Thermodynamics and Kinetics of Martensite

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I. Introduction

Troiano and Greninger [1] and Kurdjumov [2] considered kinetics to be as important as crystallography in defining the characteristics of martensitic reactions. In supporting this view, I shall ignore the exigencies of the time-table and look backwards to nucleation as well as forwards to today's papers. I take as my starting point the excellent survey of kinetics and nucleation theory in ferrous martensite presented by Magee [3]. He distinguished two kinds of kinetic behaviour, "dynamically stabilized" and "isothermal", and further sub-divided the latter into cases where martensite forms predominantly in bursts during cooling and those in which most of the transformation is isothermal. To these categories, we must add thermoelastic martensite which occurs in many non-ferrous systems.

Magee concluded, in contrast to earlier theories, that the average volume of a martensite plate is independent of the volume fraction of martensite and that nucleation sites which are autocatalytically activated by previously formed plates are overwhelmingly more important than randomly-distributed pre-existing sites. He suggested that the rate-limiting step may be the propagation of the interface.

II. Thermodynamics

Although some displacive phase transitions may be thermodynamically second or higher order, the transformations which the metallurgist recognizes as martensitic involve large distortions of the unit cell and changes in symmetry and are all first order. It is then possible to define an equilibrium T_o temperature by the intersection of two independent free energy curves, and to define a driving force as the difference between these curves (see Fig. 1). The free energy as a continuous function of configuration along some path from A to B in Fig. 1 may, more controversially, be given by a Landau expansion [4]

$$\Delta G = P\eta^2 + Q\eta^3 + R\eta^4 + \ldots \qquad (1)$$

where η is an appropriate order parameter which in the case of martensite represents a finite homogeneous deformation. Fig. 2 shows the relation between ΔG and η at different temperatures; the perfect parent phase becomes mechanically unstable at T_u when the minimum at $\eta = 0$ changes

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into a maximum and the free energy decreases continuously from $\eta = 0$ to $\eta = \eta_\alpha$. At T_u, $P = 0$, and writing $P = \alpha(T-T_u)$ and neglecting higher terms in (1) $T_o - T_u = Q^2/4\alpha R$. If the parent lattice remains mechanically stable at M_s, $T_u < M_s < T_o$; it is an open question whether even, in principle, T_u exists for most transformations.

Figs. 1 and 2 show the free energies of homogeneous, stress-free volumes of the parent, product and intermediate structures. When a martensite region forms within a constraining matrix, additional energy arises from the non-uniformity of the structure and may be approximately divided into coherency strain energy, surface energy and defect energies. In evaluating experimental thermodynamic data, it is important to take account of this additional stored energy.

2.1. Enthalpies and Free Energies in Ferrous Alloys

According to early calculations [5], the difference ΔG_c in chemical free energies of austenite and martensite is $\sim$1200 J mol^{-1} at the M_s of all binary Fe-C alloys. Later work [6-7] has shown, however, that for both Fe-C and Fe-N alloys, ΔG_c at M_s increases strongly from $\lesssim$ 1100 J mol^{-1} in pure iron (see below) to $\sim$2400 J mol^{-1} at 10 at % solute. Early estimates for substitutional alloys gave too large a variation of ΔG_c with composition; it now appears that ΔG_c increases slightly with solute content and reaches $\sim$1450 J mol^{-1} at Fe-10 at % Cr. Ternary solutes in Fe-Ni may either raise or lower ΔG_c [8].

There is still uncertainty about the value of M_s and hence ΔG_c for pure iron. The limiting arrest temperature of $\sim$820K found in very fast cooling curves [9-15] represents a reasonable extrapolation of the Fe-N data [6], but if M_s varies rapidly with interstitial content at low levels, the experimental values may be lowered by residual interstitials [1]. An alternative is $M_s \simeq$970-1000K which is consistent with extrapolation of dilute substitutional alloy data; much depends on whether the arrest temperatures observed in these alloys represent bainitic or martensitic reactions [16-18]. In recent work, four different arrest plateaux are reported by Wilson [13,19] and three by Morozov et al [14-15] who used high purity zone refined iron. Both groups obtained metallographic evidence that the transformation at 820K produces lath martensite, and in a rapidly cooled Fe-0.01% C alloy Morozov et al also found an arrest at 690K which is attributed to lenticular martensite. The value of 820K for M_s appears more probable and hence $\Delta G_c \simeq$1100 J mol^{-1} [20]. If M_s is 970K, ΔG_c is $\sim$400 J mol^{-1} and calorimetric data on alloys indicate that this is inadequate to produce heavily dislocated lath martensite.

Recent calorimetric measurements [21] indicate that the stored energy of ferrous martensite varies with the morphology and substructure. The heat evolved when lath martensite is formed in Fe-29 wt% Ni at 266-133K corresponds to an enthalpy of transformation (evaluated at 570K) of $\sim$1600 J mol^{-1} independent of transformation temperature and volume fraction. The enthalpy change is similar for Fe-30.3 wt% Ni transformed at 243-198K, but at lower temperatures, where plate

martensite is formed, it rises steeply to >2600 J mol^{-1}. Lee et al [21] conclude that the stored energy in lath martensites may be up to 1150 J mol^{-1} higher than in twinned martensites.

Combination of the free energy and calorimetric data suggests that the net driving force at M_s is very small for lath martensite, but may be appreciable for plate martensite. Indeed, Argent [22] has computed M_s curves for Fe-Cr and Fe-Co alloys on the assumptions that the net driving force is zero (i.e., there is no nucleation barrier), that surface and dislocation entropies may be neglected, and that the stored energy is ~1000 J mol^{-1}. The values are in reasonable agreement with experiment, and the estimated M_s for pure iron is 855K. Note that the assumption also implies that adiabatic heating [23-24] is not significant for lath martensites.

Lee et al considered the stored energy to arise from dislocations or twin boundaries, but there are also contributions from the interphase interfaces and the coherency strains. For oblate spheroidal plates of dimensions a and c, and for laths with a>b>>c, the interfacial energy per unit volume is $E_s \simeq 3\sigma/2c$ where σ is the specific interfacial free energy. With $\sigma = 200$ mJ m^{-2} and c = 1 μm, E_s is insignificant (0.3 MJ $m^{-3} \simeq 2$ J mol^{-1}), but this term is, of course, important in classical nucleation theory since if c = 1 nm, $E_s \simeq 2$ kJ mol^{-1}. The energy due to internal twinning is similarly $E_t \simeq \sigma_t/t$ where t is the twin separation, and if σ_t = 200 mJ m^{-2} and t = 20 nm, E_t is only ~100 J mol^{-1}.

The elastic energy per unit volume of a transformed oblate spheroid with the same shear modulus μ and Poisson's ratio as the isotropic constraining matrix is usually quoted as $E_e = Ac/a$ where [25-26]

$$A = [\pi(2-\nu)/8(1-\nu)]\mu s^2 + (\pi/4)\mu\xi^2 \simeq \mu(s^2+\xi^2) \qquad (2)$$

and s and ξ are the shear and normal strains in the unconstrained invariant plane strain (IPS) shape deformation. With $\mu = 5.10^{10}$ Pa, s = 0.18, ξ = 0.05, we obtain E = 85 MJ $m^{-3} \simeq 600$ J mol^{-1} for a typical c/a = 0.05. This may be an overestimate since linear elastic theory has been used for large strains, and the energy may also be decreased by plastic deformation or by formation of plates in groups, or of laths (which otherwise have larger E_e) in self-accommodating packets.

Eqn (2) is derived by replacing the stress-free strains of the martensite plate by the strains of the average or shape deformation, and in the real situation additional strain energy arises from the alternating twins or from the interface dislocations. Mura el al [70] have treated the twin case in which the stress free strain is periodic and they find that the elastic energy does not tend to zero as c/a→0, but rather to a constant value per unit volume given by

$$E_e = f(1-f)(C_{11}-C_{12})(\varepsilon_1-\varepsilon_2)^2 \qquad (2a)$$

where f is the volume fraction of one orientation. C_{11} and C_{12} are the anisotropic elastic stiffnesses of the plate and ε_1, ε_2 are the

principal strains of the lattice (Bain) deformation. Numerical estimates from eqn (2a) give a very large energy of $\sim$14 kJ mol^{-1} for steels, and although the use of linear elastic theory severely restricts the accuracy, it is noteworthy that the estimate considerably exceeds the available driving force. An even larger energy was obtained by Kato et al [73] from a somewhat unusual model of slipped martensite.

The reason for the apparent paradox is that for a plate of finite thickness, the additional energy should be incorporated into the surface energy, as is implied but not clearly stated in the work of Khachaturyan and Shatalov [74] who also used anisotropic elasticity and gave the first treatment of the periodic twin structure. They showed that the strain energy caused by the heterogenity of the plate arises from strains located near the habit plane so that it is proportional to the area of this interface. The interface dislocations of a single crystal of "slipped" martensite, or the periodic structure of twinned martensite, thus raise the interfacial free energy from a low value characteristic of a fully coherent interface to an effective value (assumed above to be 200 mJ m^{-2}) appropriate to the semi-coherent interface. If the twin thickness is now held constant as $c \to 0$, the energy per unit volume tends to a large constant value. It follows that the energy of eqn (2a) whilst relevant to some nucleation models, does not enter into the free energy balance for appreciable volumes of transformed product, and it is justifiable for most purposes to use eqn (2) together with an appropriate value for the effective surface free energy. The formulation of the theory developed by Khachaturyan is not restricted to an ellipsoidal shape, and in a later paper [75] he has shown how to calculate the habit plane shape which minimizes the strain energy.

Lath martensites contain dense tangles of lattice dislocations, the untwinned regions of plate martensites contain arrays of screw dislocations, and accompanying plastic deformation causes dislocation tangles and pile-ups in the surrounding austenite. For a dislocation density ρ, the energy is

$$E_d = (\rho\mu b^2/4\pi K)[\ln(R/r_o) + B] \qquad (3)$$

where $1>K>1-\nu$, R and r_o are outer and inner cut-off radii and B varies with assumptions about pile-ups. With $\rho = 10^{16-17}$ m^{-2} and $R/r_o = 10^4$, Li et al estimate E_d as 120-2800 J mol^{-1}; the large uncertainty arises mainly from the measured dislocation densities in lath martensites [27] which at the upper limits give very high stored energies. The origin of the dislocations inside laths and partly twinned plates is unknown, but if they are also due to induced plastic deformation, any contribution of E_d to stored energy should be balanced by a greater reduction in E_e. Thus $E_e + E_s + E_f \simeq E_e$ (for macroscopic plates) should represent the upper limit of stored energy, and any difference between laths and plates might only be due to the better elastic accomodation of the latter. The conclusion fails, however, if the dislocations do not accommodate the shape change.

For an Fe-13.7% Ni-0.86% C steel transformed at 297-188K, the

measured enthalpy change at 507K decreases dramatically from 4650 to 1600 J mol^{-1} as the volume of plate martensite increases from 7 to 59% [21]. The implied increase in stored energy is attributed to the high work-hardening and high dislocation densities in regions of deformed austenite which have subsequently to be transformed to martensite. Further experiments we needed to clarify and extend these results.

2.2. Other Martensitic Transformations

ε-martensite forms in some steels at smaller driving forces than α-martensite e.g. 270 J mol^{-1} in Fe-Mn [8] and 210 J mol^{-1} in Fe-Ru [28]. The similar transformation in cobalt begins at ∿5 J mol^{-1} in single crystals [29-30] but ΔG_c increases slightly in subsequent cycles. Measurements in which the enthalpy change during the heating transition exceeded that during cooling by ∿125 J mol^{-1} have been interpreted as the stored enthalpy of defects accumulated during a cycle [30], However, the result seems doubtful since at such low ΔG_c only high entropic defects could form.

Transformations from a bcc to a hcp or an orthorhombic phase in Ti, Zr and Hf alloys constitute another major group. For all Ti-Zr alloys, $\Delta G_c \simeq 220$ J mol^{-1}; M_s falls more steeply with solute content in Ti-Mn, Ti-Mo, Ti-Ta, etc., and ΔG_c is presumable larger. Many other non-ferrous transformations take place with little hysteresis and thus have small ΔG_c. Thermoelastic martensites come into this category; typical values for ΔG_c in Au-Ag-Cd alloys of varying Au:Ag ratio are 12-30 J mol^{-1}.

2.3. Thermoelastic Martensite

The concept of thermoelastic martensite, originally due to Kurdjumov and Khandros [33] has assumed increased importance in recent years because of the interest in shape-memory and related effects. In a thermoelastic transformation the assembly attains a minimum free energy at some finite volume fraction of product, so that a variation in the (thermal or mechanical) driving force produces a corresponding increase or decrease in the volume of martensite. This requires that ΔG_c, or most of it, is stored reversibly as surface, elastic and twin energies, but not as dislocation energy. I previously suggested [34] that thermoelastic martensite is characterized by a small driving force, small values of s and ξ, and a high matrix yield stress. Wayman [35] has pointed out that s is not always small.

In discussing the thermodynamics of thermoelastic martensite, Tong and Wayman [36-37] and Olsen and Cohen [38-39] have disagreed about whether A_f can be below T_o. Olsen and Cohen follow early treatments in supposing that as a plate of constant length a_1 thickens, the energy E_e per unit volume increases until a minimum in total free energy is attained. If this happens without dislocation sources operating, the plate has attained thermoelastic equilibrium with the matrix, and its thickness is given by $c = a_1 \Delta g/2A$ where Δg is the net chemical and mechanical driving force per unit volume. Olsen and Cohen assume that as Δg is reduced by raising the temperature, the plate becomes unstable when it attains the dimensions of a critical nucleus, i.e., when $c^2 =$

$a_1\sigma/A$, and that if there is no interface frictional stress it will then spontaneously contract to zero dimensions. The net driving force at this condition is $\Delta g = 2(A\sigma/a_1)^{\frac{1}{2}}$ so that the longest plates disappear last. In the absence of frictional stresses, this theory gives $A_f < T_o$, but it should perhaps be emphasized that for reasonably large plates $T_o - A_f$ is very small. For example, if $A = 2.10^9$ J m^{-3} and $\sigma = 0.2$ J m^{-2}, Δg at A_f is $\sim$40 MJ m^{-3} for $a_1 = 1$ μm and $\sim$1 MJ m^{-3} for $a_1 = 1$ mm; $T_o - A_f$ is appreciable in the first case, but very small in the second.

A difficulty with this theory is that the shrinking plate is treated as if it had nucleated homogeneously and no allowance is made for the energy of any residual defect. Nucleation is believed to be heterogeneous and the reproducibility of the hysteresis loop and of the microstructure in successive cycles of transformation implies that the nucleation sites retain their identities. It follows that the free energy may not begin to decrease with decreasing length when the classical saddle point is reached.

Tong and Wayman neglect the coherency strain energy for the initial transformation at M_s and consider the lengthening of a plate of constant thickness; they also point out that new plates may be nucleated in any increment of Δg, It is not clear how either of these processes could result in thermoelastic equilibrium but Wayman [71] has emphasized that plate lengthening is found experimentally to be a dominant growth process in many thermoelastic alloys. In terms of the model just described, lengthwise growth and nucleation can not be separated, and both represent increments in transformed volume which are additional to those produced by thermoelastic growth. Thus, although the volume of an individual thermoelastic plate increases linearly with Δg, the overall relation between volume transformed and driving force need not be linear. There will also be a deviation from linearity during heating because of the progressive disappearance of the smaller plates.

The alloy Fe_3Pt is thermoelastic when ordered but not when disordered. Olsen and Owen [40] suggest that the lower shear modulus leads to the virtual absence of a plastic accommodation zone around a plate in the ordered matrix. In a further development, Ling and Owen [41] consider in outline the effects of an assembly of partly self-accommodating plates.

In Cu-14 Al- 2.5 Ni alloys, the transformation is normally thermoelastic but single interface transformation without elastic strain energy can be obtained in suitable single crystals held in a temperature gradient. Salzbrenner and Cohen [72] have used the single interface transformation to bracket T_o between the interface advance temperatures on cooling and heating, the hysteresis being attributed to the frictional resistance to interface motion. Multiple interface transformations in a single crystal involve elastic strain energy which depresses the transformation curves both on cooling and heating, but since the martensite apparently nucleates first at a free corner of the single crystal, there are no strain energy terms in the energy balance at M_s and at A_f, and T_o may be bracketed between these temperatures, as

postulated by Tong and Wayman. This is no longer true in polycrystalline specimens where elastic energy affects both M_s and A_f and the latter may also be below T_o.

The net heat evolution measured in a differential scanning calorimeter was 515 J mol^{-1} in the single interface transformation and some 40-90 J mol^{-1} smaller in polycrystalline specimens of various grain sizes [72]. The difference is attributed to the stored elastic enthalpy, which thus has a mean value of ∿15% of the chemical enthalpy change. There is, however, an unexplained difficulty which exactly parallels that arising from the results on cobalt mentioned above [30], namely that this estimate of the stored elastic enthalpy is much larger than would be predicted from the chemical free energy difference between the phases. From the transformation temperatures, the free energy driving force is estimated as only ∿26 J mol^{-1} for growth, 29 J mol^{-1} for corner nucleation and 39 J mol^{-1} for interior nucleation.

III. Nucleation

3.1. The Strain Spinodal

It is sometimes difficult to convince a solid state physicist that there is any difficulty in nucleating martensite, whilst a metallurgist, after substituting a few numbers into the equations of classical nucleation theory, is likely to conclude that nucleation is impossible! The truth must lie between these extremes, but the best approach to an acceptable model is by no means obvious. Pre-existing embryo theories [5] have been discarded and it is generally accepted that nucleation is probably heterogeneous. In a classical model, the interaction between a defect and an embryo may be divided, somewhat arbitrarily, into an effective addition to the driving force and an effective lowering of σ. According to Guimaraes and Alves [42], the former is negligible and the latter is estimated from experimental data [43] for steels as ∿125 mJ m^{-2} which is rather more than one-half of the assumed interfacial energy.

Various authors have speculated that the concept of a strain spinodal, which exists for example at the temperature T_u defined above, might be relevant to the nucleation of martensite. In particular, Suzuki and Wuttig [44] have proposed that a strain-gradient energy, analogous to the gradient energy of spinodal decomposition, should be introduced. If this term were positive, it would have a stabilizing effect on shorter wave-length strain fluctuations below T_u; however, Nakanishi [45] has pointed out that even in alloys which show pre-transformation anomalies, the elastic constant which softens remains finite at M_s so that simple soft mode instabilities could only arise with a negative strain gradient energy.

The present author believes that there is very strong evidence that the parent lattice as a whole does not become mechanically unstable when martensite begins to form, and this is reinforced by the morphology of the product. However, Fig. 2 suggests another possibility, namely that if some local region of the lattice at temperature T_1 is

given a finite deformation to a configuration η_1 beyond which $\partial^2\Delta G/\partial\eta^2$ is negative, this region may then spontaneously transform to martensite. Clapp [46] suggested that the strains near lattice defects bring some regions close to the strain spinodal; he specifically considered the free surface and grain boundaries as likely nucleating agents, but it is perhaps more probable that a dislocation configuration is responsible. The important point about this approach, however, is that the strain field of the defect need not resemble the structure of the final product, and the critical (saddle-point) configuration for a nucleus just outside the region of instability would be very different from the classical model of the nucleus. The theoretical treatment should then resemble Cahn and Hilliard's theory of nucleation just outside the ordinary spinodal [47]; the interface would be diffuse and the work required to form the critical configuration would tend to zero continuously as the pre-existing (defect) strain approached the value where $\partial^2\Delta G/\partial\eta^2 = 0$. Moreover, thermally-activated nucleation would occur in the region just outside the strain spinodal, whilst if the spinodal were crossed by continued cooling, the local lattice near the defect would be mechanically unstable and nucleate spontaneously.

Whilst this approach appears promising, it is difficult to make it quantitative since neither the ΔG-η curves (which are strictly not one-dimensional curves but surfaces in six-dimensional configuration space) nor the detailed nature of the nucleating defect are known. Recent calculations of the finite strains needed to produce instabilities between the fcc and bcc structures have been made for the alkali metals by McDonald [48] using a uniaxial strain and by Ledbetter and Suzuki [49] using a general Bain strain, and represent the first stage in the construction of a theoretical curve of the type of Fig. 2. In order to deal with an inhomogeneous system, it may be necessary to use a suitable trial function for the variation of strain with distance, as proposed by Cahn and Green [50], and it will also be necessary to introduce the strain gradient energies about which almost nothing is known at present.

3.2. Specific Models of Nucleation

The traditional approach to heterogeneous nucleation is to calculate the energy of a nucleus forming in the vicinity of a likely defect configuration as a function of size in order to find the saddle point condition. The catalytic effect of the defect may be expressed in terms of surface or core energy which is destroyed and of elastic interaction energy between the defect and the nucleus. Another type of theory considers a nucleating defect with a highly specific strain field which either closely approximates the final structure or else is assumed to represent a critical stage in its formation. The most highly developed model of this kind is probably that of Olsen and Cohen [51], whose basic postulates are that nucleation begins with faulting on the close-packed planes of the parent lattice, the fault displacement being derived from existing defects, and that in the subsequent readjustments the fault plane remains unrotated.

The model is first applied to the fcc → hcp transformation and is formulated in terms of classical nucleation theory, the energy per unit

area of a fault which has n planes in hcp configuration being written as the sum of volume and interfacial free energies

$$\gamma(n) = n\rho(\Delta G + E_e) + 2\sigma(n) \qquad (4)$$

where ρ is the number of mols per unit area of the close-packed planes, E_e is the strain energy additional to that of the nucleating defect, and the interfacial energy $\sigma(n)$ is later assumed to be independent of n for faults greater than two layers thick. ΔG is negative below T_o and $\gamma(n)$ becomes negative at $T_2 < T_o$ where T_2 increases as n increases. Using parameters appropriate to Fe-Cr-Ni alloys and assuming that spontaneous dissociation occurs at $M_s = T_2$, the critical thickness is 7-10 lattice planes and thus corresponds to the dissociation of 4-5 lattice dislocations.

The most interesting part of the Olsen-Cohen theory is the proposal that the fcc → bcc, bcc → hcp, and related transformations also begin with faulting on the close-packed planes of the parent structure. The theory is partly based on the Bogers-Burgers hard-sphere model for the fcc → bcc transition [52-53] which involves two successive IPS deformations on intersecting close-packed planes. In the Olsen-Cohen theory, the first of these faulted regions is produced by dislocation dissociation, and is then supposed to change spontaneously into the bcc structure by a modified form of the Bogers-Burgers second IPS which is heterogeneous on a scale of every eight close-packed planes. This leaves the original fault planes unrotated and generates a bcc structure in the Kurdjumov-Sachs orientation but with an incorrect lattice parameter. The long-range stress field produced by this second IPS is next compensated by screw dislocations in the interface; this corresponds to the lattice invariant deformation of the phenomenological theories, and the structural model at this stage is close to Frank's model of martensite. Finally, adjustments of the lattice parameter to the equilibrium value and establishment of an IPS shape deformation to allow growth to continue require rotation away from the Kurdjumov-Sachs orientation and simultaneous rotation of the habit plane out of the close-packed plane. This last step is assumed to occur at a later time than the others, which are simultaneous with the formation of the initial fault, and it may possibly account for the different crystallography of e.g. {3,10,15} and {225} plates. Estimates of the various contributions to the energy of the fault embryo again lead to the conclusion that 4 or 5 properly spaced dislocations should dissociate spontaneously at M_s in Fe-Ni alloys.

Similar descriptions are given for crystallographic transitions between the other common metallic structures. Consideration of various possible rate-limiting steps in the formation of the nucleus leads to the tentative conclusion that the frictional resistance to the growth of the embryo in the fault plane may be the most important factor. Spontaneous growth of the fault would then take place only at some finite negative value of $\gamma(n)$; alternatively, if this growth were thermally activated, isothermal growth of the sub-critical nuclei would be expected above the temperature of athermal nucleation. In contrast to classical theories of nucleation, the activation energy would vary approximately linearly with driving force, as sometimes observed [3].

The Olsen-Cohen model is based on a very specific nucleating defect, namely a short wall of correctly spaced dislocations, which the authors consider may be present as part of a grain boundary, at a particle-matrix interface, or as a dislocation pile-up on several parallel slip planes. For the fcc → hcp transformation, the theory differs only slightly from earlier descriptions [54-55] and more recent rival models [56-57]. Experimental evidence in support of dislocation dissociation has accumulated steadily [58-60], but sometimes indicates that the hcp region develops by random accumulation of single faults. Brooks et al [60] have recently analyzed the fault contrast and shown there is a displacement normal to the fault, proportional to n and in the same sense as the deviation of the hcp structure from the ideal axial ratio of $(8/3)^{\frac{1}{2}}$, thus supporting the hcp model of a fault.

It is much more difficult to assess the validity of the faulting hypothesis for the formation of semi-coherent martensites where a single IPS will not produce the product structure. The basic posulate that nucleation is catalysed by a group of lattice dislocations seems very plausible and is supported by recent evidence from in situ experiments [60-61] that α martensite forms near dislocation pile-ups and also by the absence of transformation in small particles constrained by a matrix unless they are sheared [62-64]. However, it is not clear that the specific role of the dislocations is to generate the strain field of a stacking fault, and the experimental observation that the close-packed planes of the two structures remain nearly parallel, does not seem to the present author to be of great significance. Direct evidence of dislocation dissociation may be difficult to obtain, but in support of the model Olsen and Cohen [51] summarize various observations which have been made of fault-like embryos on close-packed planes. An embryo on the {110} planes of the ordered bcc structure of Au-Cd later assumed the macroscopic morphology [76]. Thus the faulting mechanism may apply to bcc structures despite the absence of metastable configurations in the calculated γ-surfaces for single layer faults [65].

There have been several other recent attempts to apply classical nucleation theory to the heterogeneous nucleation of martensite by dislocations. Easterling and Tholen [66] considered an embryo formed inside a growing dislocation loop, and concluded there would be no nucleation barrier for a twinned martensite plate. However, this result is obtained by the assumption that the interfacial free energy of twinned martensite is only $\sim$ 20 mJ m^{-2} whereas a value similar to that calculated for the dislocation model of the interface ($\sim$ 200 mJ m^{-2}) is actually appropriate; moreover, the energy of the dislocation loop has been omitted from the free energy expression [67]. When these corrections are made, this model leads to a very large barrier. Suzuki et al [61] calculated the condition for the net free energy, including the elastic interaction with the stress field of the pile-up, to be zero, and concluded this requires $\sim$ 22 dislocations which is consistent with their experimental observations on stainless steel. However,

their calculation appears to be invalid since the interfacial free energy is neglected, and indeed the finite number of dislocations results only from the arbitrary assumption that the oblate spheroidal nucleus has $a/c \simeq 10$.

In a recent calculation, Suezawa and Cook [67] treat a dislocation pile-up as a superdislocation and use Fourier methods to calculate the interaction energy with an oblate spheroidal nucleus described by the averaged strain field of two twin-related Bain strains. The dislocation stress field falls off as $1/r$ and when multiplied by the volume of an embryo, an interaction which behaves in certain respects like a negative interfacial free energy results and so facilitates nucleation. The free energy of an embryo containing q atoms is $C\,q + D\,q^{2/3}$ where C contains the chemical and coherency strain energies and D is proportional to the effective interfacial energy σ_e. For N dislocations, $\sigma_e = \sigma + N\sigma_i$ where the negative term σ_i varies with a/c and represents the interaction with a single dislocation. In order for C to be negative, which is necessary for nucleation, Suezawa and Cook estimate $a/c \simeq 20$ for Fe-29% Ni; this fixes σ_e as ~ 20 mJ m^{-2} and hence $N \simeq 10$ if $\sigma = 200$ mJ m^{-2}. The model predicts isothermal (thermally-activated) nucleation if $C < 0$ and $D > 0$, and athermal nucleation if both C and D are negative. C contains $E_e = Ac/a$ (see eqn. 2) and thus decreases with increasing a/c, whereas D increases with increasing a/c. At temperatures where nucleation first becomes possible, C is only negative at relatively large a/c for which D is necessarily positive. However, C also decreases with increasing driving force as the temperature is lowered, whereas D is insensitive to temperature, so that a temperature may be reached where for some value of a/c, both C and D are negative. The activation barrier to nucleation has then disappeared.

Most models of nucleation predict a temperature range of isothermal nucleation above that of athermal nucleation, whereas in some steels and possibly other alloys only athermal nucleation is observed. Magee [3] pointed out that athermally nucleated steels always contain interstitials which are mobile at the M_s temperature, and he suggested that the mobility of these interstitials prevents thermally activated nucleation of martensite either by lowering the driving force or by pinning the interface. The result is a bainitic transformation in the temperature range where isothermal martensite would otherwise be formed.

IV. Kinetics of Athermal Transformation

The kinetic description given by Magee [3] in which emphasis was laid on the effects of auto-catalytic nucleation has been further extended by Guimaraes and Gomes [69] who have considered specifically the effects of prior austenitic grain size. Experimental results [68-69] show that as the grain size decreases, the burst temperature and the volume fraction of martensite formed in the initial burst both decrease. The variation is due mainly to changes in the fraction of grains which contain martensite; this fraction is small in fine-grained material where the initial transformation is thus very heterogeneous. The fraction of partly transformed austenitic grains increases with

decreasing temperature, but remains smaller in the fine-grained materials over an appreciable temperature range ($\sim$ 50K in Fe-31.9% Ni-0.02% C). The volume fraction of martensite in those grains which have partly transformed is appreciably less dependent on grain size; the increase in this fraction with decreasing temperature is referred to as "fill-in", whereas the spreading of transformation into neighboring, previously untransformed grains, is called "propagation". It follows that the influence of propagation is more pronounced in the fine-grained material.

Guimaraes and Gomes consider that their results support the concept that propagation is mainly due to autocatalytic nucleation across grain and twin boundaries, and they develop a simple equation to represent the variation of the volume fraction of partly transformed grains with temperature. In this theory, the rate of propagation is proportional to the square of the volume fraction, and the greater effectiveness of the first formed plates in the larger grained austenite is attributed to their larger sizes and hence the greater extents of their accompanying stress fields.

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Erratum

The very high dislocation densities assumed for lath martensites [21-2] are incorrectly quoted from [27] and if the actual measured densities [27,77] are used, the calculated stored energy due to dislocations is reduced by a factor of $\sim$20. This strongly reinforces the conclusion that any difference in stored energies of lath and plate martensites is likely to have its origin in the better elastic accommodation of the plates. I am greatly indebted to Dr Bhadeshia for bringing this mistake and reference [77] to my attention.

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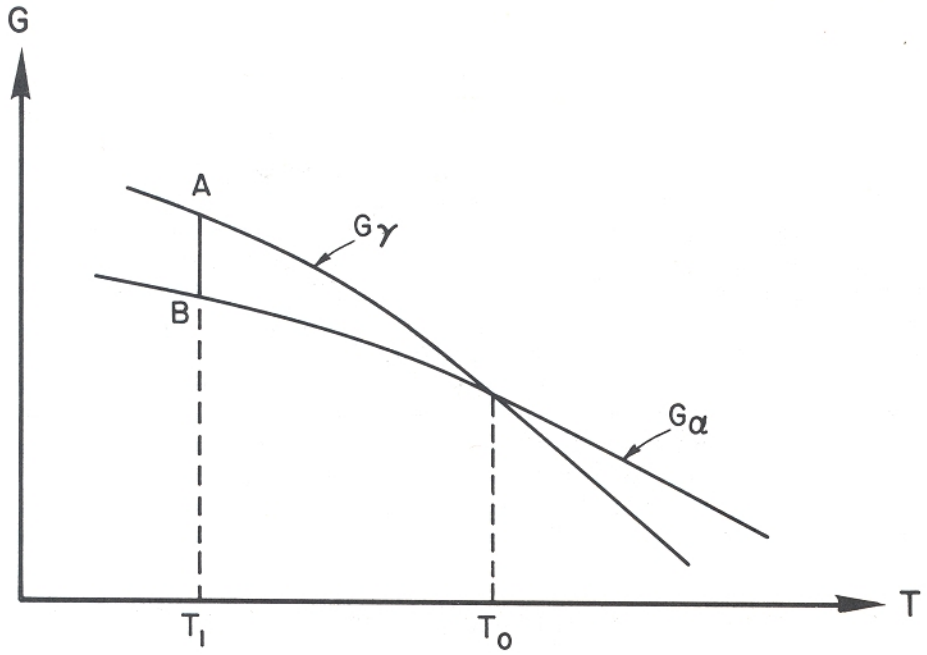

Fig. 1. Schematic free-energy vs temperature relations for a first order phase transformation $\alpha \overset{\rightarrow}{\leftarrow} \gamma$.

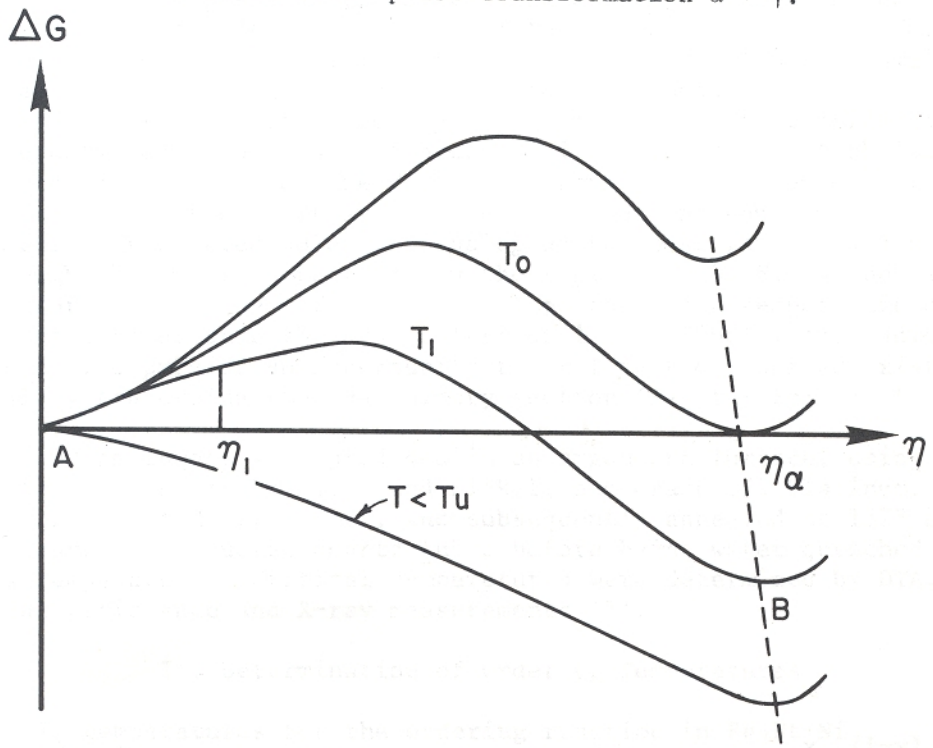

Fig. 2. Schematic free-energy vs order-parameter relations for a first order transformation. The order-parameter (η) represents continuous deformation along some path from γ to α.

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