CLASSICAL AND NONCLASSICAL MECHANISMS OF MARTENSITIC TRANSFORMATIONS

G.B. Olson and Morris Cohen
MIT, Cambridge, MA, USA

Abstract.- Theoretical approaches to the nucleation of martensitic transformations have considered two types of nucleation paths: (a) the classical path, involving a nucleus of fixed structure and increasing size, and (b) nonclassical paths, involving a nucleus of varying structure. A unified approach is outlined which allows for the theoretical treatment of homogeneous and heterogeneous nucleation of coherent and semicoherent martensitic transformations by both types of nucleation paths, and identifies the circumstances favoring each. Nonclassical paths would be favored in the special case of homogeneous coherent nucleation near a mechanical instability; however, quantitative treatment requires further knowledge of the energetics of homogeneous lattice deformations and the strain-gradient energies which control diffuse interfaces. Heterogeneous nucleation, which governs martensitic transformations in bulk materials, favors the classical path and involves relatively sharp interfaces. Classical heterogeneous nucleation is adequately treated by linear-elastic continuum and dislocation descriptions. Defect-nucleus interaction leads to "barrierless" nucleation with kinetics controlled by interfacial motion. Details requiring further attention are the microscopic mechanisms of martensitic interfacial motion in discrete crystals, and the precise nature of the nucleating defects, both those initially present and autocatalytically generated.

Introduction.- Martensitic transformations have been defined as a subset of diffusionless displacive phase transformations, with sufficiently large lattice-distortive shear displacements such that the transformation kinetics and morphology are dominated by strain energy (1). It then follows that martensitic transformations are first-order solid-state reactions occurring by nucleation and growth.

While the growth stage of first-order transformations generally takes place by the motion of interfaces which convert the parent phase to the fully-formed transformation product, two types of paths have been considered for the case of nucleation. The "classical" nucleation path, analogous to the growth stage, involves a nucleus of the same structure and/or composition as the fully-formed product, increasing in size by the motion of its interface. A "nonclassical" path involves a continuous change in structure and/or composition in a finite region. The two types of paths are illustrated in Figure 1 where composition, structure, and size are denoted by C, \( \eta \), and \( n \). Path "a" depicts the classical path, while paths "b" and "c" represent nonclassical paths. For the simple case of purely compositional transformations, nucleation via nonclassical paths has been treated quantitatively by Cahn and Hilliard (2).

The current status of the theory of martensitic nucleation by both classical and nonclassical paths has been recently reviewed (3). While the theory of nucleation via classical paths is now well-developed for both homogeneous and heterogeneous martensitic nucleation, speculation regarding the possible relevance
of nonclassical nucleation paths has not yet evolved a quantitative theory. We here outline a unified approach to the quantitative treatment of martensitic nucleation, which allows for both classical and nonclassical paths, and identifies the circumstances under which each mode of behavior will prevail.

Lattice-Deformation Energetics. - Of importance to both the energy of a nonclassical nucleus and the interfacial energy of a classical nucleus are the energetics of intermediate configurations in the lattice deformation of the martensitic transformation. The free-energy change per unit volume, \( \Delta g \), accompanying homogeneous distortion of the parent phase to the product structure along a deformation path (defined by the structural parameter \( \eta \)) is depicted in Figure 2, with \( \eta=0 \) and \( \eta=1 \) representing the parent and product structures. The value of \( \Delta g \) at \( \eta=1 \) corresponds to the chemical free-energy change of the transformation, \( \Delta g_{\text{ch}} \), and the maximum in the curve represents a "homogeneous lattice deformation barrier" of height \( \phi \). When \( \Delta g_{\text{ch}}=0 \) (as indicated for the temperature \( T=T_0 \)), the barrier is designated \( \phi_0 \). When \( \Delta g_{\text{ch}}<0 \), \( \phi \) is less than \( \phi_0 \); and for \( \Delta g_{\text{ch}} \) sufficiently negative, the condition \( \phi=0 \), can (in principle) be reached whereby the parent lattice becomes mechanically unstable as illustrated for an "instability temperature", \( T=T_i \), in Figure 2. While some transforming materials show an anomalous temperature dependence of elastic constants such that a shear constant extrapolates to zero at a finite \( T_i \) temperature (4), many systems do not exhibit such anomalies and then a \( T_i \) temperature does not exist. As discussed in ref. 3, however, any metastable lattice can become unstable if the thermodynamic driving force is made sufficiently large, as for example by the application of stress. As indicated by the curve for \( T=M_s \) in Figure 2, martensitic transformations in bulk materials typically nucleate under thermodynamic driving forces which are far removed from the conditions for general mechanical instability of the parent lattice.

Recent progress has been made in the quantitative estimation of the energy curves represented by Figure 2, based on higher-order elastic constants (5,6), interatomic potentials (7), and electronic calculations (8-11). The barrier height \( \phi \) is sensitive to the nature of the lattice deformation path. Paths examined so far include "proportional strain" paths along intermediate configurations defined by the deformation \( \eta B \), where \( B \) is the total deformation relating parent and product lattices, and "sequential shear" paths involving close-packed shear systems as proposed by Bogers and Burgers (12). Calculations to-date suggest
lower barriers for proportional strain paths, with \( \phi_0 \) values as low as \( 10^2 \) to \( 10^3 \) J/mole for FCC\#BCC transformations. The lower barrier for the proportional strain path compared to the sequential shear paths complicates the interrelation of thermodynamic stability (\( \Delta g^{ch} \)) and the behavior of second-order elastic shear constants, such as \( C_{11} = C_{12}, C_{11} - C_{12} \) in BCC alloys. Analysis of load-path bifurcations during homogeneous lattice deformation, as studied by Milshtein and Farber (7), may clarify this matter.

The energetic calculations suggest that \( \Delta g(\eta) \) can be reasonably approximated by a fourth-order Landau expansion:

\[
\Delta g = A\eta^2 - B\eta^3 + C\eta^4 ,
\]

where the coefficients \( A, B, \) and \( C \) are related to the second, third, and fourth order elastic constants of the parent phase. The dependence of \( \Delta g \) on thermodynamic conditions can be approximated by expressing these coefficients as functions of \( \Delta g^{ch} \) constrained to give local minima at \( \eta = 0 \) and \( \eta = 1 \). The simplest approximation, which is most appropriate near a mechanical instability, is to take the coefficient \( A \) (controlling mechanical stability of the parent lattice) as a linear function of \( \Delta g^{ch} \). This gives expressions of the form:

\[
\begin{align*}
A/\phi_0 &= 16 (1 - \alpha) \\
B/\phi_0 &= 32 (1 - \alpha) - 4\alpha \beta \\
C/\phi_0 &= 16 (1 - \alpha) - 3\alpha \beta \\
\alpha &= \Delta g^{ch}/\Delta g^{ch}_i \\
\beta &= \Delta g^{ch}_i/\phi_0
\end{align*}
\]

where \( \Delta g^{ch}_i \) is the critical \( \Delta g^{ch} \) for instability. The latter can be estimated from the critical driving force for instability under stress at \( T^* \), giving \( \beta = -3.08 \) (3). Energies normalized to \( \phi_0 \) can then be simply expressed as functions of the dimensionless parameter \( \alpha \), where \( \alpha = 0 \) corresponds to equal free energies of the parent and product phases (\( \Delta g^{ch} = 0 \)) and \( \alpha = 1 \) represents mechanical instability of the parent phase.

Coherent Interfacial/Gradient Energy.— As discussed in ref. 3, and also developed by Roitburd (13,14), the lower energy of intermediate configurations accompanying the reduction of \( \phi \) near a mechanical instability will promote diffuseness of a coherent martensitic interface. The behavior of the interface is then best described by adopting a gradient-energy formulation similar to that originally applied to diffuse interfaces in diffusional (compositional) transformations by Cahn and Hilliard (15). The volume and surface energy terms of a classical description are then replaced by a functional of the form:

\[
\int \left[ \Delta g + \kappa (\nabla \eta)^2 \right] dv
\]

where \( \kappa \) is a gradient-energy coefficient and \( \Delta g \) is the local free-energy density.* When the interface is the invariant plane of an invariant-plane strain (IPS) lattice deformation, \( \Delta g \) corresponds to the function of Figure 2 and equation 1. For a non-IPS coherent interface additional strain energy arises from distortions in the interfacial plane as required by compatibility of the deformation across the interface. The gradient energy \( \kappa (\nabla \eta)^2 \) is attributable to an harmonic many-body interaction (16).

*The simple form adopted for equation 3 is based on the assumption that all deformation states lie along the path corresponding to the variable \( \eta \). This will be valid for the simple cases considered here. More general cases are describable via the gradients of the complete strain tensor (13,14).
Adopting the approximation that $\kappa$ is independent of $\eta$ (and neglecting gradient-energy terms of higher power than $(\nabla \eta)^2$), we can estimate a value for $\kappa$ from knowledge of the coherent surface energy at $T_0(3)$. For a flat coherent IPS interface in the $z=0$ plane, the surface energy is:

$$\sigma_0 = \int_{-\infty}^{\infty} \left[ \Delta g + \kappa (\eta')^2 \right] dz \quad . \tag{4}$$

Solving the Euler equation for the variation $\eta(x)$ which minimizes $\sigma_0$, and assuming $\Delta g$ is of the form of equation 1, a solution for $\sigma_0$ is obtained (3) which identifies $\kappa$ as:

$$\kappa = \frac{9\sigma_0^2}{18\phi_0} \tag{5}$$

and gives an interfacial width of:

$$\delta_0 = \sqrt{\frac{\kappa}{\phi_0}} \tag{6}$$

For $\sigma_0$ values of a few mJ/m$^2$ (typical for coherent interfaces), the estimated $\phi_0$ values discussed earlier give $\kappa \approx 10^{-12} - 10^{-11}$ J/m with a $\delta_0$ of a few $\AA$. By fitting $\kappa$ to the interfacial behavior at $T_0$, the gradient-energy formulation will account for both the classical interface at $\alpha=0$ and the diffuse-interface behavior at $\alpha=1$.

A problem of relevance to martensitic nucleation is that of a thin slab of martensite centered on the $z=0$ plane where $\eta = \eta_0$. This geometry is illustrated in Figure 3. For a coherent IPS particle, the total free-energy functional of interest is now:

$$F_A = \int_{-\infty}^{\infty} \left[ \Delta g + \kappa (\eta')^2 \right] dz. \tag{7}$$

Boundary conditions for the variation $\eta(z)$ are $\eta(0) = \eta_0$, $\eta(\infty) = 0$, and $\eta'(\infty) = 0$ with $\eta' < 0$ for $z > 0$. A fixed total displacement across the particle corresponds to the condition:

$$\int_{-\infty}^{\infty} \eta \, dz = u \quad , \tag{8}$$

where $u$ is the displacement parameter identified in Figure 3. The latter condition defines a fixed effective semithickness of the slab expressed as:

$$c = \frac{u}{\eta_0} \quad . \tag{9}$$

The form of the Euler equation for determining the variation $\eta(z)$ which minimizes the functional $F_A$, equation 7, subject to the constraint of equation 8 is:

$$\frac{d\Delta g}{d\eta} - 2\kappa \frac{d\eta'}{dz} + \lambda = 0 \quad , \tag{10}$$

where $\lambda$ is a multiplier introduced by the fixed displacement constraint. This yields a differential equation for $\eta(z)$ of the form:

$$\eta'' + \frac{\lambda}{\kappa} \eta = 0 \quad . \tag{11}$$
For a given \( n_0 \), the minimum energy variation for \( n(z) \) corresponds to the additional boundary condition \( n'(0)=0 \), whereby \( \lambda=-\Delta g_0/n_0 \).

Solution of equation (11) for \( n(z) \) as a function of \( n_0 \) and \( \lambda \) is given by the integration:

\[
z = -\sqrt{\frac{2}{n_0}} \int_{n_0}^{n} \left[ \Delta g + \lambda n \right]^{-1/2} \, dn.
\]  

(12)

Substitution of variables according to equation (11) determines \( F_A \) and \( u \) as:

\[
F_A(n_0, \lambda) = \sqrt{\frac{2}{n_0}} \int_{n_0}^{n} \frac{2\Delta g + \lambda n}{\Delta g + \lambda n} \, dn
\]

(13)

\[
u(n_0, \lambda) = \sqrt{\frac{2}{n_0}} \int_{n_0}^{n} \frac{n}{\Delta g + \lambda n} \, dn
\]

(14)

The effective semithickness \( c=\frac{u}{n_0} \) can be used to define an interfacial energy:

\[
\sigma(n_0, \lambda) = F_A(n_0, \lambda) - \frac{\Delta g_0}{n_0} - u(n_0, \lambda).
\]

(15)

These relations provide the basis for a treatment of the energy of a martensitic nucleus, which allows for both classical and nonclassical nucleation paths.

Coherent Nucleation.- The major contribution to the interfacial energy of a thin-plate IPS particle arises from its broad interfaces as opposed to the plate periphery, while the elastic energy accommodating the transformation strain resides primarily in the region of the matrix beyond the periphery. Accordingly
the total energy of a thin-plate nucleus of radius \( r \), lying in the \( z=0 \) plane, can be reasonably approximated by the energy of a one-dimensional variation \( \eta(z) \) within a cylinder of radius \( r \) combined with the elastic energy associated with the long-range strain field of a particle of semithickness \( c \) producing the net displacement defined by \( u \). This approximation will fit best when the interfacial width \( \delta \) is much less than \( r \). Relating the matrix elastic constants to the coefficient \( A \) in equation 1, the nucleus energy can then be expressed by:

\[
\Delta G(r, \eta_0, \lambda) = 2\pi r^2 F_A(\eta_0, \lambda) + 2\pi r\xi A[u(\eta_0, \lambda)]^2
\]

(16)

where \( \xi \) is an accommodation factor equal to \( \pi(2-v)/(4(1-v)) \) for the case of a simple shear. The functions \( F_A \) and \( u \) can be evaluated from equations 13 and 14 using equations 1 and 2 to express \( \Delta G \). The activation energy for homogeneous coherent nucleation \( \Delta G^* \) can then be evaluated from a saddle point of \( \Delta G(r, \eta_0, \lambda) \) at \( (r^*, \eta_0^*, \lambda^*) \) corresponding to a maximum of \( \Delta G \) with respect to \( r \) and a minimum with respect to \( \eta_0 \) and \( \lambda \). The coefficients of equations 2, 5, and 7 are most conveniently fitted to the classical interfacial parameters at \( \alpha=0 \) by normalizing energies (per volume) with respect to \( \phi_0 \) and distances with respect to \( \delta_0 \) (equation 6).

Inspection of these equations reveals certain features of a coherent nucleus which parallel the Cahn-Hilliard diffusional nucleation behavior as discussed in ref. 3. Since \( F_A \) must be negative for a critical nucleus, \( \eta_0^* \) must be sufficiently large that \( \Delta G_0<0 \). As indicated by Figure 2, this condition is met by progressively smaller \( \eta \) as \( \alpha \to 1 \). While a critical nucleus at low \( \alpha \) will require \( \eta_0^* \) and \( \delta^* \) for a nonclassical nucleus \( (\eta_0<1) \) vanishes at \( \alpha=1 \) as depicted by the dashed line in Figure 4. Thus, while classical nucleation theory generally predicts a \( \Delta G^* \) which is too high for thermal activation of homogeneous nucleation in most circumstances, deviations from classical behavior near in instability can reduce \( \Delta G^* \) enough so that thermally-activated homogeneous coherent nucleation will precede the actual instability. This result obtains for the simple case of an IPS lattice deformation. It is not clear that the additional strain energy associated with interfacial distortions in a non-IPS coherent transformation will vanish at \( \alpha=1 \), but it can be expected that nonclassical behavior will generally allow a substantial reduction in \( \Delta G^* \) for homogeneous coherent nucleation near a mechanical instability.

It is of course well established that martensitic transformations typically nucleate heterogeneously. The high \( \alpha \) levels necessary for homogeneous nucleation can only be reached if nucleation at imperfections is eliminated. Theoretical predictions (17,18) and experimental observations (19-23) indicate that the most common nucleation sites are linear defects which can be modelled as groups of dislocations. Heterogeneous nucleation of the coherent nucleus considered here can be modelled by treating its interaction with the stress field \( \sigma_d \) of the defect in the \( z=0 \) plane. The interaction energy for a ribbon-shaped nucleus of length \( \lambda \), width \( a \), and semithickness \( c \) lying along a defect parallel to the \( y \) axis is then:

\[
E_{\text{int}} = -2ck\gamma T \int_{r_0}^{a} \sigma_d \eta_0 dx
\]

(17)

*Within the approximation of equation 16, \( \Delta G^* \) of a classical nucleus \( (\eta =1) \) also vanishes as \( A \to 0 \). This arises from neglect of the surface energy contribution of the plate periphery. A more realistic (nonvanishing) behavior of the classical \( \Delta G^* \) near \( \alpha=1 \) is obtained by adding a \( 4\pi r\sigma_0 c \) term to equation 16, with \( \sigma \) defined by equation 17. The nonclassical \( \Delta G^* \) still vanishes at \( \alpha=1 \).
where \( \gamma_f \) is the transformation strain and \( r_0 \) is the defect core radius. The total nucleation energy change \( \Delta G \) can be expressed by combining \( E_{\text{int}} \) with the two terms of equation 16 modified for the ribbon shape. For a dislocation defect with \( a \sim x^{-1} \) strain field, equation 17 introduces a negative energy contribution proportional to \( \ln a \) which substantially reduces \( \Delta G^* \), promoting nucleation at lower \( \alpha \) values.

As equation 17 indicates, the nucleus-defect interaction energy is proportional to \( \eta_0 \) and heterogeneous nucleation thus favors classical nucleation. The range of \( \alpha \) required for classical heterogeneous nucleation can be estimated from a dislocation-dissociation model of heterogeneous nucleation (17) in which nuclei form at a constant thickness determined by the number of dislocations in the nucleating defect. The classical barrier \( \Delta G^* \) goes abruptly to zero when the fault energy associated with the dissociation becomes negative. For the simple coherent transformation considered here, this occurs at a critical driving force of \( \Delta G^*_C = -\sigma_0/c \). Taking \( \sigma_0 = 4\phi_0 \delta_0 / 3 \) from equations 5 and 6, the critical \( \alpha \) for nucleation is then:

\[
\alpha_C = \frac{4\phi_0}{3\delta_0} .
\]  

(18)

The behavior predicted for various values of \( c / \delta_0 \), corresponding approximately to the number of dislocations in the nucleating defect, is shown by the solid lines in Figure 3. For defects of the size which accounts for bulk nucleation in steels, \( \alpha_C \) is of the order of 0.1. In addition to the strong interaction energy favoring a classical \( \eta_0 = 1 \) nucleus, the occurrence of nucleation at such low \( \alpha \) values will favor sharp interface behavior such that no significant deviation from a classical nucleation path is expected for heterogeneous coherent nucleation.

To summarize the results depicted in Figure 4, heterogeneous coherent nucleation at low \( \alpha \) will favor nucleation via the classical path. If heterogeneous nucleation can be suppressed, homogeneous coherent nucleation at high \( \alpha \) will then favor a nonclassical path and the associated nucleation barrier is expected to reach a thermally-surmountable level before general lattice instability can be reached.

Semicohercet Nucleation.- With the exception of FCC-HCP and some BCC+9R transformations, the lattice deformation accompanying most martensitic transformations is not sufficiently close to on IPS to allow fully coherent transformation. Under the thermodynamic conditions where these transformations are known to occur, the volume strain energy associated with distortions in a fully coherent interface would exceed the chemical driving force, and so a martensitic particle can only be stable in a semicoherent form with sufficiently reduced strain energy.

Semicohercence is achieved through a lattice-invariant deformation by slip or twinning which alters the net transformation shape strain, generally toward an IPS. A necessary consequence of the lattice-invariant deformation is a modification of the interfacial structure, introducing a short-range interfacial elastic strain field (with range comparable to the spacing of the twins or slip dislocations in the interface) which contributes a substantial increment to the interfacial energy. In contrast to the behavior of fully coherent interfaces just discussed, the interfacial energy of a semicoherent particle in an anisotropic crystal will generally have contributions from elastic constants which do not vanish at an instability. Similarly, nonvanishing elastic constants will also likely contribute to the accommodation strain energy associated with the net transformation strain (shape change). Thus the interfacial energy and strain energy will remain finite, and the nucleation barrier \( \Delta G^* \) for homogeneous nucleation of a semicoherent martensitic particle will not vanish at \( \alpha = 1 \). Nonclassical diffuse-interface behavior should play only a secondary role in semicoherent martensitic nucleation, as reflected by just a moderate reduction in interfacial energy accompanying a widening of the cores of interfacial dislocations. Classical calculations indicate
that homogeneous nucleation of semicoherent martensitic transformations is highly improbable under the thermodynamic conditions where these transformations typically occur (24).

For the case of heterogeneous nucleation, the considerations previously discussed for coherent nucleation combined with the properties of semicoherent interfaces just described make it highly unlikely that semicoherent nucleation will deviate significantly from the classical nucleation path. The essential features of heterogeneous classical nucleation of semicoherent transformations at dislocation-like linear defects are now well established, based on both specific dislocation-dissociation models (17,25,26) and general continuum-elastic calculations (18,27,28). A general result is that (a) $\Delta G^*$ for heterogeneous nucleation will vanish at a relatively modest (compared to that for $\alpha=1$) critical driving force which depends on the defect size, and (b) the critical condition will be preceded by the formation of stable subcritical classical embryos at very low driving forces. The short-range interaction with dislocations is so strong that the latter embryos may exist above $T_0$ ($\Delta G_{CH}>0$). The prediction of pre-existing classical embryos and the greater interaction energy for classical vs. nonclassical embryos discussed earlier reinforce the conclusion that heterogeneous semicoherent nucleation will follow a classical rather than non-classical nucleation path.

The detailed behavior of $\Delta G^*$ for heterogeneous nucleation is sensitive to the constraints applied to the nucleus. Dislocation-dissociation models for heterogeneous nucleation are based upon a discrete-dislocation description of nucleus interfacial structure, intended to reflect discrete-crystal constraints on the interfacial mobility and morphology of a microscopic particle. A specific nucleus model (25) for semicoherent FCC-BCC transformation is depicted in Figure 5. The transformation lattice deformation is accomplished by a homogeneous array of coherency dislocations (29) with approximate Burgers vectors $a_\parallel [121]$ and $a_\perp [121]$, each array producing an IPS on crystal planes of closest packing (30). A semicoherent interface is obtained by the superposition of a periodic array of (anticoherency) slip dislocations with Burgers vectors $a_\parallel [110]$ and $a_\perp [011]$, accomplishing a lattice-invariant deformation. The major component of the transformation net shape strain arises from the $a_\parallel [121]$ coherency dislocations. If the nucleation of individual loops of these dislocations is difficult at small sizes, the habit of a microscopic particle will be confined to the close-packed (111) plane. A fixed number of the latter dislocations can be derived from the dissociation of a group of existing dislocations as represented in Figure 6a, allowing formation of a ribbon-shaped nucleus of width $a$ and thickness $2c$. If the difficulty of forming additional $a_\parallel [121]$ coherency dislocations is removed at larger particle sizes by an athermal mechanism (to be discussed), the kinetics of nucleation will be controlled by the
Figure 6 Geometry of nucleus and defect for heterogeneous nucleation, describing nucleus as (a) discrete dislocation array, and (b) continuum particle.

widening of the nucleus at constant thickness. As described earlier for the case of heterogeneous coherent nucleation by dissociation, this geometric nucleation path has the characteristic that the free-energy barrier $\Delta G^*$ drops abruptly to zero when the effective fault energy accompanying dissociation becomes negative. Widening of the nucleus is then controlled by the discrete-crystal kinetic processes governing the motion of the $\Delta G^*$ coherency dislocations and the concomitant formation of the interfacial dislocations of Figure 5. The thermodynamic conditions for the fault energy to become negative can be expressed as a function of defect size (as for the coherent case in equation 18) via classical nucleation theory (17,25). By this dissociation mechanism, the nucleation kinetics are governed not by heterogeneous fluctuations surmounting the barrier $\Delta G^*$, but rather by the microscopic processes of interfacial motion at a pre-formed classical embryo where $\Delta G^*=0$.

Numerical continuum elastic calculations by Suezawa and Cook (18) also predict that $\Delta G^*$ can vanish for heterogeneous classical nucleation at a linear defect, but the behavior of $\Delta G^*$ differs in detail from the above dislocation-dissociation model due to different constraints applied to the nucleus; nucleus thickness is unconstrained in the Suezawa-Cook treatment, but an oblate-spheroidal nucleus shape is imposed. Ling and Olson (27) have demonstrated with similar calculations that a ribbon-shaped nucleus has a lower energy than an oblatespheriodal nucleus when forming in the strain field of a linear defect. Barrierless nucleation of a ribbon-shaped particle will occur even when $\Delta G^*$ for the oblate spheroid is still finite. These results are supported by a simple analytical treatment of the problem by Roitburd (28).

The calculations of Ling and Olson (27) demonstrate that the discrete-dislocation and continuum-elastic nucleus descriptions are energetically equivalent when identical constraints are employed. This was shown by computing the energy of a continuum particle with a net transformation strain $\epsilon_{ij}$ equivalent to that of the nucleus of Figure 5 interacting with the same defect as in Figure 6. Using parameters appropriate to steels, the calculated total free-energy change per length, $G_0$, vs. nucleus width, $a$, are plotted in Figure 7 for three levels of chemical driving force. The curves are for various fixed nucleus thicknesses, with the numbers indicating the thickness in number of crystal planes. The dotted curves denoting a thickness of 15 planes correspond to a nucleus thickness equal to the height $h$ of the defect (Figure 6) as adopted in the dislocation-dissociation description (25). The computed energies include a strain-energy contribution arising from elastic distortions in the interface (habit) plane
Figure 7  Total free-energy change per unit nucleus length for heterogeneous FCC-BCC nucleation in steels at three levels of driving force. Numbers identify nucleus thickness in terms of crystal close-packed planes. Shear modulus, $\mu$; FCC lattice parameter, $a_0$. Dislocation defect in mixed orientation.
imposed by the constraints of a rational (111) crystal-plane habit. The behavior of the dotted curves is identical to that derived from the dislocation-dissociation model (15,25).

Comparison of the curves for different thicknesses verifies that the short-range interactions favor the formation of a subcritical embryo with a thickness equal to the defect height at low driving force, as indicated by the arrow (a/h=10) in Figure 7a. Once an embryo of this thickness is established, the difficulty of nucleating additional coherency dislocations will constrain the thickness so that the embryo is still subcritical (with a/h=30) under the driving-force conditions of Figure 7b even though a thicker embryo would be supercritical. For the conditions of Figure 7c, the embryo in question becomes supercritical, with a negative fault energy then driving the process of interfacial motion.

A plausible dislocation pole mechanism for embryo thickening has been proposed based on the intersection with forest dislocations when the conditions for unrestricted nucleus widening are met (26). Once thickening can readily occur, the particle can adopt a minimum-energy habit and morphology, thereby allowing the attendant reduction in strain energy to accelerate the growth process. In situ electron microscopy observations of heterogeneous nucleation in thermoelectric Au-Cd (19) indicate a change from the close-packed habit to the macroscopic habit without evidence of a pole mechanism. Nucleation of additional coherency dislocations may in this case be stimulated by the free surfaces of the thin-foil specimen. The increasing separation of the curves of Figure 7c at large a signifies an increasing thickening force which might ultimately drive coherency-dislocation generation under bulk conditions. However, classical (linear-elastic) dislocation-nucleation calculations have not yet accounted for such a process (26).

Defining the end product of nucleation as an "operational nucleus," the nucleation kinetic behavior discussed here can be described within the framework of general nucleation theory, adopting a nucleation-rate equation of the form (3):

\[ J = \sum_{i} N_i \chi_i \beta_i, \]  \hspace{1cm} (19)

where \( N_i \) is the number of nucleation sites of the \( i \)th type, \( \chi_i \) is the fraction of these sites occupied (at a given instant) by operational nuclei, and \( \beta_i \) is a frequency factor controlling the rate at which nuclei become operational. In classical nucleation, the fraction of sites \( \hat{\chi} \) occupied by nuclei of operational size \( \hat{n} \) is expressed by:

\[ \hat{\chi} = Z \exp\left(-\Delta G^*/kT\right) \]  \hspace{1cm} (20)

where \( Z \) is a nonequilibrium factor (expressing the fraction of critical nuclei which reach \( \hat{n} \)) and \( \Delta G^* \) is as previously defined. The frequency factor \( \beta \) is the rate at which these nuclei arrive at \( \hat{n} \), and is expressed as:

\[ \beta = \nu \exp\left(-Q_m/kT\right) \]  \hspace{1cm} (21)

where \( Q_m \) is the activation energy controlling motion of the nucleus/matrix interface and \( \nu \) is an associated attempt frequency. In diffusional transformations, \( Q_m \) is the activation energy for atomic diffusion, while for martensitic transformations it is the activation energy for motion of a dislocation interface.

The operational nucleus in martensitic transformations has come to be defined by the point at which rapid growth begins, i.e. the condition that leads to a macroscopically detectable event (31). The strong defect/nucleus interaction in heterogeneous martensitic nucleation indicates that operational nucleation will occur under the condition \( \Delta G^*=0 \) whereby the nucleation kinetics (equation 19)
are controlled entirely by interfacial motion. Further progress in our understanding of the kinetics of martensitic nucleation requires better knowledge of the microscopic processes of interfacial motion subject to the constraints of the discrete crystal.

The kinetics of nucleus-interfacial motion have been modelled in terms of the generation of dislocations producing the lattice-invariant deformation (24,32) and the motion of coherency dislocations producing the lattice deformation (26). Either mechanism can account for the experimental nucleation kinetics which show a linear dependence of activation energy on driving force. As discussed in reference 3, no attempt to account for this behavior in terms of a smoothly changing $\Delta G^*$ (as opposed to $Q_m^*$) has succeeded so far.

Nucleation kinetic experiments on the coherent FCC→HCP transformation in Fe-Ni-Mn alloys (33), where the lattice-invariant deformation is absent, indicate the same behavior as does the semicoherent FCC→BCC transformation in the same alloy system. This finding suggests that rate control is by the lattice deformation in both cases, and favors the coherency dislocation motion model. Recent experiments on the mobility of macroscopic martensitic interfaces in thermoelastic B CuAlNi alloys reveal the same kinetic behavior as thermally-activated dislocation motion (34).

Analogous to the classical and nonclassical paths which describe the history of a nucleus as an entity, the microscopic fluctuations governing interfacial motion of a classical nucleus may be of either "heterophase" or "homophase" character(3). Hence, although the overall nucleus follows a classical path, nonclassical diffuse-interface concepts may have some relevance to the interfacial mobility, particularly if widening of the interfacial core structure increases mobility as suggested by estimates of the coherent interface Peirls barrier (14). The macroscopic interfacial mobility experiments (34) suggest an anomalous mobility increase at low temperatures where elastic softening effects are encountered.

While observed heterogeneous nucleation sites of low potency possess many characteristics of the nucleation-site models (19,23), the most potent sites which initiate transformation at the $M_s$ temperature in steels are known to be sparsely distributed with a number density of $\sim 10^6$ cm$^{-3}$ (one per 100μm grain) and are therefore virtually unobservable. Efforts to artificially produce crystallographically well-defined potent sites in pre-strained synthetic Fe30Ni bicrystals have been hampered by interference from an unusual isothermal autocatalytic mode of transformation (formation of paired martensitic units or "butterflies") which obscures the initial events (35). Earlier detection of initial events by acoustic emission measurements might circumvent this difficulty.

Although autocatalytic nucleation often interferes with investigations directed at the initial nucleation events, the fact that the majority of martensitic units are autocatalytically generated makes this an important phenomenon worthy of study in its own right. It is clear that the stress-assisted and strain-induced modes of nucleation which normally account for transformation during deformation will make an important contribution to autocatalysis, but the autocatalytic nucleation accompanying rapid growth events in "bursting" alloys is suggestive of an overdriven process for which classical nucleation kinetic concepts may be inadequate. Autocatalytic nucleation may represent a fertile ground for exploration of possible nonclassical phenomena.

As a final remark, we have here focussed on nucleation mechanisms for transformations in bulk materials. It is well established that free surfaces can provide a strong stimulating effect on martensitic nucleation. While it is evident that surface image forces will reduce the strain energy of a classical nucleus, a quantitative theory of surface nucleation has not yet been developed. This is another area which is ripe for further investigation.
Closure. - This survey of the theoretical possibilities for martensitic nucleation sets some definite guidelines for the circumstances favoring classical and nonclassical nucleation paths. Nonclassical paths will be favored in the case of homogeneous coherent nucleation near a mechanical instability, but this will require the suppression of heterogeneous nucleation. This special condition might be achieved experimentally in the case of small defect-free metastable particles precipitated in a solid matrix, (as in the case of FCC iron in copper, or of partially stabilized zirconia) which are known to transform at quite high driving forces. A more quantitative treatment of nonclassical nucleation would benefit from further calculations of the energetics of homogeneous lattice deformations and measurements of higher-order elastic constants in metastable alloys, as well as the development of strain-gradient energies.

The heterogeneous nucleation which controls martensitic transformations in bulk materials will favor nucleation by the classical path, particularly in semicoherent transformations. In view of the fact that classical behavior, involving relatively sharp interfaces, is adequately described by linear-elastic continuum and dislocation theories, the essential features of heterogeneous martensitic nucleation are considered to be well understood. Although the detailed discrete crystal constraints which apply to a microscopic particle merit further attention, theoretical and experimental evidence point to nucleation-rate control by interfacial motion. Consequently, a better understanding of the mechanism and kinetics of heterogeneous martensitic nucleation requires further investigation of the complete process of martensitic interfacial motion in a discrete crystal; this interfacial motion may involve nonclassical phenomena in some circumstances.

Isolation of the sparsely distributed highly potent nucleation sites which initiate transformation in the bulk will require the fabrication of synthetic nucleation sites in carefully designed experiments guided by specific site models. While existing models appear to reasonably account for nucleation in deformation-induced transformations, further work is needed on the mechanisms and kinetics of autocatalytic nucleation (especially in materials exhibiting bursting behavior) as well as the special case of martensitic nucleation at free surfaces.

Acknowledgements. - This research is sponsored by the National Science Foundation under Grant #DMR79-15196. The authors are also indebted to Dr. H.C. Ling of Western Electric Engineering Research Labs for the elastic calculations quoted in Figure 6, and to Dr. J.W. Cahn of the National Bureau of Standards for helpful discussions concerning nonclassical nucleation behavior. Conclusions regarding nonclassical behavior near a mechanical instability are based on preliminary numerical calculations performed by Mr. K. Ballou as an undergraduate research project.

References.-

34. GRUJICIC, M., OLSON, G.B., and OWEN, W.S., this conference.
35. CLARK, H.R., this conference.