

Precipitation at Interphase Boundaries

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Three problems in precipitation at interphase boundaries are examined. 1) The classic argument as to the particular phase in which such a precipitate nucleates is shown to be irrelevant; except in a special situation, the critical nucleus must normally penetrate both phases forming the interphase boundary. 2) The relative penetrations into the two phases achieved during growth can be very different than those expected during nucleation; hence, deductions about the nucleation process based upon observations on growth morphologies can be quite misleading. 3) The observations of Honeycombe and others that the nucleation of carbides at austenite : ferrite boundaries occurs predominantly at the low energy, immobile broad faces of ledges rather than at the higher energy, mobile risers of ledges are accounted for theoretically on the basis of the high velocities of the risers preventing nucleation. Example calculations on a Ti-Ni alloy indicate that precipitation at the risers of ledges may become possible in substitutional systems, but only at lower homologous temperatures, and if the migration of these boundaries is still controlled by volume diffusion while nucleation is controlled by interfacial diffusion.

INTERPHASE boundary precipitation is an important process during the bainite reaction in ferrous^{1,2} and nonferrous³ eutectoid decomposition and during the formation of a sequence of precipitate phases in alloys undergoing aging reactions.^{4,5} The nucleation aspect of this process, originally treated by Gibbs,⁶ albeit for liquids, was recently reexamined for solids in the presence of faceting⁷ and has been studied in some detail for the special case of precipitate nucleation at a matrix : GP zone boundary.⁸ Continuing controversies about carbide precipitation during the bainite reaction in steel,² parallel studies of the equivalent process during eutectoid decomposition in Ti-base alloys^{9,10} and the finely detailed electron microscopic studies of Honeycombe and coworkers¹¹ on interphase boundary precipitation in Fe-C-X alloys have stimulated consideration of some key aspects of precipitation at interphase boundaries. Three problems will be examined: the phase in which nucleation occurs, the extent to which the relative precipitate penetration into the parent phases during growth may reflect that obtaining during nucleation, and nucleation at moving interphase boundaries. The two matrix phases forming the interphase boundaries will be designated α and γ , with the α taken to have formed in a γ matrix, and the precipitate nucleated at these boundaries will be termed C (since it is often an intermetallic compound). For example purposes, attention is focused on eutectoid decomposition in Fe-C and Ti-Ni alloys; however, the concepts involved are equally applicable to sequential precipitation during aging.

DOES THE NUCLEUS FORM IN THE γ OR THE α PHASE?

In considering nucleation at an interphase boundary, let the boundary be planar and first assume that the

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energy of the α : C and the γ : C boundaries is independent of boundary orientation. The critical nucleus will accordingly consist of two abutting spherical caps with different radii, as illustrated in Fig. 1(a). Since these radii are proportional to the energies of the α : C and γ : C boundaries, and these energies are usually not very different,^{12,13} the shape of the nucleus will normally not be markedly assymetrical. Even if it is, however, achievement of the equilibrium shape, which is normally a very good approximation of the critical nucleus shape, requires that the C nucleus penetrate both α and γ phases.* If the energy of the

At small driving forces, e.g., when the free energy of activation for nucleation, ΔG^ , is 40 to 60 kJ, the equilibrium shape and the critical nucleus shape should be in very close correspondence. Some deviations may develop at larger driving forces. It should also be noted that unless the volume strain energy attending nucleation exceeds ca. $\frac{1}{3}$ the absolute value of the volume free energy change, no effect of strain energy upon critical nucleus shape is anticipated¹⁴; the strain energy will act only to reduce the driving force for nucleation.

nucleus : matrix boundaries passes through a cusped minimum at one or more boundary orientations,

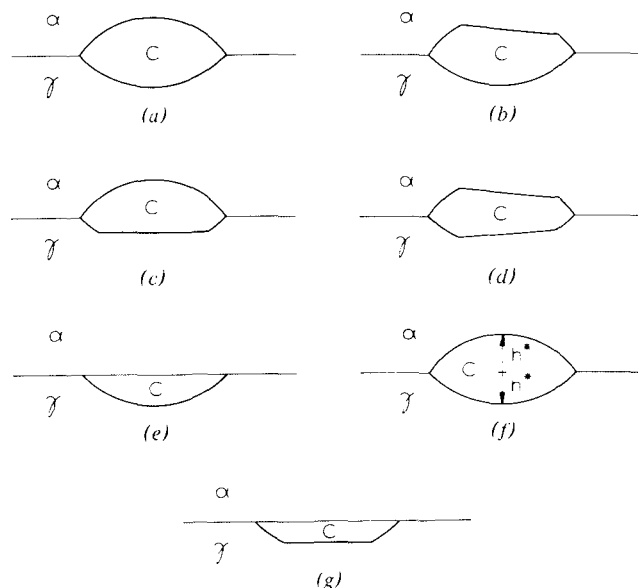


Fig. 1—Models for critical nuclei of C phase formed at interphase (α : γ) boundaries.

nuclei faceted in α (Fig. 1(b)), in γ (Fig. 1(c)) or in both phases (Fig. 1(d)) will develop instead of the un-faceted morphology of Fig. 1(a).⁷ In the special case of Fig. 1(e), where a facet lies in the plane of the interphase boundary (this occurs when the facet interfacial energy is half or less than that of the $\alpha : \gamma$ boundary¹⁵), the nucleus is excluded from the phase against which the facet formed (here α). However, the phase not invaded has obviously played a vital role in the nucleation process. Hence, we conclude that the prolonged debate as to whether bainitic carbides nucleate in austenite or in ferrite (recently reviewed²) is irrelevant: *interphase boundary precipitates nucleate in both phases.*

Figure 1 shows that demonstration of an orientation relationship between the C nucleus and the α , γ or both phases proves only that the energy of the $\alpha : C$ and/or $\gamma : C$ boundaries is orientation-dependent. Such data give no information on the penetration of the C nucleus into either phase. Observation of but one variant of a particular form of orientation relationships amongst carbides precipitated at planar austenite : ferrite boundaries^{16,17} is explained by the pronounced influence of the angle between a facet and the interface at which nucleation occurs upon the free energy of activation for nucleation.¹⁸

COMPARISON OF NUCLEATION AND GROWTH MORPHOLOGIES OF INTERPHASE BOUNDARY PRECIPITATES

Since observations on interphase boundary precipitates are normally made after they have developed well into the growth stage, it is important to recognize that the growth morphology, which is controlled by kinetic considerations, will usually differ from the critical nucleus morphology, which is normally controlled predominantly by interfacial energy minimization. For simplicity, assume that both the $\alpha : C$ and the $\gamma : C$ boundaries are disordered, planar and of infinite extent.* Using Zener's²⁰ linearized gradient

*When the aspect ratio of the C crystals is less than ca. 1/3, departure from planarity produces only a minor acceleration of growth kinetics.¹⁹

approximation for this case, omitting a factor which is nearly unity and varies slowly with supersaturation, and simplifying the concentration terms by making use of the circumstance that the mole fraction of solute in C is normally much greater than in α or γ :

$$\frac{G_\alpha}{G_\gamma} = \left(\frac{D_\alpha}{D_\gamma} \right)^{1/2} \cdot \frac{(x_\alpha^{\alpha\gamma} - x_\alpha^{\alpha C})}{(x_\gamma^{\gamma\alpha} - x_\gamma^{\gamma C})} \quad [1]$$

where G_α and G_γ = growth rates of C into the α and γ phases, $x_\alpha^{\alpha\gamma}$ and $x_\alpha^{\alpha C}$ = mole fractions of solute in α at the $\alpha/(\alpha + \gamma)$ and at the $\alpha/(\alpha + C)$ phase boundaries and $x_\gamma^{\gamma\alpha}$ and $x_\gamma^{\gamma C}$ = mole fractions of solute in γ at the $\gamma/(\alpha + \gamma)$ and the $\gamma/(\gamma + C)$ phase boundaries. Equation [1] is based upon volume diffusion control of solute directly to the C precipitates. This relationship should be appropriate when α and γ are interstitial solid solutions down to quite low homologous temperatures.^{19,21} However, when α and γ are substitutional solutions, particularly fcc and probably also hcp, interfacial diffusion along the $\alpha : \gamma$, and thence along the $\alpha : C$ and $\gamma : C$ boundaries, will accelerate growth

kinetics to an increasing degree as the reaction temperature falls below ca. $0.9 T_m$ when these boundaries have a largely disordered structure.^{22,23} Modeling the C crystals now as oblate ellipsoids (since this interfacial diffusion-aided growth mechanism is inapplicable to the infinite planar boundary case), and assuming, for lack of more detailed information, that the various interphase boundary diffusivities involved are equal, the ratio of the thickening rates of the ellipsoids into the two phases is approximately:

$$\frac{G_\alpha}{G_\gamma} = \frac{x_\alpha^{\alpha C}}{x_\gamma^{\gamma C}} \quad [2]$$

Equations [1] and [2] are evaluated numerically in Fig. 2 for Fe_3C precipitates at austenite : ferrite boundaries in Fe-C alloys from 573 to 973 K and for Ti_2Ni precipitates at $\alpha : \beta$ boundaries in Ti-Ni from 573 to 1023 K on the basis of available ancillary data.²⁴⁻³¹ (Note that both ratios are independent of alloy composition within a given system.) G_α/G_γ is seen to fall with decreasing temperature in both systems when volume diffusion is dominant and to fall in the Fe-C system and to rise in Ti-Ni when growth is controlled by interfacial diffusion. The interfacial diffusion mechanism is probably applicable to Ti-Ni and that of volume diffusion should be appropriate for Fe-C. Overall, the compound particles are predicted to thicken with marked preference into γ irrespective of growth mechanism, except near 300°C in Ti-Ni when growth is controlled by interfacial diffusion and near 700°C in Fe-C when growth is controlled by volume

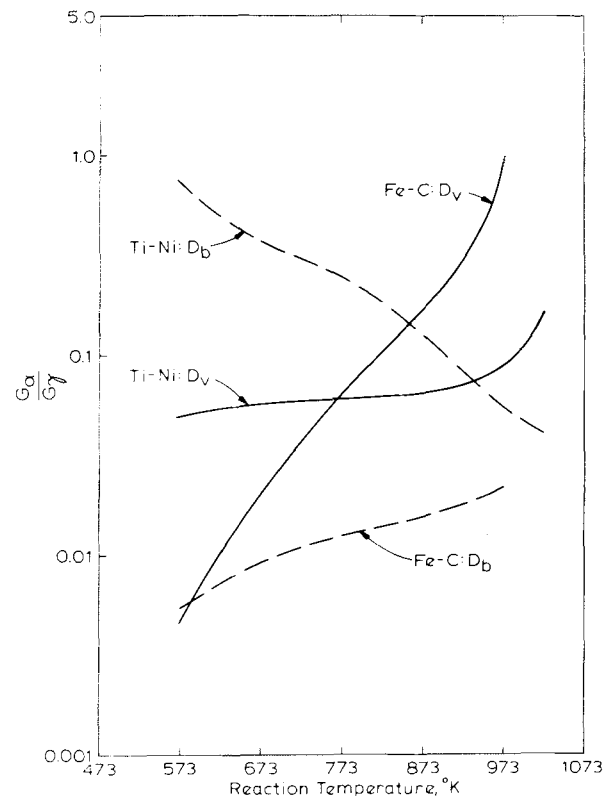


Fig. 2—Variation with reaction temperature of the ratio of the growth rate of interphase boundary-nucleated C into α (G_α) to its growth rate into γ (G_γ) for Fe-C and Ti-Ni alloys under conditions of volume diffusion (v) and of boundary diffusion (b) control.

diffusion. This prediction is consistent with experimental observations in Ti-Ni and many other Ti-X alloys;^{9,10} the much smaller size of the compound particles and the far more rapid rates of α growth in Fe-C alloys make comparison with experiment more difficult in this system but limited observations at higher reaction temperatures tend to support the results of Fig. 2. However, available information on disordered ferrite : cementite¹² and austenite : ferrite¹³ boundary energies indicates that the energies of disordered ferrite : cementite and austenite : cementite boundaries are similar. Hence, prior to the imposition of facets, cementite nuclei should extend about equally into austenite and ferrite. On physical grounds, a similar result is to be expected in Ti-Ni and other Ti-X eutectoid systems. One may thus conclude that the relative penetrations of compound particles precipitated at interphase boundaries into the phases forming these boundaries during growth will often bear little resemblance to the penetrations likely to have obtained during nucleation.

PRECIPITATE NUCLEATION AT MOVING INTERPHASE BOUNDARIES

During isothermal decomposition of austenite in Fe-C-X alloys containing several wt pct of a strong carbide-forming element, growth of ferrite takes place predominantly by the ledge mechanism.¹¹ Convincing metallographic evidence has been presented to show that interphase boundary carbides formed in these alloys nucleate predominantly on the relatively low energy broad faces of these ledges, rather than on their high energy risers^{11,17,32-34} (Fig. 3). Honeycombe¹¹ recognized that the high mobility of the risers makes them unsatisfactory nucleation sites for carbides relative to the immobile broad faces. More detailed support will now be developed for this doubtlessly correct reasoning.

Since ledge-free partially or fully coherent interphase boundaries separating crystals with different structures and/or markedly different degrees of long-range order are immobile,^{35,36} this problem is reduced to ascertaining the conditions under which nucleation is feasible at moving disordered interphase boundaries. The shape of the critical nucleus must very closely approximate the equilibrium shape in order to minimize the free energy needed to form the critical nucleus. Therefore, the restriction that the mi-

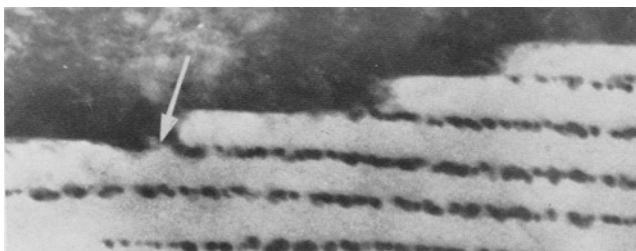


Fig. 3—Precipitation of Cr_{23}C_6 at broad faces but not at the risers of ledges in Fe-0.2 wt pct C-12 wt pct Cr reacted 30 min at 650°C. Dark field transmission electron micrograph, magnification 100,500 times. K. Campbell, Ph.D. thesis, Cambridge, 1971. Courtesy of R. W. K. Honeycombe.

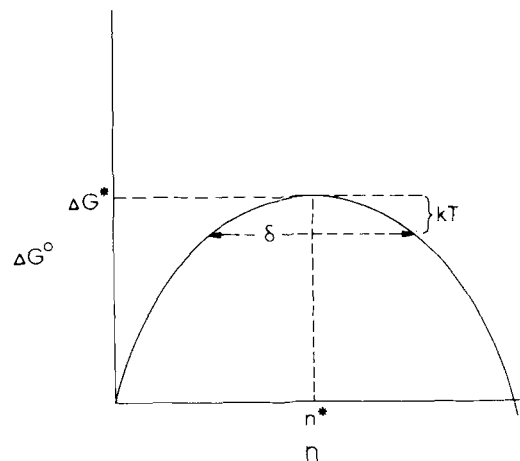


Fig. 4—Definition of δ , after Feder *et al.*³⁷

gration rate of the $\alpha : \gamma$ boundary, $G_{\alpha:\gamma}$, at which nucleation may take place must not exceed that which displaces this boundary a distance of, say, one lattice parameter, a , in the time required for an embryo to develop to (and safely beyond³⁷) the critical nucleus size should be satisfied. Hence:

$$G_{\alpha:\gamma} = a\bar{G}/h^* \quad [3]$$

where \bar{G} = average radial growth rate of an embryo (*i.e.*, thickening rate) and h^* = maximum perpendicular distance from the interphase boundary to the surface of the critical nucleus (indicated in Fig. 1(f)), for a symmetrical nucleus; facets are not considered here to avoid unnecessary complication). Feder *et al.*³⁷ show that fluctuational growth of an embryo must proceed beyond critical nucleus size until the molar free energy change accompanying embryo formation $\Delta G^0 = \Delta G^* - kT$ (where k = Boltzmann's constant and T = absolute temperature) in order to prevent probable destruction of the nucleus by thermal fluctuations. It will be shown in the derivation of \bar{G} , however, that under conditions of likely interest here the additional growth is small enough to be disregarded; hence the use of h^* in Eq. [3] does not introduce a significant approximation.

Volume Diffusion-Controlled Nucleation

Bhattacharyya *et al.*³⁸ have derived an expression for \bar{G} using the approach of Hillig³⁹ in which the embryo is taken to be a perfect sink. Here the considerations of Feder *et al.*³⁷ are employed in order to ensure distinction between nucleation, which is a fluctuational process and hence provides a highly imperfect sink, and growth of a disordered interphase boundary, to which the perfect sink concept is much more accurately applicable. Feder *et al.*³⁷ recognized that most of the time required for development to critical nucleus size is spent traversing the region δ in Fig. 4, where δ = the number of atoms required for growth from $n^* - \delta/2$ to $n^* + \delta/2$, and $\Delta G^0 = \Delta G^* - kT$ at both of these sizes; thus the total incubation time for nucleation, τ , was taken as the time needed to accomplish this portion of the process. Hence one may write:

$$\bar{G} \cong \frac{\text{net number of atoms impinging on nucleus surface/time} = \delta/\tau}{\text{average surface area of nucleus/area per atomic site at surface} = \bar{A}/a^2} \quad [4]$$

$$\times \frac{\text{thickness} = a}{\text{atomic layer}} = \frac{\delta a^3}{\tau \bar{A}}$$

The average area of an embryo during this fluctuational growth process is:

$$\bar{A} = 4\pi \left(\frac{r_f^2 + r_i^2}{2} \right) (1 - \cos \psi) \quad [5]$$

where r_f and r_i = radii of embryos or nuclei containing $n^* + \delta/2$ and $n^* - \delta/2$ atoms and $\cos \psi = \gamma_{\alpha\gamma}/2\gamma_{\alpha C} = \gamma_{\alpha\gamma}/2\gamma_{\gamma C}$, in which $\gamma_{\alpha\gamma}$, $\gamma_{\alpha C}$ and $\gamma_{\gamma C}$ = interfacial energies of disordered $\alpha : \gamma$, $\alpha : C$ and $\gamma : C$ boundaries. From Johnson *et al.*,⁷

$$r_f = \left[- \left(\frac{2\gamma_{\alpha C}}{\Delta G_v} \right)^3 + \frac{6}{(\Delta G_v)^2} \left(\frac{kT\gamma_{\alpha C}^3}{\pi K} \right)^{1/2} \right]^{1/3} \quad [6a]$$

$$r_i = \left[- \left(\frac{2\gamma_{\alpha C}}{\Delta G_v} \right)^3 - \frac{6}{(\Delta G_v)^2} \left(\frac{kT\gamma_{\alpha C}^3}{\pi K} \right)^{1/2} \right]^{1/3} \quad [6b]$$

where ΔG_v = volume free energy change and K = ratio of the volume of the double spherical cap critical nucleus to that of a sphere of the same radius. Substituting into Eq. [4] expressions for τ and δ from Johnson *et al.*⁷ and Eqs. [5] and [6],

$$\bar{G} = \frac{16(\pi kT\gamma_{\alpha C}^3 K)^{1/2}}{a^3 \Delta G_v^2} \times a^3 \times \frac{a^5 \cdot \Delta G_v^2 \cdot Dx(1 - \cos \psi)}{8kT\gamma_{\alpha C} a^4 K} \times \frac{1}{2\pi \xi(1 - \cos \psi)}$$

$$= \frac{a^2 \gamma_{\alpha C}^{1/2} Dx}{(\pi kTK)^{1/2} \xi} \quad [7]$$

where Dx = product of the diffusivity and the solute concentration in either the α or the γ phase, whichever is smallest; the term v_α , the average volume of an atom in the nucleus phase, used by Johnson *et al.*⁷ has been approximated as a^3 ; the volume strain energy attending nucleation of C is incorporated into ΔG_v and $\xi = r_f^2 + r_i^2$. Taking $\gamma_{\alpha C} = 750$ ergs/cm² = 0.75 J/m², $T = 1000$ K and $\Delta G_v = 1, 10$ and 100 cal/cm³ = (4.19, 41.9 and 419) $\times 10^{-6}$ J/m³, the first term in Eqs. [6a] and [6b] is greater than the second by factors greater than 400 at the smallest $|\Delta G_v|$ and 4 at the largest when $K = 10^{-2}$ and by 40 and 4 at the smallest and the intermediate $|\Delta G_v|$ even when $K = 10^{-4}$. Hence it usually appears acceptable to omit the second term in these expressions, thereby simplifying Eq. [7] to:

$$\bar{G} = \frac{a^2 Dx \cdot \Delta G_v^2}{8(\pi kT\gamma_{\alpha C}^3 K)^{1/2}} \quad [8]$$

This is just the relationship obtained when \bar{A} is taken as $4\pi r^{*2}(1 - \cos \psi)$. The foregoing conclusion, that r_f is usually very little larger than r_i , justifies the use of h^* in Eq. [3]. Substituting Eq. [8] into Eq. [3] yields the highest growth rate of a disordered $\alpha : \gamma$ boundary at which a crystal of C can nucleate:

$$G_{\alpha:\gamma} = \frac{-a^3 Dx \cdot \Delta G_v^3}{16(1 - \cos \psi) (\pi kT\gamma_{\alpha C}^5 CK)^{1/2}} \quad [9]$$

When the disordered $\alpha : \gamma$ boundary is planar and of infinite extent, $G_{\alpha:\gamma}$ diminishes with time as $t^{-1/2}$, thus ensuring that the condition of Eq. [9] will eventually be fulfilled. Using Zener's²⁰ linearized gradient relationship for $G_{\alpha:\gamma}$, again omitting the constant of order unity and rearranging:

$$t = \frac{256\pi kT\gamma_{\alpha C}^5 CK(1 - \cos \psi)^2 (x_\gamma^{\gamma\alpha} - x_\gamma)^2 D_G}{(a \cdot \Delta G_v)^6 (D_J x)^2 (x_\gamma^{\gamma\alpha} - x_\alpha^{\alpha\gamma})(x_\gamma - x_\alpha^{\alpha\gamma})} \quad [10]$$

where x_γ = mole fraction of solute in the alloy, D_G = diffusivity applicable during growth of α into γ (if D in γ varies with composition, then an averaged diffusivity becomes appropriate) and D_J = diffusivity applicable during nucleation (in α at $x_\alpha^{\alpha\gamma}$ or in γ at $x_\gamma^{\gamma\alpha}$). This equation yields the earliest isothermal reaction time at which nucleation of C at planar, disordered $\alpha : \gamma$ boundaries of effectively infinite extent becomes feasible.

When the disordered boundary forms the riser of a ledge, $G_{\alpha:\gamma}$ is both constant and high.^{35,40} The only option available for diminishing $G_{\alpha:\gamma}$ sufficiently to make C nucleation feasible is that of reducing the supersaturation driving the growth of α into γ , and this alternative entails the twin risks of excessive reduction in the supersaturation for carbide nucleation and discouraging the formation of ledged boundaries, which are customarily more prominent at higher supersaturations.^{11,35,41} Substituting the Jones-Trivedi⁴⁰ equation for the lateral velocity of a ledge in the absence of a barrier to growth at the riser into Eq. [9],

$$(x_\gamma^{\gamma\alpha} - x_\gamma)_{\max} = \frac{-a^3 (x_\gamma^{\gamma\alpha} - x_\alpha^{\alpha\gamma}) \alpha l \cdot \Delta G_v^3 \cdot D_J x_\gamma}{16(1 - \cos \psi) (\pi kT\gamma_{\alpha C}^5 CK)^{1/2} \cdot D_G} \quad [11]$$

where α = a constant which varies with supersaturation and l = ledge height.⁴⁰ This equation permits evaluation of the highest driving force, expressed as $(x_\gamma^{\gamma\alpha} - x_\gamma)_{\max}$ at which C nucleation at the risers of ledged $\alpha : \gamma$ boundaries may occur.

Interfacial Diffusion-Controlled Nucleation

Operation of this mechanism is expected when the participating phases are substitutional and a sufficient proportion of the boundary area involved is disordered.⁴² In order to permit a more direct comparison with the results for volume diffusion-controlled nucleation, growth of the disordered $\alpha : \gamma$ boundaries along which compound nucleation is attempting to occur will continue to be considered as controlled by volume diffusion. This assumption is valid when grain boundary allotriomorphs have largely

replaced the grain boundaries in the matrix phase, when individual allotriomorphs are very long or when compound nucleation is being considered at a quite limited area of disordered boundary which is wholly surrounded by a partially (or fully) coherent area. Russell^{43,44} has concluded that the principal effect upon nucleation kinetics which attends replacement of volume by interfacial diffusion as the dominant transport mechanism is exerted through β^* . For this quantity, Vander Velde *et al*⁴² write:

$$\beta^* = 2\pi r^* D_b x_b \lambda \cdot \sin \psi / a^4 \quad [12]$$

where D_b = boundary diffusivity in whichever interface involved in mass transport has the lowest $D_b x_b$ product, x_b = solute concentration in that interface and λ = boundary thickness $\approx a$. Since $r^* = -2\gamma_{\alpha C} / \Delta G_v$, substituting these relationships into the Johnson *et al*⁷ relationship for τ yields:

$$\tau = - \frac{32kT\gamma_{\alpha C}^2}{a^3 D_b x_b \cdot \Delta G_v^3 \cdot \sin \psi} \quad [13]$$

Replacing the third term in Eq. [7] with this equation:

$$\bar{G} = \frac{-a^3 D_b x_b \cdot \Delta G_v^3 \cdot \sin \psi}{32(1 - \cos \psi)(\pi k T \gamma_{\alpha C}^5)^{1/2}} \quad [14]$$

when the same approximation is made with respect to ξ . Substituting Eq. [14] into Eq. [3]:

$$t = \frac{4096\pi k T \gamma_{\alpha C}^7 K D_G (1 - \cos \psi)^4 (x_{\gamma}^{\gamma\alpha} - x_{\gamma})^2}{(a \cdot \Delta G_v)^8 (D_b x_b \sin \psi)^2 (x_{\gamma}^{\gamma\alpha} - x_{\alpha}^{\alpha\gamma})(x_{\gamma} - x_{\alpha}^{\alpha\gamma})} \quad [15]$$

This relationship replaces Eq. [10] when interfacial diffusion controls nucleation. Similarly, Eq. [11] becomes:

$$(x_{\gamma}^{\gamma\alpha} - x_{\gamma})_{\max} = \frac{a^4 D_b x_b \alpha l \cdot \sin \psi \cdot \Delta G_v^4 (x_{\gamma}^{\gamma\alpha} - x_{\alpha}^{\alpha\gamma})}{64 D_G (1 - \cos \psi)^2 (\pi k T \gamma_{\alpha C}^5)^{1/2}} \quad [16]$$

NUMERICAL EVALUATIONS AND COMPARISONS WITH EXPERIMENT

Volume Diffusion-Controlled Nucleation

To compare these equations with experimental observations, t will be evaluated from Eq. [10] and $(x_{\gamma}^{\gamma\alpha} - x_{\gamma})_{\max}$ from Eq. [11], both as a function of reaction temperature, for the proeutectoid ferrite reaction in an Fe-0.10 wt pct C alloy, wherein volume diffusion is expected to control nucleation at interphase boundaries over much of the temperature range of interest. These quantities are also computed for a Ti-2 wt pct alloy, in which interfacial diffusion should control this nucleation process. For both alloys, the following values are employed: $\psi = 60$ deg ($\gamma_{\alpha\gamma} = \gamma_{\alpha C} = \gamma_{\gamma C}$), $\gamma_{\alpha C} = 750$ ergs/cm² = 0.75 J/m², $a = 0.33$ nm, $x_b = x_{\gamma}$ (in view of the uncertainty as to the solute concentration in an interphase boundary⁴⁵⁻⁴⁷) and $\alpha = 0.1$.* In the Fe-C alloy, the molar volume of

*The supersaturations which obtain during compound nucleation at interphase boundaries in these alloys range from 0.7 to nearly unity. These exceed the range for which Jones and Trivedi⁴⁰ have computed a vs. supersaturation; an average value of $\alpha = 0.1$ was estimated by approximate graphical extrapolation.

Fe₃C, the compound assumed to form at disordered

austenite : ferrite boundaries, is 2.34×10^{-5} m³/mole, the range of reaction temperatures covered by the calculations is 573 to 973 K, $x_{\gamma}^{\gamma\alpha}$ and $x_{\alpha}^{\alpha\gamma}$ were evaluated from new calculations²⁶ based upon the experimental and theoretical studies of McLellan and Dunn,⁴⁸⁻⁵⁰ D_{Jx} was taken as $D_{\gamma} x_{\gamma}^{\gamma\alpha}$ at 973 K and as $D_{\alpha} x_{\alpha}^{\alpha\gamma}$ at 923 K and below (on the criterion that the smaller product is the correct one to employ) and D_G was specified, consistently with the use of Zener's²⁰ linearized gradient model for the growth of an $\alpha : \gamma$ boundary, as D_{γ} at $(x_{\gamma}^{\gamma\alpha} + x_{\gamma})/2$, computed from the relationship for the effects of temperature and composition upon D_{γ} developed by Kaufman, Radcliffe and Cohen.²⁴ In the Ti-Ni alloy, the compound was assumed to be Ti₂Ni, the molar volume of this compound is 2.74×10^{-5} m³/mole, calculations were made for reaction temperatures from 573 to 1023 K (the eutectoid temperature in Ti-Ni is 1043 K (Ref. 28) as compared with 996 K in Fe-Fe₃C), $x_{\beta}^{\beta\alpha}$ and $x_{\alpha}^{\alpha\beta}$ (the equivalents in Ti-Ni of $x_{\gamma}^{\gamma\alpha}$ and $x_{\alpha}^{\alpha\gamma}$) were calculated on the approach of Kaufman and Bernstein,³¹ $x_{\alpha}^{\alpha C}$ was taken from the phase diagram²⁸ and $x_{\beta}^{\beta C}$ was extrapolated graphically from this diagram, for D_G the relationship $D_{\beta} = 0.0093 \times \exp(-29,600/RT)$ cm²/s (Ref. 29) was employed and D_b was taken to have a D_o the average of those for D_{α} (Ref. 30) and D_{β} and a ΔH somewhat larger than one-half the average of the ΔH 's for volume diffusion in α and β , namely $D_b = 0.026 \exp(-22,000/RT)$ cm²/s. For the calculations on both alloys, K and l were considered as variables and were grouped with the unknowns. Since experience is beginning to indicate that K , the critical nucleus shape factor, is often < 0.1 ,^{51,52} however, the model of Fig. 1(e) was used, rather than that of Fig. 1(a) (with the two spherical caps having equal radii) used in the derivations. Accordingly, the term $(1 - \cos \psi)$ must be multiplied by $1/2$.⁷ Hence Eqs. [10] and [11] should be multiplied by $1/4$ and 2 , respectively, and Eqs. [15] and [16] are multiplied by $1/16$ and 4 for this specific nucleus morphology.

Figure 5 shows the variation of t/K with reaction temperature calculated from Eq. [10] for proeutectoid ferrite nucleated at austenite grain boundaries in Fe-0.10 wt pct C and Fe-0.80 wt pct C. (K is in effect left as a variable because our information on the actual shape of critical nuclei at interfaces is still so scanty.) For an Fe-0.13 wt pct C alloy reacted ca. 30°C below the Ae₃ ($\gamma/(\alpha + \gamma)$ equilibrium temperature), Lange⁵¹ has recently found that K is somewhat less than 10^{-4} for a nucleus of the type illustrated in Fig. 1(g), *i.e.*, one facet coplanar with the grain boundary and a second on the remaining spherical cap. This means that the available ΔG_v is insufficient to permit the presence of as much as one monolayer of disordered boundary on the nucleus, though the existence of such a thin strip of disordered boundary is in itself physically unrealistic. Since there are now many alternate nucleus shapes which can be hypothesized, and there is not yet any means available for distinguishing among them, it is useful to retain the basic models of Fig. 1 even though nonphysical values of K must sometimes be employed. We shall continue to use Fig. 1(e), with K ranging from 10^{-1} to 10^{-4} . Applying the smallest K of this range to the lowest value of t/K in Fig. 5, encountered at 873 K, yields $t \sim 200$ s. In an Fe-0.11 wt pct C alloy reacted at this temperature, the

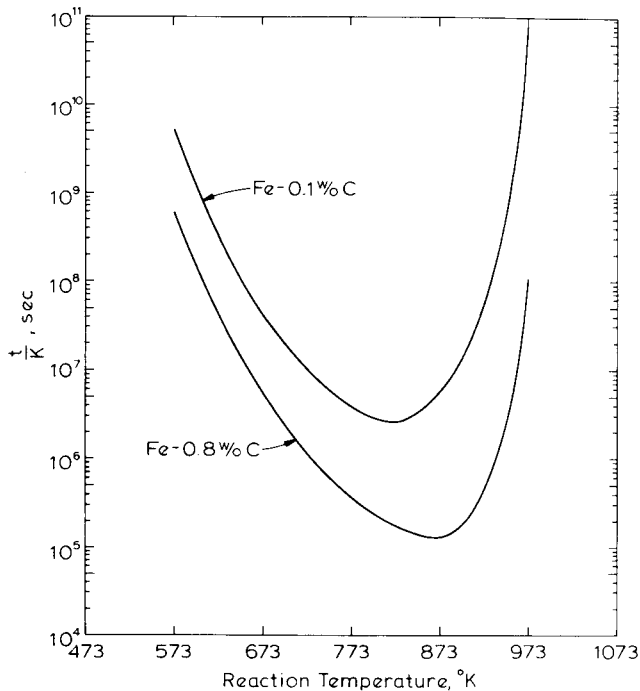


Fig. 5—Effect of reaction temperature upon t/K , the ratio of the growth time which must elapse prior to nucleation to the critical nucleus shape factor, for nucleation of Fe_3C at moving planar, disordered austenite : ferrite boundaries in Fe-0.10 wt pct C and Fe-0.80 wt pct C.

time required to decompose the austenite phase completely is not much greater than 4 s.⁵³ The discrepancy between these two times is still greater at the other reaction temperatures investigated. Hence nucleation of Fe_3C at planar, disordered austenite : ferrite boundaries does not appear to be feasible in this alloy. Increasing the carbon content of the alloy to the eutectoid composition is seen, in Fig. 5, to reduce t/K noticeably, particularly at higher temperatures. However, even when $K = 10^{-4}$, the calculated values of t exceed those required for complete decomposition of the matrix austenite, albeit by smaller margins. Thus the unsuitability of these boundaries as nucleation sites for cementite appears to be general.

Figure 6 shows the variation of $(x_{\gamma}^{\gamma\alpha} - x_{\gamma})K^{1/2}/l$ with reaction temperature for the Fe-C alloy. Ledges on the broad faces of ferrite sideplates formed in Fe-C alloys have been observed to be as much as ca. 5×10^{-7} m high.⁵⁴ When $K = 10^{-4}$, $x_{\gamma}^{\gamma\alpha} - x_{\gamma}$ is thus $\leq 5 \times 10^{-5}$ multiplied by the values of $(x_{\gamma}^{\gamma\alpha} - x_{\gamma})K^{1/2}/l$ graphed in Fig. 6. Comparison of the maximum allowable $(x_{\gamma}^{\gamma\alpha} - x_{\gamma})$ with that computed from the phase diagram is made in Fig. 7. Even at the largest value of $(x_{\gamma}^{\gamma\alpha} - x_{\gamma})_{\text{max}}$, the actual supersaturation is still over an order of magnitude too high for nucleation of Fe_3C to occur at the edge of a moving ledge on an $\alpha : \gamma$ boundary. Hence nucleation of Fe_3C at the edge of a moving ledge cannot occur except at negligible undercooling below the Ae_3 or its metastable equilibrium extrapolation.

The results obtained in respect of Fe_3C precipitation at both configurations of moving austenite : ferrite boundaries in Fe-C alloys cannot be compared with experiment in more detail, since the refined metallographic observations on Fe-C-X alloys summarized by

Honeycombe¹¹ have yet to be reported on Fe-C alloys—and indeed would be considerably more difficult to make because transformation processes are so much more rapid in the latter alloys. It therefore appears desirable to give some consideration to the applicability of the calculations to Fe-C-X alloys. The steels in which such studies were made invariably contained an appreciable proportion of an alloying element which is a strong carbide-former and markedly decreases the activity of carbon in austenite. Such elements can significantly reduce the growth rates of proeutectoid

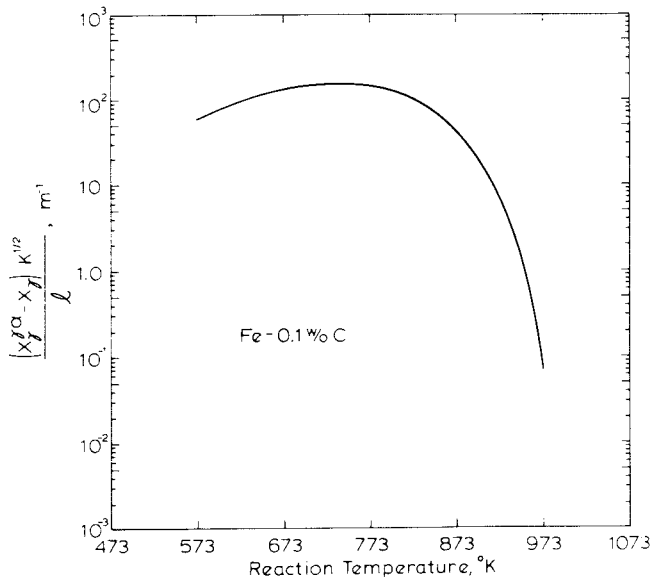


Fig. 6—Influence of reaction temperature upon the product of the maximum driving force, $(x_{\gamma}^{\gamma\alpha} - x_{\gamma})_{\text{max}}$, at which Fe_3C can nucleate at the risers of ledges on $\alpha : \gamma$ boundaries in Fe-C alloys, and $K^{1/2}/l$, where K is the critical nucleus shape factor and l is the ledge height.

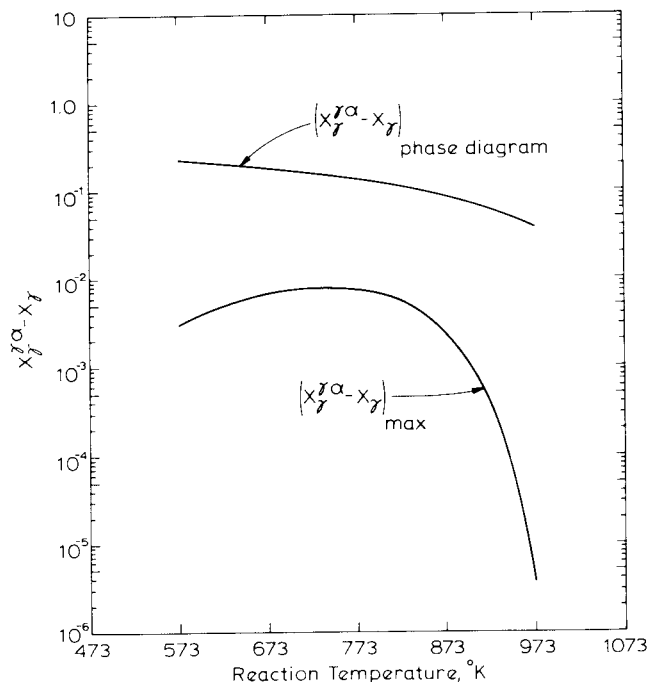


Fig. 7—Comparison of the maximum level of $(x_{\gamma}^{\gamma\alpha} - x_{\gamma})$ at which Fe_3C nucleation can take place at the risers of ledges on $\alpha : \gamma$ boundaries when $l/K^{1/2} = 5 \times 10^{-5}$ m with the values of $(x_{\gamma}^{\gamma\alpha} - x_{\gamma})$ computed from the extrapolated $\gamma/(\alpha + \gamma)$ phase boundary.

ferrite, even in the absence of carbide precipitation,⁵⁵ by a solute drag-like effect.^{56,57} (A quantitative description of this effect is not yet available, thus preventing its incorporation in the present treatment.) Hence these elements should facilitate carbide precipitation at austenite : ferrite boundaries unless (somewhat implausibly) this effect reduces equally or even more the growth kinetics of carbide embryos. Particularly at the higher reaction temperatures, interphase boundary carbides in Fe-C-X alloys are alloy carbides whose formation appears to be facilitated by diffusion of the alloying element along the advancing austenite : ferrite boundaries.¹¹ Provided that boundary diffusion of alloying element rather than volume diffusion of carbon controls nucleation, as the calculations to follow will make clear this process will also facilitate alloy carbide nucleation at interphase boundaries. At high reaction temperatures, when the solute drag effect is less important, the ability of the alloying elements in question to raise even the no-partition Ae3 to temperatures above that of the Ae3 in Fe-C (Ref. 58) will hinder interphase boundary carbide nucleation through acceleration of the growth kinetics of proeutectoid ferrite. However, the temperature range in which this effect is important appears to be limited,⁵⁶ particularly in the high alloy steels used by Honeycombe and coworkers. Finally, an effect which can easily be at least as important as any of the foregoing is the influence of alloying elements upon K , as exerted through alterations in the various interfacial energies involved. Unfortunately, data on this effect are not yet available. In the absence of such information, however, we may tentatively conclude that the sum of the other effects of carbide-forming alloying elements will usually tend to facilitate interphase boundary carbide nucleation at disordered austenite : ferrite boundaries. The experimental finding that such boundaries are *not* preferred sites for carbide nucleation in these Fe-C-X alloys¹¹ suggests that the analyses presented in terms of Fe-C may in fact be applicable in the large to Fe-C-X alloys.

Interfacial Diffusion-Controlled Nucleation

When growth of the disordered boundary at which compound nucleation may occur takes place under long range volume diffusion-control but compound nucleation at this boundary takes place by means of interfacial diffusion the foregoing picture is partially reversed. Figure 8 displays the variation of t/K with reaction temperature calculated from Eq. [15] for a Ti-2 wt pct Ni alloy. K is again taken as 10^{-4} . The time for Ti_2Ni spheres to grow to a radius of 2.5×10^{-7} m, at which they should be resolvable with optical microscopy, was computed. The sum of the resulting times for nucleation and for growth was compared with the interval between C-curves for the start of the proeutectoid α reaction and that for the onset of compound precipitation at $\alpha : \beta$ boundaries in a Ti-3.3 wt pct Ni alloy.¹⁰ The calculated time for nucleation and growth was less than the experimental time at temperatures of 723 K and above. Allowance for the higher Ni content of the experimental alloy would somewhat increase the temperature range in

which compound nucleation is feasible.

Figure 9 shows the dependence of $(x_{\beta}^{\beta\alpha} - x_{\beta})_{\max} K^{1/2}/l$ upon reaction temperature, calculated for a Ti-2 wt pct Ni alloy from Eq. [16]. Assuming, as in Fe-C, that

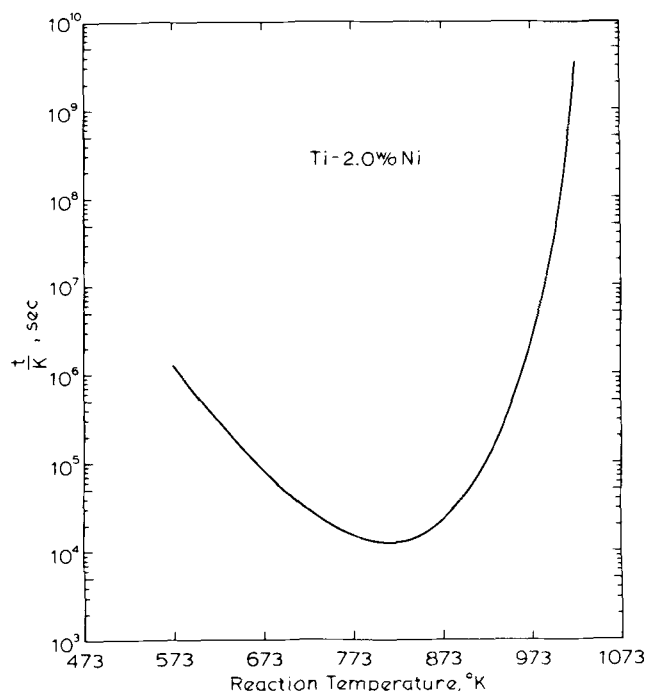


Fig. 8—Variation of t/K for nucleation of Ti_2Ni at moving planar, disordered $\alpha : \beta$ boundaries in a Ti-2 wt pct Ni alloy when mass transport during nucleation takes place by interfacial diffusion. t is the growth time which must elapse prior to precipitate nucleation and K is the critical nucleus shape factor.

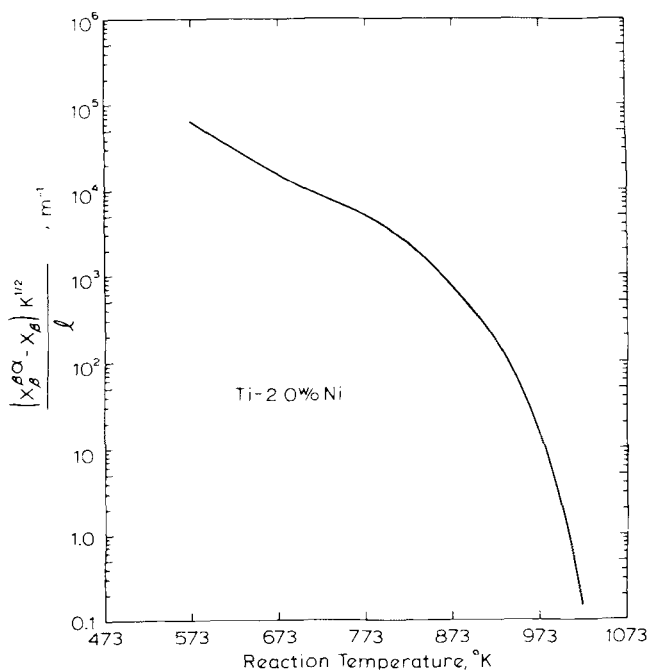


Fig. 9—Effects of reaction temperature upon the product of the maximum driving force, $(x_{\beta}^{\beta\alpha} - x_{\beta})_{\max}$, at which Ti_2Ni can nucleate upon moving risers of ledges on $\alpha : \beta$ boundaries in a Ti-2 wt pct Ni alloy when mass transport during nucleation takes place by interfacial diffusion, and $K^{1/2}/l$, where K is the critical nucleus shape factor and l is the ledge height.

$l/K^{1/2} = 5 \times 10^{-5}$ m, Fig. 10 shows the maximum value of $x_{\beta}^{\alpha} - x_{\beta}$ vs reaction temperature at which Ti_2Ni can nucleate at the risers of ledges. For comparative purposes, Fig. 10 also includes a plot of $x_{\beta}^{\alpha} - x_{\beta}$ computed from the extrapolated $\beta/(\alpha + \beta)$ phase boundary. These two plots are seen to intersect at ca. 840 K. Hence compound nucleation at risers should be feasible at all lower reaction temperatures.

These results indicate that precipitation at moving, disordered interphase boundaries in substitutional alloys with physical constants roughly comparable to those for Ti-Ni should be feasible under some conditions when the boundary growth rates are controlled by volume diffusion but precipitate nucleation at these boundaries is governed by interfacial diffusion. The metallographic observations needed to test this prediction properly are not yet available in sufficient detail. It is expected, however, that current research¹⁰ will provide this information in the Ti-Ni and in a number of other Ti-X eutectoid systems.

SUMMARY

Three problems in precipitation at interphase boundaries have been considered on the basis of theories of diffusional nucleation and growth. Where feasible, illustrative calculations have been made for Fe_3C precipitation at austenite : ferrite boundaries in Fe-0.10 wt pct C and 0.80 wt pct C alloys and for Ti_2Ni precipitation at $\alpha : \beta$ boundaries in a Ti-2 wt pct Ni alloy.

Simple, approximate expressions were derived for relative growth rates of precipitate into the two parent phases under the conditions of volume diffusion and interfacial diffusion-control. These expressions were

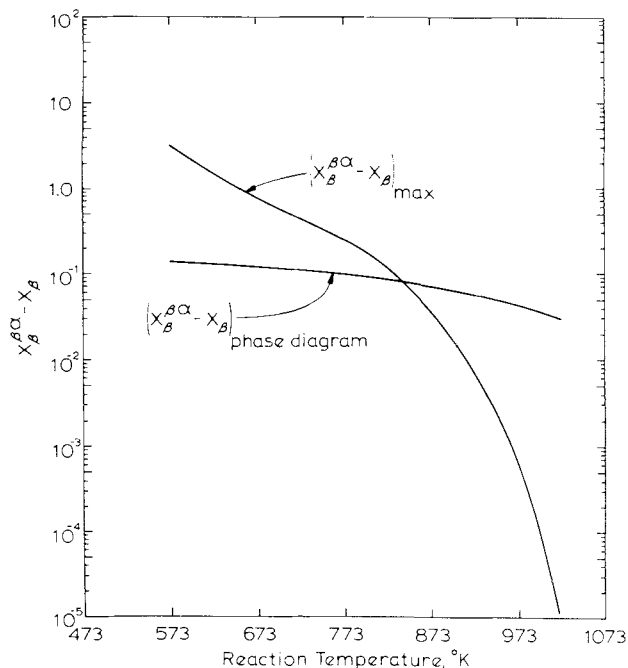


Fig. 10—Comparison of the maximum values of $(x_{\beta}^{\alpha} - x_{\beta})$ at which Ti_2Ni nucleation can take place at the risers of ledges on $\alpha : \beta$ boundaries when $l/K^{1/2} = 5 \times 10^{-5}$ m, with the values of $(x_{\beta}^{\alpha} - x_{\beta})$ computed from the extrapolated $\beta/(\alpha + \beta)$ phase boundary.

evaluated numerically as a function of reaction temperature for the relative growth kinetics of Fe_3C into austenite and ferrite in Fe-C alloys and of Ti_2Ni into α and β in Ti-Ni alloys. Under nearly all conditions examined, growth takes place predominantly into the parent phase whose existence range is larger, even though, in the case of Fe-C, the diffusivity is considerably higher in the lower solubility phase. Available information on relative interfacial energies indicates, however, that the critical nucleus should usually penetrate about equally (facets aside) into both phases. Hence the relative penetration into these phases during growth, the only stage of precipitation which can usually be observed experimentally, can give a quite misleading impression of the relative penetration which occurred during nucleation.

Equations have been derived, based upon the approach of Feder *et al.*,³⁷ for the average growth rate of an embryo through the critical nucleus size under the alternative assumptions that mass transport takes place by volume diffusion and by interfacial diffusion. The criterion is proposed that migration of the interphase boundary at which nucleation is attempting to occur through a distance greater than one lattice parameter during growth of an embryo through critical nucleus size would distort the nucleus shape sufficiently to cause a kinetically unacceptable increase in the free energy of activation for nucleation. Relationships are then obtained for the maximum growth rate of an interphase boundary at which precipitate nucleation is feasible and incorporated with equations for the growth kinetics of two different configurations of disordered interphase boundary: the planar boundary of infinite extent²⁰ and the riser or edge of a ledge.⁴⁰ The time is obtained at which motion of the infinitely extended planar boundary is slowed sufficiently to permit precipitate nucleation through each mass transport mechanism. Risers of ledges grow at constant velocity, so expressions are obtained for the maximum ratio of the driving force to the ledge height at which precipitate nucleation is feasible, again for both mechanisms. It is found that for interstitial systems, *e.g.*, Fe-C, where nucleation should be controlled by volume diffusion except possibly at very low homologous temperatures, nucleation of precipitate at moving interphase boundaries should not be feasible. However, calculations for Ti-2 wt pct Ni suggest that in substitutional systems, when mass transport during nucleation takes place along interfaces, precipitate crystals may form under certain conditions at moving interphase boundaries. The detailed metallographic studies of Honeycombe and coworkers¹¹ on Fe-C-X alloys support the conclusion obtained for interstitial systems; counterpart information is not yet available in sufficient detail for substitutional systems.

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