>
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Fe–Ni, Fe–Ni–C, Fe–Ni–Cr and Fe–Ni–Mn alloys as a function of temperature, superimposed magnetic field, superimposed elastic stress and prior plastic deformation of austenite [11–24]. The compositions of such alloys and the experimental conditions are listed in Table 1. The phenomenological rate equations employed for a singly-activated nucleation-controlled isothermal martensitic transformation kinetics are given by [15, 25]

$$
\frac{dN_t}{dt} = \left[n_t + Pf - N_t\right]v \exp\left(-\frac{Q}{RT}\right) \quad (6)
$$

$$
\frac{df}{dt} = \frac{dN_t}{dN_t} \frac{dP}{dN_t} = \left[n_t + Pf - N_t\right](1-f)
\times \left(\frac{P + dP}{d\ln N_t}\right)v \exp\left(-\frac{Q}{RT}\right). \quad (7)
$$

where $N_t$ is the number of martensite plates per unit volume, $n_t$ is the density of most-potent initial nucleation sites, $P$ is an autocatalytic nucleation factor, $f$ is the volume fraction of martensite, $\hat{P}$ is the mean volume of the martensite plates, $Q$ is the activation energy. The $P + dP/d\ln N_t$ term represents instantaneous volume of the martensite plates. Equations (6) and (7) represent the nucleation rate and the overall transformation rate, respectively. Traditionally, the attempt frequency $v$ has been taken as the lattice vibrational frequency of $10^{13}$ s$^{-1}$. Based on small particle experiments, Magee [17] proposed that $v$ should be about $10^{15}$ s$^{-1}$. From the conventional slip deformation data over a wide range of strain rates, Kocks et al. [9] found that $v$ lies between $10^4$ to $10^6$ s$^{-1}$. In this work $v$ is taken as $10^5$ s$^{-1}$ as proposed by Olson and Cohen [26] based on interfacial mobility experiments.

In addition to the alloys listed in Table 1, the kinetics of isothermal martensitic transformation has been studied in several other Fe–Ni–Mn, Fe–Ni–Mn–C and Fe–Ni–Cr–C alloys [27–30]. These studies did not include sufficient stereological information for analysis in terms of the phenomenological kinetic theory, however, and were not considered in the present analysis. The activation energies reported by Chang and Meyers [24] for isothermal nucleation under pulsed tensile stress in an Fe–21.63 at.% Ni–4.108 at.% Mn alloy appeared anomalously small. Also, there is considerable uncertainty regarding the driving force contribution of the large tensile pulse stresses (1.4 or 2 GPa) employed. For these reasons the activation energies under tensile pulse stress conditions in Fe–30.88 at.% Ni–0.165 at.% C [22] and Fe–21.63 at.% Ni–4.108 at.% Mn [24] alloys were not considered in the present analysis, even though these experiments were conducted apparently at very high driving forces where data is needed.

4. DRIVING FORCE–ACTIVATION ENERGY RELATIONSHIP FOR MARTENSITIC NUCLEATION

In our previous analysis [2] we considered the kinetics of interfacial mobility controlled heterogeneous nucleation when the interfacial frictional work is only athermal in nature. However, at relatively lower temperatures thermal activation will play an important role in determining the interfacial frictional work, and hence the total critical driving force for nucleation $-\Delta G_{crit}$. The Gibbs energy difference between b.c.c. and f.c.c. forms of pure iron is a very important parameter to evaluate the chemical driving force for martensitic transformation in Fe–base alloys. The lattice stability of pure iron has been evaluated in several studies [31–33]. In view of the recent measurements of the specific heats of pure iron [32], we have evaluated the Gibbs energy difference and the results are shown in Fig. 2 along with other literature data. It may be seen that at very high temperatures all lattice values are very similar and also our values are very similar to those of Kaufman et al. [31] and Bendick and Pepperhoff [32] over the whole temperature range. However, at very low temperatures a disparity up to about 2.0 kJ/mol can be noticed between our values and those reported by Fernandez-Gillmer and Gustafson [33].

The thermal component of the interfacial work will arise from the short-range interaction forces. In order to estimate the thermal component of the interfacial work, it is necessary to determine some of the fundamental parameters describing the profile of short-range interaction forces. Analogous to slip deformation, the driving force–activation energy function for the motion of a martensitic interface can be written in terms of the discrete obstacle-dislocation interaction model as [34]

$$
Q(\Delta G, T) = Q_0(T)[1 - (\Delta G_0/\Delta G)^n]
$$

Fig. 2. Gibbs energy difference between b.c.c. and f.c.c. forms of pure iron.
where $Q(Ag,T)$ is the activation energy of the obstacle at a volume driving force $-\Delta g$, $Q_0(T)$ is the activation energy in the absence of a driving force, $-\Delta g_0$ is the net volume driving force, $-\Delta g$ is the net “threshold” volume driving force where $Q(Ag,T) = 0$. The temperature dependence of $Q_0(T)$ is again given by scaling with the shear modulus $\mu(T)$, and is generally weak. The quantities $\Delta g_0$ and $\Delta g$ for the martensitic nucleation process are schematically shown in Fig. 3. In line with our earlier notation [2], the corresponding molar quantities are represented as $\Delta G_0$ and $\Delta G$, respectively. In the case of heterogeneous martensitic nucleation, $\Delta g_0$ and $\Delta g$ can be expressed as

$$\Delta g_0 = \Delta g_{th} + \left( w_p + g^d + \frac{2\sigma}{nd} \right)$$  \hspace{1cm} (9a)$$

$$\Delta g = -w_d,$$  \hspace{1cm} (9b)$$

where the quantities $w_p$, $g^d$, $\sigma$, $n$ and $d$ have already been defined in Part I [2]. In equations (9a) and (9b) the Gibbs energy change $\Delta g_{th}$ is negative, the quantities $w_p$, $g^d$ and $(2\sigma)/(nd)$ are always positive, and hence $\Delta g_0$ must be negative for transformation to occur. The quantity $\Delta g$ is also taken as negative so that the ratio $\Delta g_0/\Delta g$ is always positive. Based on the behavior of the athermal contribution of interfacial friction determined in our earlier study [2], we assume an $X^{0.5}$ concentration dependence of $W_0$ (or $w_d$) for each solute and adopt the same form of superposition law for multicomponent systems. We then express the molar quantity $W_0$ as

$$W_0 = W_{th} + \sqrt{\sum_i (K_i X_i^{0.5})^2} + \sqrt{\sum_j (K_j X_j^{0.5})^2} + \sum_k (K_k X_k^{0.5}) + K_0 X_0^{0.5},$$  \hspace{1cm} (10)$$

where $i = C, N$; $j = Cr, Mn, Mo, Nb, Si, Ti, V$ and $k = Al, Cu, Ni, W, W_{Fe}$ is the level of $W_0$ for pure Fe, and the $K_0$ coefficients determines the thermal components of interfacial work due to various solute atoms at absolute zero. Assuming these forms, the results of a comprehensive analysis of the kinetic data from the studies of Table 1 are shown in Fig. 4(a, b) which plot normalized activation energy $Q(T)/\mu(T)$ vs normalized driving force $\Delta g_0/\Delta g$. This type of universal nature of driving force-activation energy relationship has also been observed in slip deformation. In normalizing the activation energy, $\mu(T)$ for paramagnetic austenite was taken from Korenko [20]. As shown in Fig. 4(a, b), the literature data describing $Q-(\Delta g)$ behavior fits very well with $p = 0.5$ and $q = 1.5$ with very similar $Q_0(T)$. These values of $p$ and $q$ are theoretically predicted [9] for the case of strain interaction with solutes. The theoretical predictions of $p$ and $q$ for different types of interaction mechanisms are listed in Table 2. This implies that, in the alloys considered here, the martensitic

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**Fig. 3.** Schematic representation of the parameters $\Delta g_0$ and $\Delta g$.

**Fig. 4.** Plot of normalized activation energy vs normalized driving force for martensitic nucleation: (a) based on the results of Refs [11, 12, 14, 15, 18, 19, 23] and (b) based on the results of Refs [13, 16, 17, 20].
nucleation kinetics is governed by the interaction of interfacial dislocations with the strain field of solute atoms.

By analyzing a number of Fe-Ni and Fe-Ni-Mn alloys we find that \( W^{\text{Fe}} \) is 836 J/mol, and \( K_{\alpha}^{\text{Fe}} \) and \( K_{\alpha}^{\text{Mn}} \) are 345 and 4107.4 J/mol, respectively (expressed here as molar rather than volume quantities). Since the \( K_{\alpha} \) for other substitutional elements could not be determined directly, a scaling procedure was adopted. It is found that \( K_{\alpha}^{\text{Fe}}/K_{\alpha}^{\text{Ni}} \approx 2.1 \), \( K_{\alpha}^{\text{Mn}}/K_{\alpha}^{\text{Ni}} \approx 2.006 \) and \( K_{\alpha}^{\text{Mn}}/K_{\alpha}^{\text{Fe}} \approx 2.0707 \), which are very similar. Therefore, by taking an average scaling factor \( K_{\alpha}/K_{\alpha} = 2.058 \) the \( K_{\alpha} \) for the other substitutional elements were derived. In the case of the interstitial element C, the ratio \( K_{\alpha}^{\text{Fe}}/K_{\alpha}^{\text{C}} \) was found to be much higher at 5.573. Using this value \( K_{\alpha}^{\text{C}} \) was derived. All these values are listed in Table 3.

Another fundamental parameter for any deformation process is the activation volume \( V^*(T) \) which defines the volume of the thermally activated event. Following the concept of thermally-activated deformation, a slightly different definition of activation volume is employed for martensitic transformation. As has been discussed by Grujevic et al. [35], due to the three-dimensional nature of the problem of interfacial motion it is convenient to define an activation volume as the derivative of activation energy with respect to volume net driving force. This quantity can easily be obtained from equation (8)

\[
V^*(T) = -\left[ \frac{\partial Q}{\partial (\Delta g_{\alpha})} \right]_T
\]

\[
= \left[ \frac{Q_{\alpha}(T)}{\Delta g} \left( \frac{\Delta g_{\alpha}}{\Delta g} \right)^{\lambda(T)} \right] \left[ 1 - \left( \frac{T}{T_p} \right)^{\lambda(T)} \right]^{\lambda(T)} \quad (11a)
\]

\[
= \frac{Q_{\alpha}(T)}{\Delta g} \left( \frac{T}{T_p} \right)^{1-\lambda(T)} \left[ 1 - \left( \frac{T}{T_p} \right)^{\lambda(T)} \right]^{\lambda(T)} \quad (11b)
\]

where \( T_p \) is the temperature above which the frictional work is only athermal in nature. For \( p \neq 1, q \neq 1 \), the curvature of \( Q(\Delta g) \) defines a temperature dependent \( V^*(T) \) function. Figure 5 shows the observed temperature dependence of the activation volume for the f.c.c. \( \rightarrow \) b.c.c. martensitic nucleation process, as derived from equation 11(a) for different alloys. A temperature dependent activation volume for f.c.c. \( \rightarrow \) b.c.c. martensitic nucleation was first reported by Ghosh and Raghavan [23]. From data of Fig. 5, we find that the activation volume lies between 26 and 1950 (\( \Omega \) is the atomic volume taken as \( 11.8 \times 10^{-29} \text{m}^3 \)) in temperature range of 77-270 K. These values are much smaller than that for slip deformation (62-229 \( \Omega \)), in an Fe-35 at.% Ni alloy, in the same temperature range [36]. From Fig. 4(a, b) we obtain \( Q_{\alpha} \approx 1.2 \text{eV} \) for isothermal f.c.c. \( \rightarrow \) b.c.c. martensitic nucleation. Plastic deformation studies [37] of Fe-Ni-C alloys near \( M_s \) yields \( Q_{\alpha} \approx 1.68 \text{eV} \) [38] for slip.

A commonly observed phenomenon in solid solution strengthening is “stress equivalency” [4]. If two alloys containing different solutes in the same solvent have the same yield stress at a given temperature, they will have the same activation volume. Based on equation (8) and taking \( p = 0.5 \) and \( q = 1.5 \), Fig. 6 shows a unique variation of activation volume,

![Graph showing temperature dependence of activation volume](image-url)

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**Table 2: Dislocation-obstacle interaction mechanisms and the corresponding values of \( p \) and \( q \)**

<table>
<thead>
<tr>
<th>Mechanism of interaction</th>
<th>Theoretical values of ( p ) and ( q )</th>
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<tr>
<td>Friction</td>
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<tr>
<td>Strain</td>
<td>1/2, 3/2</td>
</tr>
<tr>
<td>Modulus</td>
<td>1/2, 2</td>
</tr>
<tr>
<td>Interface step</td>
<td>2/3, 2</td>
</tr>
<tr>
<td>Core energy</td>
<td>3/2, 2</td>
</tr>
<tr>
<td>Internal fault, APB</td>
<td>1/2, 3/2</td>
</tr>
</tbody>
</table>

**Table 3: The athermal and thermal strengths of different solutes for f.c.c.-b.c.c. martensitic interface in Fe-base system**

<table>
<thead>
<tr>
<th>Element</th>
<th>( K_{\alpha} ) (J/mol)</th>
<th>( K_{\alpha} ) (J/mol)</th>
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<tbody>
<tr>
<td>C</td>
<td>3807 ± 68</td>
<td>21,216</td>
</tr>
<tr>
<td>N</td>
<td>3048 ± 85</td>
<td>16,958^b</td>
</tr>
<tr>
<td>Mo</td>
<td>1989 ± 79</td>
<td>4107</td>
</tr>
<tr>
<td>Si</td>
<td>1879 ± 215</td>
<td>3867^b</td>
</tr>
<tr>
<td>Cr</td>
<td>1868 ± 72</td>
<td>3923</td>
</tr>
<tr>
<td>Nb</td>
<td>1635 ± 90</td>
<td>340^b</td>
</tr>
<tr>
<td>V</td>
<td>1613 ± 122</td>
<td>3336^b</td>
</tr>
<tr>
<td>Ti</td>
<td>1473 ± 204</td>
<td>3031^b</td>
</tr>
<tr>
<td>Mo</td>
<td>1418 ± 55</td>
<td>2914^b</td>
</tr>
<tr>
<td>Co</td>
<td>752 ± 12</td>
<td>1548^b</td>
</tr>
<tr>
<td>W</td>
<td>714 ± 93</td>
<td>1469^b</td>
</tr>
<tr>
<td>Al</td>
<td>280 ± 41</td>
<td>576^b</td>
</tr>
<tr>
<td>Ni</td>
<td>172 ± 35</td>
<td>345</td>
</tr>
<tr>
<td>Co</td>
<td>−352 ± 110</td>
<td>−724^b</td>
</tr>
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^a Based on a scaling parameter \( K_{\alpha}/K_{\alpha} = 2.058 \).

^b Based on a scaling parameter \( K_{\alpha}/K_{\alpha} = 5.573 \).
for the alloys having very similar $\Delta G$, with net driving force for the martensite kinetics as well. Deviation from straightline behavior at higher activation volumes in this plot suggests a deviation of the obstacle interaction profile form the "tail" region \[9\] Experimental data on slip deformation also suggests this kind of deviation from model behavior \[5\]. It should be noted that unlike slip deformation, activation volume data at a constant temperature over a wide range of driving force does not exist for martensite kinetics.

5. DISCUSSION

At low temperatures thermal activation plays an important role in determining the critical driving force for martensite nucleation. Figure 7 shows a comparison between the calculated and experimental \[39-46\] $M_t$ temperatures in multicomponent alloys with $M_t$ below 300 K. In this case the molar critical driving force is given by

$$-\Delta G_{tot} = K_t + W_p(K_o, X_t) + W_m(K_o, X_t, T, T_o).$$ (12)

The constant $K_t$ and athermal work $W_p(K_o, X_t)$ have already been discussed in our previous analysis \[2\]. In analogy to equation (5) we can describe the thermal component of interfacial friction $W_m(T)$ as

$$W_m(T) = W_m \left[1 - \left(\frac{T}{T_o}\right)^{\frac{1}{\alpha}}\right]^{\frac{1}{\alpha}}.$$ (13)

where $W_m$ is evaluated according to equation (10) in conjunction with the $K_o$ coefficients listed in Table 3. The quantity $T_o$, which is interfacial rate dependent, is taken here to be 500 K. The calculated behavior of $W_m$ is not sensitive to $T_o$ due to the long tail of the function of equation (13). Similar to our previous analysis \[2\], the scatter in $M_t$ prediction in the thermal regime of Fig. 7 is $\pm 40$ K.

In the previous study \[2\] we summarized various microstructural elements that can influence martensite interface mobility. A generalized expression for the net driving force for the motion of a martensite interface can be written as

$$\Delta G_{tot} = \Delta G_{th} + \Delta G^a + \Delta G^M +$$

$$\left[ w_0(X_t) + w_0(\rho) + w_{pre} + \sigma \frac{2\alpha}{m_l} \right],$$ (14)

where $\Delta G^a$ and $\Delta G^M$ are the Gibbs energy contributions due to a superimposed elastic stress ($\sigma$) and magnetic field ($M$), respectively, both of which increase the net driving force. The $w_0(\rho)$ and $w_{pre}$ are the contributions to the frictional work due to forest dislocations and precipitates, respectively, both of which will reduce the net driving force. As a first-order approximation, the contributions to the frictional work due to forest dislocations and precipitates are assumed to be only athermal in nature. In considering the effect of various microstructural elements on the frictional work, we must address the issue of possible superposition laws. Following Kocks \[47\], we write the following possible expressions for the total athermal interfacial frictional work $W$ (a molar quantity)

$$W = W_p(X_t) + W_a(\rho) + W_{pre}(f, \Gamma, \epsilon, \Psi, \theta)$$ (15a)

$$W = W_p(X_t) + W_{pre}(f, \Gamma, \epsilon, \Psi, \theta)$$ (15b)

$$W^{\prime} = W_p(X_t) + W_a(\rho) + W_{pre}^{\prime}(f, \Gamma, \epsilon, \Psi, \theta)$$ (15c)

where $W_p(\rho)$ is a function of dislocation density $\rho$, and $W_{pre}(f, \Gamma, \epsilon, \Psi, \theta)$ is a function of volume fraction of precipitates $f$, average precipitate size $\bar{r}$, particle position with respect to the interface $\Gamma$.
lattice mismatch (for coherent precipitates) $\epsilon$, particle crystallographic orientation with respect to the interface $\Psi$, and a shape factor $\theta$. In equation (15b), $[1 + A(X)]$ represents an interaction of solute atoms and forest dislocations, and $[1 + B(p)]$ represents an interaction of forest dislocations and precipitates. In equation (15c), $m$ is an exponent. For the sake of simplicity, equation (14) is written on the assumption of a simple additivity law of the form of equation (15a). If the microstructural elements, such as dislocation forests, precipitates, etc., have only athermal contributions then only $\Delta G_n$ will be affected, otherwise $\Delta G$ will also be influenced.

The effect of a superimposed elastic stress on the activation energy for isothermal martensitic nucleation was measured by Ghosh and Raghavan [23]. The observed decrease in activation energy with increasing stress was not in good agreement with the commonly employed assumption of an optimal nucleus orientation [48]. A more recent analysis employing a random orientation model [49] predicts that the effective driving force contribution $\Delta G^e$ is a non-linear function of stress level, and generally smaller than the optimum orientation model. Employing an analytical fit [50] to the random orientation model for $\Delta G^e$ [49], Fig. 8 shows the correlation of $Q(T) - Q(T, \sigma)$ with $-\Delta G^e V^e(T)$ at two temperatures, where $Q(T)$ and $Q(T, \sigma)$ are the activation energies with and without stress, respectively. The model reasonably accounts for the kinetic behavior under applied stress, of importance to the quantitative modeling of transformation plasticity phenomena.

The effect of prior plastic strain of austenite on the activation energy for subsequent isothermal martensitic nucleation was measured by Ghosh and Raghavan [23]. Figure 9(a) shows the strain hardening behavior of an Fe-22.3 at% Ni-2.888 at% Mn alloy deformed in axisymmetric tension at 293 K. As expected for polycrystalline f.c.c. alloys, the strain hardening behavior can be described by $\Delta \sigma \propto \epsilon^{0.5}$ [51]. Strain hardening of the matrix results in an increase in activation energy for isothermal martensitic nucleation [23]. This increase in activation energy was attributed to the $\Delta \sigma$ increase in athermal stress for the interfacial motion which was calculated on the assumption of validity of the Cottrell-Stokes law [52]. Equivalently, it is possible to account for the increase in activation energy due to the reduction of net driving force. With $Q$ a unique function of $\Delta G_n$, from equation (9) we have

$$
\frac{Q(\epsilon = 0)}{Q'(\epsilon = \epsilon')} = \frac{[1 - (\Delta G_n/\Delta G')^p]}{[1 - (\Delta G_n/\Delta G')^q]} \quad (16)
$$

where $Q'$ and $\Delta G_n'$ are the activation energy and net driving force due to a plastic strain $\epsilon'$ in austenite, respectively. From equation (16) it is possible to
calculate $\Delta G^*$ if the other quantities are known. Since the interface interacts with remote dislocations, the resulting increase in interfacial work will be predominantly long-range or athermal in nature. Therefore, for a given alloy $\Delta G$ will remain unaltered in the presence of forest dislocations. Figure 9(b) plots the $W_s(p)$ estimates thus obtained from experimental activation energies at three transformation temperatures. The behavior of $W_\eta(p)$ shows a similar $\epsilon^{0.5}$ strain dependence. Within the scatter of Fig. 9(b), a linear superposition of forest hardening $W_s(p)$ on the athermal $W_\eta$ and thermal $W_\theta$ contributions to solution hardening appears to be a reasonable approximation.

The $\Delta \sigma$ of Fig. 9(a) can be converted to a shear resistance $\Delta \tau (\approx \Delta \sigma/M)$ using a Taylor factor of $M = 3.06$ [53] appropriate to slip in an f.c.c. polycrystal. Treating the forest hardening as an athermal backstress acting on the transformation shear strain $\gamma_\tau = 0.2$ the interfacial frictional work $w_\eta(p)$ (per volume, $V_\eta = 6.9 \times 10^{-6}$ m$^3$/mol) is expressed as $A \Delta \gamma_\tau$ (per volume). Figure 10 shows the plot of $w_\eta(p)$ vs $A \Delta \gamma_\tau$, where $w_\eta(p)$ is estimated from the isothermal-kinetic data of Ghosh and Raghavan [23] in the Fe-Ni-Mn alloy deformed in tension and recent athermal kinetic data of Tsuzuki et al. [54] on Fe-Mn and Fe-Ni alloys deformed by rolling at 773 K. For the best fit straight line passing through the origin, the parameter $A$ is $1.42 \pm 0.1$ for the Fe-Ni-Mn alloy. The best fit straight line representing the data of Tsuzuki et al. [54] gives a similar $A$ of $1.28 \pm 0.3$. However, in the latter case there is an intercept level below which deformation aids transformation. This behavior is consistent with the earlier reports [55, 56] that a small pre-strain at elevated temperature results in a small increase in $M$. Indeed Tsuzuki et al. [54] carried out the deformation at the elevated temperature of 773 K, while Ghosh and Raghavan [23] performed pre-straining at 293 K and observed only a retarding effect on the isothermal transformation kinetics at all strain levels (0.005-0.05). In an effort to correlate the effect of pre-strain on subsequent martensitic transformation kinetics, Breedis [57] carried out a transmission electron microscopy investigation of the substructure in deformed metastable stainless steels. It was observed that small pre-strain leads to the development of planar dislocation pile-ups with long-range stress fields which can aid nucleation (effectively increasing the nucleation site potency $n$ of equation 9(a)). With increasing level of pre-strain the substructure changes from planar pile-up to dislocation forest and/or cells. Evolution of such substructures can be influenced by several factors such as the stacking fault energy, interstitial content, deformation temperature and the strain state during deformation. The planar pile-ups may be promoted by the plane-strain deformation conditions of the rolling experiments for Tsuzuki et al. [54] compared to the axisymmetric deformation experiments of Ghosh and Raghavan [23].

To relate the forest hardening contribution $w_\eta(p)$ to the dislocation density, the strain hardening behavior of the Fe-base f.c.c. alloys can be described as $\Delta \sigma = B \rho^{1/2} \eta$ with $B$ the shear modulus (taken as $8 \times 10^{10}$ N/m$^2$), $\rho$ the Burgers vector of lattice dislocations ($\alpha/\sqrt{2} \approx 0.254$ nm). Using a value $B = 0.4$ [51] gives an estimated $\partial \rho/\partial c$ of $9.2 \times 10^{10}$ m$^{-3}$ for the Fe-Ni-Mn alloy deformed in axisymmetric tension at 293 K [23] while $\partial \rho/\partial c$ is $2.9 \times 10^{10}$ m$^{-3}$ for the Fe-Ni and Fe-Mn alloys deformed by rolling at the higher temperature of 773 K [54], where $c$ is the equivalent strain. These inferred levels of dislocation production are comparable to the levels of $2 \times 10^{18}$ m$^{-3}$ directly measured in polycrystalline Ag [58] and Cu [59] after axisymmetric deformation at room temperature. The slope of the Fe-Ni-Mn alloy in Fig. 10 then implies $w_\eta(p) = C \sqrt{\rho}$ with $C = 1.29 \pm 0.2$ J/m$^2$.

In our previous analysis [2] and here we have demonstrated the importance of interfacial friction in controlling heterogeneous nucleation at low or moderate driving forces ($\Delta G \approx 2-3$ kJ/mol). However, nonclassical mechanisms [26] can become operational at very high driving forces approaching conditions of lattice instability. Very recently, evidence of homogeneous nucleation in coherent Fe-Co precipitates in a Cu matrix has been reported [60] at a driving force of about 10 kJ/mol, approaching the theoretical instability driving force of 14 kJ/mol (for pure iron). It is expected that at very high driving force interfacial friction will no longer control nucleation kinetics. Rather, other dissipating mechanisms, such as, interaction of the moving interface with phonons and, at low temperatures with electrons, will become rate controlling [34]. This condition might apply in the tensile pulse experiments of Thadhani and Meyers [22] and Chang and Meyers [24].

![Fig. 10. The variation of $w_\eta(p)$ as a function $A \Delta \gamma_\tau$ in Fe-Ni, Fe-Mn and Fe-Ni-Mn alloys.](image-url)
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6. CONCLUSIONS

The similarities between the kinetics of martensitic transformation and the kinetics of slip deformation in solid solutions has been demonstrated. The universal nature of the normalized activation energy $Q(T)/\mu(T)$ vs normalized driving force $Ag\Delta g$ relationship has been established for heterogeneous martensitic nucleation. The behavior is consistent with nucleation rate control by solute atoms acting as discrete obstacles to interfacial motion. The frictional work for f.c.c. → b.c.c. martensitic nucleation in multicomponent alloys has been modeled adopting a scaling between thermal and athermal contributions. The model behavior is consistent with the observed effect of applied elastic stress on isothermal martensitic kinetics and the effect of plastic pre-strain acting as athermal backstress inhibiting interfacial motion.

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