Introduction to

"A Modification of the Lifshitz-Slyozov-Wagner Equation for Predicting Coarsening of γ' and Other Precipitates with Compositions Similar to that of Their Matrix"

The story behind this article is instructive, and even a bit troubling. I wrote it in 1991 as a continuation of part of my Doctoral thesis, which I'd completed a few years earlier. During that research, I'd found that scientists who'd done very fine laboratory work on Ostwald ripening during the 1960s had made a curious error in simple mass balances when deriving a rate equation for Ostwald ripening starting from the minimum-entropy-production-rate (MEPR) principle.

That error led the 1960s scientists to reject (with commendable honesty) their hypothesis that the MEPR principle is applicable to Ostwald ripening. Like all the rest of us metallurgists back then, I didn't catch that error, until I examined the derivation of the MEPR-based rate equation in detail during my thesis work. However, I didn't manage to re-derive the rate equation fully until I took up the subject again in the early 1990s. The scientists who did such fine lab work in the 1960s would no doubt have been pleased to learn that their empirical results agreed quite well with predictions made by the corrected equation. Thus, those scientists were correct in their hypothesis about the MEPR principle's applicability.

I continue to wonder how we metallurgists overlooked, for more than two decades, the simple error that led those scientists to conclude, mistakenly but honestly, that they'd been wrong.

I never did manage to publish this article, but the same derivations and analyses were published by other researchers within a few years. Some of the reviewers' comments on the article are addressed in the second article in this document, "Comments on 'Ostwald Ripening Growth Rate for Nonideal Systems with Significant Mutual Solubility'".

A MODIFICATION OF THE LIFSHITZ-SLYOZOV-WAGNER EQUATION FOR PREDICTING COARSENING RATES OF γ' AND OTHER PRECIPITATES WITH COMPOSITIONS SIMILAR TO THAT OF THEIR MATRIX

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Abstract — This study modifies the Lifshitz-Slyozov-Wagner (LSW) equation to determine how coarsening rates are affected by partitioning of elements between matrix and precipitate. The modified equation does not require the assumption that one element's diffusivity controls coarsening. Important aspects of conservation of matter during coarsening are presented. Actual coarsening data are analyzed according to the modified LSW equation, yielding reasonable interfacial energies (~0.01 J/m^2) for several Ni-base γ/γ' alloys, but an anomalous high value (perhaps caused by elastic interactions) for one Re-containing superalloy. Analysis of data from a study that measured both coarsening rate and rate of change of mean-field supersaturation yielded consistent, independent values of surface energy and effective diffusivity. It is commonly assumed that diffusion of Al controls coarsening of γ', but the present study suggests that diffusion of elements that partition to the matrix (like Re) is equally important.

1. INTRODUCTION

The LSW coarsening equation [1,2] and its modifications are solutions to a diffusion problem in which the growth rate of particles with radius a is

$$\frac{dr}{dt} = -DC^*\Omega\nabla X \Big|_{r=a} \tag{1}$$

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and the solute concentration in equilibrium with a particle of radius a is

$$X(a) = X_\infty + \frac{\eta}{a},$$ (2)

where

C^* = number of atoms (of both solute and solvent) per unit volume in the matrix;

Ω = molar volume of the precipitate;

X = concentration of the precipitate species in the matrix;

X_∞ = concentration of precipitate species in equilibrium with a planar interface; and

η = thermodynamic factor, equal to $2\sigma\Omega/RT$ for pure-material precipitates.

For $X(a) - X_\infty \ll 1$, Reference [1] showed that the average radius ($<r>$) of an ensemble of coarsening precipitates increases with time according to

$$<r>^3 - <r>_o^3 = K(t - t_o),$$ (3)

where t_o is the time at which steady-state behavior begins and

$$K = \frac{4}{9}DC^*\Omega\eta.$$ (4)

Although the LSW equation is useful for predicting coarsening rates in many metallic systems, it is difficult to apply to γ' precipitates in Ni-base alloys because γ' is nonstoichiometric and because its coarsening may not always be controlled by γ'-formers. Elements that partition to the matrix phase (γ) must diffuse away from growing precipitates, and some authors suggest that this process can control coarsening [3].

When using the LSW equation to study coarsening of γ', authors have attempted to deduce which element controls coarsening, after which they have used X_∞ and D of the "controlling" element in the LSW equation [4,5]. One weakness of this approach is that the

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classic LSW equation cannot account for control of coarsening by diffusion of elements that partition to the matrix.

A more-important weakness is that coarsening needn't be controlled by a single element. Each element, whether it partitions to matrix or to precipitate, should have an influence that depends upon its diffusivity, concentration in the matrix, and extent of partitioning between matrix and precipitate. Without accounting for partitioning explicitly, its importance in Ni-base alloys cannot be assessed accurately. The purpose of this study is to derive an equation that accounts more satisfactorily for the role of each element.[†]

The derivation presented in this study is based upon the analyses of References [7] and [8] for precipitates coarsening under a compositional constraint. A key concept in their analysis is the minimization of entropy-production rate (MEPR) principle from irreversible thermodynamics.

The LSW theory's assumptions and limitations apply to the present derivation as well. In particular, coarsening is a near-equilibrium process that occurs after growth is complete, and there is local equilibrium between each precipitate and its surrounding matrix. Therefore, supersaturations in the matrix are much smaller than differences between equilibrium compositions of matrix and precipitate.

For simplicity, this derivation assumes that molar volumes of matrix and precipitate are equal when expressed in terms of volume per mole of atoms. This assumption is approximately true for Ni-baseγ/γ' alloys. References [7] and [8] describe modifications of the treatment for unequal molar volumes. The present derivation also assumes constant activity coefficients, as

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[†] Since the present paper was first submitted, Umantsev and Olson have treated a similar (and in some ways more general) problem in Reference [6], which also summarizes previous treatments of multicomponent alloys.

does the original LSW theory. References [6] and [9] discuss modifications for non-Henrian behavior as well as its importance.

2. DERIVATION

The first step in the derivation is to relate elemental fluxes to the elements' degrees of partitioning between matrix and precipitate. The MEPR principle is then used to combine the elements' flux ratios, mobilities, and matrix concentrations into an "effective" diffusivity. Subsequently, an equation is derived for supersaturations of each element. The equation for supersaturations is useful (a) for establishing an analogy to the LSW diffusion solution, and (b) for determining surface energies and effective diffusivities from studies that measure mean-field supersaturation as a function of time. Finally, an equation for K is derived. The derivation refers several times to the mass balances in the Appendix.

Determining Ratios of Elemental Fluxes

To determine ratios of elemental fluxes, we do a mass balance on the α matrix that surrounds the β-phase precipitates. Because coarsening is a near-equilibrium process, we may characterize α and β compositions by their equilibrium mole fractions X_i^α and X_i^β. A mass balance shows that to change N moles of atoms in the α phase surrounding a precipitate into N moles of atoms as β phase, the amount of each element that must be transferred from the matrix is Np_i, where the partitioning p_i is defined as $X_i^\beta - X_i^\alpha$. The p_i can be treated as constants if (a) supersaturations are small compared to differences between X_i^β and X_i^α, and (b) the composition of the β precipitates is essentially independent of radius, as is usually assumed. The validity of assuming constant p_i will be considered in comparisons with experimental results (Section 3).

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For constant p_i, the above mass balance shows that the ratios of atoms transferred during coarsening must be proportional to their respective p_i, thereby requiring that the fluxes J_i must satisfy the relationship

$$\frac{J_i}{J_k} = \frac{p_i}{p_k} \ . \tag{5}$$

Equation (5) seems surprising at first, for it says that the flux ratios are independent of elements' respective diffusivities and the precipitate's stoichiometry, except insofar as the latter affects p_i. Equation (5) has further implications for ratios of elements' supersaturations: the LSW theory assumes that J_i are proportional to the differences between mean-field supersaturations and supersaturations at the precipitate surfaces; therefore, Equation (5) implies that these differences must be proportional to p_i. Because the mean-field supersaturations in the LSW theory are themselves simply the supersaturations in equilibrium with particles of radius $<r>$, Equation (5) further implies that the supersaturation of each element is proportionate to its p_i. In the particular case of a binary alloy, the elements' fluxes and supersaturations must be equal in magnitude and opposite in sign if we ignore vacancy fluxes, as the LSW theory does. All of these implications are demonstrably true under the assumptions of the LSW theory, as will be demonstrated later in the main text and Appendix.

Formulating the "Effective" Diffusivity

To derive an "effective" diffusivity, we follow References [7] and [8], and write each J_i through the α matrix as

$$J_i = -B_i C^\alpha X_i^\alpha \left(\nabla \mu_i^\alpha + F_i \right), \tag{6}$$

where B_i is the mobility of component i, C^α is the total concentration of atoms in the α matrix, and the coupling forces F_i are any general forces other than Onsager-type forces that may arise between constituent elements by virtue of their relative motion.

Combining Equations (5) and (6), and multiplying both sides by p_i,

$$p_i F_i = -\frac{p_i J_i}{B_i C^\alpha X_i^\alpha} - p_i \nabla \mu_i^\alpha . \qquad (7)$$

MEPR requires $\sum_{i=1}^{n} J_i F_i = 0$, where n is the number of components. Therefore, from

Equation (5), $\sum_{i=1}^{n} p_i F_i = 0$. If we now assign one element the subscript k, and express all fluxes

in terms of J_k, then $J_i = \frac{p_i}{p_k} J_k$. Combining these ideas with Equation (7),

$$\sum_{i=1}^{n} p_i F_i = -\sum_{i=1}^{n} \left(\frac{p_i^2}{p_k}\right)\left(\frac{J_k}{B_i C^\alpha X_i^\alpha}\right) - \sum_{i=1}^{n} p_i \nabla \mu_i^\alpha = 0. \qquad (8)$$

For constant activity coefficients, $B_i = D_i /RT$. Substituting this expression for B_i and solving

for J_k,

$$J_k = -p_k \left[\frac{(DC)_{eff}}{RT}\right] \sum_{i=1}^{n} p_i \nabla \mu_i^\alpha , \qquad (9)$$

leading to

$$(DC)_{eff} = \frac{C^\alpha}{\sum_{i=1}^{n} \psi_i} , \qquad (10)$$

where $\psi_i = \frac{p_i^2}{D_i X_i^\alpha}$.

Expressing J_k in Terms of ∇X_i^α

To make use of the LSW solution to the diffusion problem, we must write Equation (9) in terms of ∇X_k^α. We can do so because the $\nabla \mu_i^\alpha$ are not independent in our case: they are related through the supersaturations dX_i^α, which in turn are related to each other through conservation of matter, as shown in the Appendix. For constant activity coefficients,

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$d\mu_i^\alpha = RT\, dX_i^\alpha / X_i^\alpha$. Also, $dX_i^\alpha = \dfrac{p_i}{p_k} dX_k^\alpha$ (see Appendix). Therefore, $d\mu_i^\alpha = \dfrac{p_i X_k^\alpha}{p_k X_i^\alpha} d\mu_k^\alpha$. In

addition, LSW demonstrated that ∇X_k^α at the particle/matrix interface is proportional to the

difference between the mean-field supersaturation and the supersaturation at the interface, both

of which are proportional to p_i, as will be demonstrated later [Equation (20)]. These ideas lead

to

$$\sum_{i=1}^{n} p_i d\mu_i^\alpha = \left[\frac{X_k^\alpha}{p_k} \sum_{i=1}^{n} \left(\frac{p_i^2}{X_i^\alpha} \right) \right] d\mu_k^\alpha \tag{11}$$

and subsequently to

$$J_k = -\left[\frac{(DC)_{eff}}{RT} \right] \left[X_k^\alpha \sum_{i=1}^{n} \left(\frac{p_i^2}{X_i^\alpha} \right) \right] \nabla \mu_k^\alpha. \tag{12}$$

Again using $d\mu_i^\alpha = RT dX_i^\alpha / X_i^\alpha$, we arrive at

$$J_k = -[(DC)_{eff}] \left[\sum_{i=1}^{n} \left(\frac{p_i^2}{X_i^\alpha} \right) \right] \nabla X_k^\alpha. \tag{13}$$

To put Equation (13) in the form of Equation (1), we recognize that one mole of atoms as α

phase is transformed into one mole of atoms as β phase for every p_k moles of element k

transferred. Therefore, the analog to Equation (1) in our case is

$$\frac{da}{dt} = -[(DC)_{eff}] \left[\frac{V_m^\beta}{p_k} \sum_{i=1}^{n} \left(\frac{p_i^2}{X_i^\alpha} \right) \right] \nabla X_k^\alpha \Big|_{r=a}, \tag{14}$$

where V_m^β is the volume per mole of atoms in the β phase. Equation (14) cannot be correct

unless $\nabla X_i^\alpha \propto p_i$ for all i. Otherwise, the coarsening rate predicted by Equation (14) would

depend upon which element is assigned subscript k. The proportionality between ∇X_i^α and p_i

will be demonstrated next.

Expressions for η_k and the Supersaturations dX_i^α

The LSW diffusion solution shows us that K for our case will be $\frac{4}{9}V_m^\beta$ times the product of η of element k (η_k) and the coefficient of $-\nabla X_k^\alpha\big|_{r=a}$ in Equation (14). When both precipitate and matrix are essentially pure substances, as in the original LSW theory, η of the precipitate species is equal to $2\sigma\Omega X_\infty/RT$. However, this is not true when matrix and precipitate have similar compositions. Nor is the corresponding increase in chemical potential necessarily equal to $2\sigma\Omega/r$ [10]. To determine η_k, we follow Reference [10] and write the changes in $d\mu_i^\alpha$ and $d\mu_i^\beta$ in terms of corresponding departures from planar-interface X_i^α and X_i^β:

$$d\mu_i^\alpha = \sum_{j \neq k} \left[\left(\frac{\partial \mu_i^\alpha}{\partial X_j^\alpha} \right)_{T,P,X_{m \neq j,k}^\alpha} \right] dX_j^\alpha \tag{15}$$

and

$$d\mu_i^\beta = \sum_{j \neq k} \left[\left(\frac{\partial \mu_i^\beta}{\partial X_j^\beta} \right)_{T,P,X_{m \neq j,k}^\beta} \right] dX_j^\beta + \overline{V}_j^\beta dP^\beta, \tag{16}$$

where dP^β is the increase in pressure on precipitates of radius r due to interfacial tension. To maintain local equilibrium, $d\mu_i^\alpha = d\mu_i^\beta$. Setting Equations (15) and (16) equal, multiplying by X_i^β, and summing over all i,

$$\sum_{i=1}^{n} \left\{ \sum_{j \neq k} X_i^\beta \left[\left(\frac{\partial \mu_i^\alpha}{\partial X_j^\alpha} \right)_{T,P,X_{m \neq j,k}^\alpha} \right] dX_j^\alpha \right\} = \sum_{i=1}^{n} \left\{ \sum_{j \neq k} X_i^\beta \left[\left(\frac{\partial \mu_i^\beta}{\partial X_j^\beta} \right)_{T,P,X_{m \neq j,k}^\beta} \right] dX_j^\beta \right\} + V_m^\beta dP^\beta. \tag{17}$$

By the Gibbs-Duhem equation, the summation on the right-hand side of Equation (17) is equal to zero [10]. In addition, for constant activity coefficients,

$$\left(\frac{\partial \mu_i^\alpha}{\partial X_j^\alpha} \right)_{T,P,X_{m \neq jk}^\alpha} = \frac{RT}{X_i^\alpha}, \ i = j; \ 0, \ i \neq j \neq k; \ \text{and} \ -\frac{RT}{X_k^\alpha}, \ i = k \ . \tag{18}$$

Therefore, Equation (17) becomes

$$\sum_{i=1}^{n} \frac{X_i^\beta}{X_i^\alpha} dX_i^\alpha = \frac{V_m^\beta}{RT} dP^\beta \ . \tag{19}$$

From conservation of matter, $\sum\limits_{i=1}^{n} dX_i^{\alpha} = 0$. Subtracting this expression from the left-hand side

of Equation (19), rearranging, and using $dX_i^{\alpha} = \frac{p_i}{p_k} dX_k^{\alpha}$ (see Appendix),

$$dX_k^{\alpha} = \frac{p_k V_m^{\beta} dP^{\beta}}{RT \sum\limits_{i=1}^{n} \frac{p_i^2}{X_i^{\alpha}}}. \tag{20}$$

Now, using $dP^{\beta} = 2\sigma d(1/r)$, we can see that

$$\eta_k = \frac{2\sigma p_k V_m^{\beta}}{RT \sum\limits_{i=1}^{n} \frac{p_i^2}{X_i^{\alpha}}}. \tag{21}$$

Note that p_k and η_k have the same sign. Therefore, as in the LSW theory, α adjacent to a

precipitate is enriched in elements that partition to the precipitate and depleted in elements that

partition to the matrix. Also, because $\nabla X_i^{\alpha} \propto dX_i^{\alpha}$, Equation (21) shows that $\nabla X_i^{\alpha} \propto p_i$ for

all i, as required for Equation (14) to be valid. An additional implication of Equation (21) is that

for elements that partition to the matrix (p_i negative), μ_i^{α} is actually *lower* adjacent to

precipitates of finite radius than adjacent to a planar interface, and it *increases* as precipitates

coarsen. Because of the Gibbs-Duhem equation, this situation also holds true in the classic

LSW situation (*i.e.*, when matrix and precipitate are essentially pure, insoluble materials), but is

seldom noted [6].

Final Expression for *K*

Combining Equations (1) through (4), (14), and (21),

$$K = \frac{8}{9} \left[\frac{(DC)_{eff} \, \sigma \left(V_m^{\beta} \right)^2}{RT} \right]. \tag{22}$$

Equation (22) is identical in form to Reference [7]'s result for stoichiometric

compounds, and can be simplified under some circumstances. For example, if β in a binary

alloy is essentially pure B and α is essentially pure A, then $p_A = -1$, $p_B = 1$, and $X_B^\alpha \ll X_A^\alpha$. Unless $D_A \ll D_B$, ψ_A is much smaller than ψ_B, and Equation (22) reduces to the standard LSW equation. Under the same conditions, Equation (21) reduces to the LSW expression for η.

Variation of Mean-Field Supersaturation with Time

References [1] and [11] note a rearrangement of Equations (21) and (22) that is useful for determining σ from coarsening studies. Following their reasoning, we can write the mean-field supersaturation in the matrix as a function of $<r>$:

$$X_k^\alpha(<r>) - X_k^\alpha(\infty) = \frac{\eta_k}{<r>} \, . \tag{23}$$

We then define $X_k^\alpha(<r>) - X_k^\alpha(\infty) = \Delta_k$ and combine Equations (22) and (23) to obtain

$$\left(\frac{1}{\Delta_k}\right)^3 - \left(\frac{1}{\Delta_k}\right)_o^3 = \frac{K}{\eta_k^3}(t - t_o) \, . \tag{24}$$

Defining $\frac{K}{\eta_k^3} = \chi_k$, we can see that χ_k is the slope of $\frac{1}{\Delta_k^3}$ versus time. Reference [11] notes that by measuring both $<r>$ and X_i^α as a function of time, one may determine K and χ_k empirically, then find η_k from $K/\chi_k = (\eta_k)^3$, which leads to an equation that we may use to calculate σ without knowing the diffusivities:

$$\sigma = \frac{\left(RT \sum_{i=1}^{n} \frac{p_i^2}{X_i^\alpha}\right)\left[\frac{K}{\chi_k}\right]^{\frac{1}{3}}}{2 V_m^\beta p_k} \, . \tag{25}$$

Similarly, we can determine $(DC)_{eff}$ without knowing σ via

$$(DC)_{eff} = \frac{9\left(p_k^3 K^2 \chi_k\right)^{\frac{1}{3}}}{4 V_m^\beta \sum_{i=1}^{n} \frac{p_i^2}{X_i^\alpha}} \, . \tag{26}$$

3. COMPARISON WITH PUBLISHED STUDIES

Equation (22) is valid only to the extent that p_i may be treated as constants. We can address this issue by considering Reference [11]'s data on concentration of Al as a function of time in the γ matrix of Ni-Al alloys. Reference [11] found that at 715°C, X_{Al}^{γ} dropped from 0.125 after 0.5 hours (the first data point) to 0.123 after 96 hours, by which time X_{Al}^{γ} was essentially indistinguishable from the equilibrium concentration. The mole fraction of Al in γ' is 0.232 [12], from which we can see that p_{Al} was within 2% of the equilibrium value throughout Reference [11]'s experiment. Because $(DC)_{eff}$ varies with the sum of squares of p_i, the error incurred by assuming constant p_i should be on the order of 5%, which is usually negligible.

Few authors of coarsening studies have provided compositions of both matrix and precipitate, as needed for use of Equations (22) and (25). Among those who did were Ardell and his co-workers [11,12] for Ni-Al alloys, Davies *et al.* [13] for Ni-Co-Al alloys, and Giamei and Anton [3] for a Re-containing Ni-base superalloy.

Reference [11]'s data are particularly valuable because the author measured both X_{Al}^{γ} and $<r>$ as a function of time, thereby enabling us to compare σ values obtained from Equations (22) and (25). Calculation of σ from Equation (25) is summarized in Table 1. $V_m^{\gamma'}$ was assumed to be 6.79 x 10^{-6} m^3 per mole of atoms, corresponding to a lattice parameter of 3.56 x 10^{-10} m. Resulting σ values are on the order of 0.01 J/m^2. For comparison with later results, Table 1 also gives values of $(DC)_{eff}$ calculated from Equation (26).

Tables 2 through 4 summarize calculation of σ from Equation (22). $(DC)_{eff}$ values given in Table 4 were calculated from Equation (10) using diffusion parameters presented in Table 2. Values presented in Table 2 provide only approximate intrinsic diffusivities for the alloys considered in this study because diffusion parameters for Al, Ti, and W were determined

by [14] from dilute binary Ni-base alloys, and values for Co, Cr, and Re are assumed equal to those of Ni, Ti, and W, respectively. C^γ was taken as 1.47×10^5 moles of atoms per m^3, corresponding to a lattice parameter of 3.56×10^{-10} m. K in Table 4 is the experimentally determined slope of $(\overline{a}/2)^3$ vs. t, where $\overline{a}$ is the average length of the sides of γ' cubes. Calculated values of σ presented in Table 3 were determined by setting the measured K equal to the right-hand side of Equation (22) and solving for σ. Coarsening rates were not corrected for volume fraction because existence of a volume-fraction effect in γ' is controversial [13,15,16].

A study of Table 3 shows that ψ_{Al} is rarely much larger than that of other elements. Because ψ is a measure of an element's contribution to coarsening resistance, this result suggests that Al diffusion may not truly control coarsening of γ', as is often assumed. Instead, ψ values for Co and other elements that partition to the matrix are often fully comparable to ψ_{Al}, suggesting that these elements can be as important as Al.

By comparing entries for Reference [11]'s data in Tables 1 and 4, we can see that $(DC)_{eff}$ values calculated from Equation (10) agree well with values from Equation (26). Similarly, σ values from Reference [11]'s data in Table 4 agree well with corresponding values from Table 1. With the exception of alloy 1444 + 4Re, σ values in Table 4 also agree reasonably well with Reference [17]'s rough estimate of 0.03 J/m^2. In contrast, σ for 1444 + 4Re is 0.16 J/m^2, approximately an order of magnitude larger than values for the Ni-Al and Ni-Co-Al alloys.

4. DISCUSSION

Like the standard LSW equation, Equations (10) and (22) predict that coarsening is inhibited most effectively by elements with low diffusivities and low concentrations in the matrix. However, Equations (10) and (22) also predict that large degrees of partitioning inhibit

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coarsening. This prediction is reasonable, since elements that do not partition need only order into the precipitate's crystal structure rather than diffuse between particles [3].

In addition, because $\psi_i \propto (p_i)^2$, Equation (22) predicts that the algebraic sign of p_i does not affect coarsening. This prediction, too, is reasonable, as low-diffusivity elements can inhibit coarsening as effectively by having to diffuse away from coarsening particles (p_i negative) as by having to diffuse toward them (p_i positive). This prediction supports suggestions by Giamei and Anton and Davies *et al.* about the roles of Co and Re, both of which partition to the matrix.

Although these qualitative predictions are reasonable, there is some discrepancy in the calculated σ values. Ni-Al and Ni-Co-Al alloys gave reasonable, consistent σ values insofar as uncertainties in diffusivities allow, and the agreement between values calculated from Equations (22) and (25) is encouraging. However, the σ value for Giamei and Anton's alloy seems anomalously large. There are several possible causes for this discrepancy, two of which are listed below as hypotheses that can be tested to assess Equation (22)'s validity:

1. Actual diffusivities in 1444 + 4Re may differ considerably from the approximate values used in this calculation.

2. Elastic effects may be important. As described by Voorhees [15], elastic effects not only can modify solute distributions around precipitates, but can create interparticle interactions that overwhelm capillarity-driven coarsening. In this connection, note that among the alloys listed in Tables 3 and 4, only 1444 + 4Re should have a negative lattice-parameter mismatch [3]. Therefore, elastic effects may be qualitatively different in this alloy.

A third possibility, raised by References [11] and [18], is that the MEPR principle is not applicable to coarsening, in which case the differences between calculated σ values would have

no physical meaning. Christian [18] noted that the applicability of the MEPR principle to complex phenomena in general is controversial, and Reference [11] questioned its applicability to coarsening of γ' in particular.

As evidence, Reference [11] noted that $(DC)_{eff}$ values calculated from Reference [11]'s versions of Equations (10) and (26) disagree by considerably more than the uncertainty in diffusivities. However, Reference [11] did not consider effects of partitioning, and its $(DC)_{eff}$ values appear to disagree primarily for that reason. In contrast, $DC)_{eff}$ values calculated in the present study from Reference [11]'s data agree well. This agreement suggests that the MEPR principle's applicability to γ' may merit reconsideration.

As noted in the Introduction, some works have applied the LSW equation to coarsening of γ' by assuming that one element (usually Al) controls coarsening. This assumption led to an inconsistent application of the LSW equation in that the calculations used Ω of Ni_3Al and D of Al. A possible reason for this inconsistency is the thought that Ni_3Al dissolves stoichiometrically in γ, yielding one mole of Al for every mole of Ni_3Al. However, the ratio of Al released to γ' dissolved is given more realistically by p_{Al}. In addition, it is not clear that Al alone controls coarsening in these alloys. For this reason, σ values calculated by other references may need to be reconsidered.

5. SUMMARY

The MEPR principle leads naturally to a modified LSW equation that makes correct qualitative predictions about the role of partitioning. The modified equation reduces to the standard LSW equation under appropriate conditions. Interfacial energies calculated from the modified equation provide testable hypotheses about diffusivities and elastic interactions in Re-containing alloys. Although it is commonly believed that diffusion of Al controls coarsening of γ', diffusion of elements that partition to the matrix may be equally important.

APPENDIX
SOME ASPECTS OF CONSERVATION OF MATTER DURING COARSENING

Proportionality between Supersaturations (dX_i^α) and Partitionings (p_i)

If equilibrium compositions of matrix phase α and precipitate phase β separated by a planar interface are X_i^α and X_i^β respectively, then the inverse lever rule, (*i.e.* conservation of matter), shows that the fraction of atoms contained in the β phase of an alloy with bulk composition X_i^o is given by $f^\beta = (X_i^o - X_i^\alpha)/p_i$, where $p_i = X_i^\beta - X_i^\alpha$. If β is in the form of precipitates of radius r, both the compositions and f^β will change [10] (although the changes in X_i^β are ignored in the LSW theory).

Again from conservation of matter, the changes in composition and f^β are related by

$$X_i^\alpha f^\alpha + X_i^\beta f^\beta = (X_i^\alpha + dX_i^\alpha)(f^\alpha + df^\alpha) + (X_i^\beta + dX_i^\beta)(f^\beta + df^\beta). \tag{A1}$$

A first-order expansion of df^β gives

$$df^\beta = \frac{\partial f^\beta}{\partial X_i^\alpha} dX_i^\alpha + \frac{\partial f^\beta}{\partial X_i^\beta} dX_i^\beta \tag{A2}$$

which leads to

$$dX_i^\beta = -\left[\frac{\delta f^\beta}{f^\beta} p_i + \frac{f^\alpha}{f^\beta} dX_i^\alpha \right]. \tag{A3}$$

Substituting this expression for dX_i^β into Equation (A1), and realizing that $df^\beta = - df^\alpha$,

$$dX_i^\alpha = - p_i df^\beta. \tag{A4}$$

This result shows that supersaturations are proportional to elements' degrees of partitioning.

Consistency between Supersaturations and Flux Ratios

For simplicity, the discussion presented here deals with a binary alloy, but the principles hold true for a multicomponent alloy. It is often believed that during coarsening of particles of A_aB_b in a binary A-B alloy, the fluxes J_A and J_B are in the ratio $J_A/J_B = a/b$. However, this idea violates conservation of matter, which requires that $J_A + J_B = 0$ (both within the matrix and at particle/matrix interfaces) if we ignore vacancy fluxes [19], as the LSW theory does. From $J_A + J_B = 0$, conservation of matter requires that $J_A = -J_B$, and that $J_A/J_B = -1$. Therefore, it is not physically possible for J_a/J_b to equal a/b in a binary alloy. This point was recognized implicitly by [6].

Instead, as was shown in the main text [Equation (5)], fluxes must be proportional to the elements' respective p_i. (In a binary alloy, $p_A = -p_B$; therefore, $J_A/J_B = -1$.) This proportionality maintains consistency in two important ways: (a) since $\Sigma p_i = 0$, $\Sigma J_i = 0$, confirming conservation of matter; and (b) since both J_i and supersaturations are proportional to p_i, $J_i \propto \nabla X_i^{\alpha}$ for all i (because ∇X_i^{α} is proportional to the difference between mean-field and interfacial supersaturations of i, both of which supersaturations are proportional to p_i).

One important (and surprising) implication of the fact that both J_i and ∇X_i^{α} are proportional to p_i is that the effective diffusivity must be the same for every element. However, that is exactly the result obtained from nonequilibrium thermodynamics in Equation (10) of the main text, again demonstrating self-consistency.

Consistency between Flux Ratios and Coarsening Rates

The self-consistency demonstrated thus far (*i.e.*, that both the supersaturations dX_i^{α} and the fluxes J_i are proportional to p_i) is essential, but not sufficient. It is also necessary to demonstrate that fluxes proportional to p_i are consistent with the mass transfers that occur during coarsening. This demonstration was made in the discussions that led to Equation (5) in the main text. Therefore, the overall conservation of matter is consistent: supersaturations are

proportional to p_i, thereby producing fluxes proportional to p_i. In turn, fluxes proportional to p_i are exactly those needed to transform the α matrix into β (or conversely, to transform β into α when a smaller-than-average particle dissolves). This necessary consistency is violated at several points by the idea that $J_A/J_B = a/b$ during coarsening of A_aB_b in a binary A-B alloy.

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Table 1. Calculation of σ and $(DC)_{eff}$ from K and χ_{Al} (Ni–6.35 and Ni-6.5 wt. % Al [11][†])

Element	X_i^{γ}	$X_i^{\gamma'}$	p_i	K, m³/sec ($\times 10^{30}$)	χ_{Al}, sec⁻¹	η_{Al}, m ($\times 10^{11}$)	σ, J/m²	$(DC)_{eff}$, moles/m-sec
898K:								
Ni	0.869	0.768	-0.101					
				2.25	868	1.37	0.0067	6.12×10^{-14}
Al	0.131	0.232	0.101					
988K:								
Ni	0.859	0.768	-0.091					
				65.4	28,500	1.32	0.0060	2.18×10^{-12}
Al	0.141	0.232	0.091					

† $X_i^{\gamma'}$ was calculated from Figure 1 of Reference [12].

Table 2. Values used for each
element in the diffusivity equation
$D = D_o \exp(-Q/RT)$ [14]

Element	D_o, m^2/sec	Q, kJ/mole
Ni	1.27 x 10^{-4}	279
Al	1.87 x 10^{-4}	268
Ti	8.6 x 10^{-5}	257
W	1.11 x 10^{-3}	321
Co	Assumed equal to Ni values[†]	
Cr	Assumed equal to Ti values[†]	
Re	Assumed equal to W values[†]	

[†] By present author.

Table 3. Calculation of ψ_i values from data of References [3,11,12,13]

Element	X_i^{γ}	$X_i^{\gamma\,'}$	p_i	D_i, m²/sec	ψ_i, sec/m²
Ardell [11], Ni-6.35 and Ni-6.5 wt. % Al†					
898K:					
Ni	0.869	0.768	-0.101	7.48×10^{-21}	1.56×10^{18}
Al	0.131	0.232	0.101	4.81×10^{-20}	1.62×10^{18}
988K:					
Ni	0.859	0.768	-0.091	2.25×10^{-19}	4.25×10^{16}
Al	0.141	0.232	0.091	1.26×10^{-18}	4.62×10^{16}
Ardell et al. [12], Ni–6.7 wt. % Al, 1023K†					
Ni	0.867	0.770	-0.097	7.20×10^{-19}	1.50×10^{16}
Al	0.133	0.230	0.097	3.86×10^{-18}	1.83×10^{16}
Davies et al. [13], Ni-Co-Al Alloys, 1073K‡					
Alloy Ni 10–13					
Ni	0.792	0.694	-0.098	3.32×10^{-18}	3.65×10^{15}
Co	0.0935	0.0605	-0.033	3.32×10^{-18}	3.51×10^{15}
Al	0.114	0.245	0.131	1.68×10^{-17}	8.94×10^{15}
Alloy Ni 22–13					
Ni	0.665	0.652	-0.013	3.32×10^{-18}	7.69×10^{13}
Co	0.238	0.109	-0.129	3.32×10^{-18}	2.10×10^{16}
Al	0.0969	0.239	0.142	1.68×10^{-17}	1.24×10^{16}
Alloy Ni 37–12					
Ni	0.508	0.541	0.0325	3.32×10^{-18}	6.25×10^{14}
Co	0.407	0.224	-0.183	3.32×10^{-18}	2.48×10^{16}
Al	0.0852	0.2355	0.150	1.68×10^{-17}	1.58×10^{16}
Alloy Ni 49–12					
Ni	0.379	0.485	0.106	3.32×10^{-18}	8.87×10^{15}
Co	0.516	0.285	-0.231	3.32×10^{-18}	3.13×10^{16}
Al	0.105	0.231	0.126	1.68×10^{-17}	8.98×10^{15}
Giamei and Anton [3], 1444 + 4Re, 1338K					
Ni	0.711	0.741	0.030	1.63×10^{-15}	7.77×10^{11}
Al	0.013	0.105	0.092	6.44×10^{-15}	1.01×10^{14}
Ti	0.010	0.028	0.018	7.96×10^{-15}	4.11×10^{12}
W	0.0654	0.0708	0.0054	3.26×10^{-16}	1.37×10^{12}
Cr	0.182	0.056	- 0.126	7.96×10^{-15}	1.09×10^{13}
Re	0.0193	0.000	- 0.0193	3.26×10^{-16}	5.92×10^{13}

† $X_i^{\gamma\,'}$ calculated from Figure 1 of Reference [12].

‡ Mole fractions were calculated from Figure 8 of Reference [13].

Table 4. Calculation of σ from data of References [3,11,12,13]

$\Sigma \psi_\iota$ (sec/m^2)	$(DC)_{eff}{}^\dagger$ (mole/m-sec)	Actual K (m^3/sec)	Calculated σ (J/m^2)
Ardell [11], Ni–6.35 and Ni–6.5 wt. % Al			
898K:			
3.18×10^{16}	4.62×10^{-14}	2.25×10^{-30}	0.0089
988K:			
8.86×10^{16}	1.66×10^{-12}	6.55×10^{-29}	0.0079
Ardell *et al.* [12], Ni–6.7 wt. % Al, 1023K			
3.33×10^{16}	4.41×10^{-12}	1.72×10^{-28}	0.0081
Davies *et al.* [13], Ni-Co-Al Alloys, 1073K			
Alloy Ni 10–13			
1.61×10^{16}	9.13×10^{-12}	2.87×10^{-28}	0.0068
Alloy Ni 22–13			
3.34×10^{16}	4.40×10^{-12}	2.65×10^{-28}	0.013
Alloy Ni 37–12			
4.12×10^{16}	3.56×10^{-12}	2.04×10^{-28}	0.012
Alloy Ni 49–12			
4.91×10^{16}	2.99×10^{-12}	1.80×10^{-28}	0.013
Giamei and Anton [3], 1444 + 4Re, 1338K‡			
1.77×10^{14}	8.32×10^{-10}	4.86×10^{-25}	0.16

† Calculated from Equation (10).
‡ K determined by plotting values for $t \geq 2$ hours from Table III of Reference [3].

COMMENTS ON "OSTWALD RIPENING GROWTH RATE FOR NONIDEAL SYSTEMS WITH SIGNIFICANT MUTUAL SOLUBILITY"

J. A. SMITH

References [1] and [2] present two extensions of the LSW theory of precipitate coarsening: (1) to alloys with large degrees of mutual solubility between precipitate and matrix; and (2) to alloys whose deviations from Henrian behavior make the LSW theory's assumption of constant activity coefficients untenable.

Although these ideas are potentially valuable, [1] and [2] contain inconsistencies and conceptual errors that restrict their usefulness and invalidate some of their equations. The most important of these errors are (1) confusion of thermodynamic and kinetic influences upon local supersaturations around precipitates; (2) diffusive flux ratios that conflict with their thermodynamic treatment; and (3) assumptions about diffusivities that lead to further inconsistencies.

Thermodynamic versus Kinetic Influences

An important part of Reference [1] and [2]'s treatment is determining the degree of supersaturations around precipitates in alloys that deviate from Henrian behavior (*i.e.*, whose activity coefficients are not constant). Reference [1] shows that it is straightforward to do so for binary alloys. However, Reference [2] notes that it is not possible to determine supersaturations in ternary alloys from thermodynamics alone; instead, one must also use mass-balance

information. Rather than do so, [2] simplifies the derivation by dividing it into various cases. In some of these cases, the supersaturation of one element or another is assumed to be essentially equal to zero. Reference [2] states that this situation can arise due to rapid diffusion.

This idea is erroneous firstly because it violates the assumption of local equilibrium on which the LSW theory is based. Equilibrium supersaturations associated with discrete precipitates depend only upon capillarity effects and conservation of matter; they are independent of kinetics. Secondly, as will be shown later, diffusive fluxes of the alloy's elements must have definite ratios that are determined by mass balances. Conservation of matter dictates that one element cannot diffuse so rapidly as to reduce its supersaturation to essentially zero without the other elements doing likewise. That being the case, one cannot assume arbitrarily that only one element's supersaturation is negligible.

In addition, this assumption is unnecessary because one can determine the supersaturations readily by establishing firstly that the supersaturation of any element i is proportional to its degree of partitioning between matrix and precipitate. To show that this is so, consider an alloy in which equilibrium compositions of matrix phase α and precipitate phase β separated by a planar interface are X_i^α and X_i^β respectively. From conservation of matter, the fraction of atoms contained in the β phase of an alloy with bulk composition X_i^o is given by $f^\beta = (X_i^o - X_i^\alpha)/p_i$, where $p_i = X_i^\beta - X_i^\alpha$. If β is in the form of precipitates of radius r, both the compositions and f^β will change [3].

From conservation of matter, these changes are related by

$$X_i^\alpha f^\alpha + X_i^\beta f^\beta = (X_i^\alpha + \delta X_i^\alpha)(f^\alpha + \delta f^\alpha) + (X_i^\beta + \delta X_i^\beta)(f^\beta + \delta f^\beta). \tag{1}$$

A first-order expansion of δf^β gives

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$$\delta f^{\beta} = \frac{\partial f^{\beta}}{\partial X_i^{\alpha}}\delta X_i^{\alpha} + \frac{\partial f^{\beta}}{\partial X_i^{\beta}}\delta X_i^{\beta} \tag{2}$$

which leads to

$$\delta X_i^{\beta} = -\left[\frac{\delta f^{\beta}}{f^{\beta}}p_i + \frac{f^{\alpha}}{f^{\beta}}\delta X_i^{\alpha}\right]. \tag{3}$$

Substituting this expression for δX_i^{β} into Equation (1), and realizing that $\delta f^{\beta} = -\delta f^{\alpha}$, we arrive after considerable manipulation at

$$\delta X_i^{\alpha} = -p_i \delta f^{\beta}. \tag{4}$$

To maintain local equilibrium, chemical potentials must remain equal in both phases. Therefore, departures from planar-interface chemical potentials must be equal: $\delta \mu_i^{\alpha} = \mu_i^{\alpha}(r) - \mu_i^{\alpha}(r = \infty) = \delta \mu_i^{\beta}$, or, in terms of the supersaturations [4],

$$\sum_{j \neq k}\left[\left(\frac{\partial \mu_i^{\alpha}}{\partial X_j^{\alpha}}\right)_{T,P,X_{m \neq j,k}^{\alpha}}\right]\delta X_j^{\alpha} = \sum_{j \neq k}\left[\left(\frac{\partial \mu_i^{\beta}}{\partial X_j^{\beta}}\right)_{T,P,X_{m \neq j,k}^{\beta}}\right]\delta X_j^{\beta} + \bar{V}_i^{\beta}\delta P^{\beta}, \tag{5}$$

where δP^{β} is the pressure on β precipitates of radius r due to interfacial tension.

If we now multiply both sides of Equation (5) by X_i^{β} and sum over all i, the summations on the right-hand side are equal to zero because of the Gibbs-Duhem equation [4], resulting in

$$\sum_i \left\{X_i^{\beta}\sum_{j \neq k}\left[\left(\frac{\partial \mu_i^{\alpha}}{\partial X_j^{\alpha}}\right)_{T,P,X_{m \neq j,k}^{\alpha}}\right]\delta X_j^{\alpha}\right\} = \Omega^{\beta}\delta P^{\beta}, \tag{6}$$

where Ω^{β} is the molar volume of β. Also from the Gibbs-Duhem equation,

3

$$\sum_i \left\{ X_i^\alpha \sum_{j \neq k} \left[\left(\frac{\partial \mu_i^\alpha}{\partial X_j^\alpha} \right)_{T,P,X_{m \neq jk}^\alpha} \right] \delta X_j^\alpha \right\} = 0 \ . \tag{7}$$

Subtracting Equation (7) from Equation (6), and using $p_i = X_i^\beta - X_i^\alpha$,

$$\sum_i \left\{ p_i \sum_{j \neq k} \left[\left(\frac{\partial \mu_i^\alpha}{\partial X_j^\alpha} \right)_{T,P,X_{m \neq j,k}^\alpha} \right] \delta X_j^\alpha \right\} = \Omega^\beta \delta P^\beta \ . \tag{8}$$

We next write the left-hand side of Equation (8) in terms of a single element's supersaturation. We do so by making use of the proportionality between supersaturations and p_i. If we write all supersaturations in terms of that of element k, the element whose mole fraction was not held constant in the above derivatives, then the supersaturation of any element i is given by $\delta X_i^\alpha = (p_i/p_k)\delta X_k^\alpha$. Substituting this result into Equation (8), and using $\mu_i^\alpha = \mu_i^o + RT \ln (X_i^\alpha \gamma_i^\alpha)$,

$$\left(\frac{\delta X_k^\alpha}{p_k} \right) \sum_i \left\{ p_i \left[\sum_{j \neq k} p_j \left(\frac{\partial \ln X_i^\alpha}{\partial X_j^\alpha} \right)_{T,P,X_{m \neq jk}^\alpha} + \sum_{j \neq k} p_j \left(\frac{\partial \ln \gamma_i^\alpha}{\partial X_j^\alpha} \right)_{T,P,X_{m \neq jk}^\alpha} \right] \right\} = \frac{\Omega^\beta \delta P^\beta}{RT} \ . \tag{9}$$

Now, $\partial \ln X_i^\alpha / \partial X_j^\alpha = 1/X_i^\alpha$ for $i = j$, 0 for $i \neq j \neq k$, and $-1/X_k^\alpha$ for $i = k$. Therefore, using $\delta P^\beta = 2\sigma/r$,

$$\delta X_k^\alpha = \frac{2\sigma p_k \Omega^\beta}{rRT \sum_i p_i \left(\frac{p_i}{X_i^\alpha} + \sum_{j \neq k} p_j \left(\frac{\partial \ln \gamma_i^\alpha}{\partial X_j^\alpha} \right)_{T,P,X_{m \neq j,k}^\alpha} \right)} \ . \tag{10}$$

The derivatives of γ_i^α can now be expressed as appropriate to the thermodynamic model for the alloy.

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<u>Diffusive Flux Ratios</u>

According to Reference [1], ratios of diffusive fluxes J_i through the matrix are equal to the stoichiometric ratios in the β phase:

$$\frac{J_A}{J_B} = \frac{X_A^\beta}{X_B^\beta} \; . \qquad\qquad (11)$$

This idea is erroneous because Equation (11) implies that in a binary alloy, both elements' fluxes must have the same algebraic sign. However, conservation of matter requires that $\delta X_A^\alpha = -\delta X_B^\alpha$. That is, if the matrix next to a precipitate is enriched in one element, it must be depleted in the other. Therefore, the concentration gradients between precipitates must be equal and opposite, and so must the fluxes in a near-equilibrium situation like Ostwald ripening. According to Equation (11) fluxes are not proportional to the supersaturations that induce them, thereby violating one of Reference [1]'s assumptions.

A second argument against Equation (11) is that it implies an unreasonable description of events at the matrix/precipitate interface. We can see this by considering a monolayer containing N moles of atoms in the α phase at the interface with a β precipitate. According to the model from which Equation (11) arises, this monolayer of α is replaced completely by one of β upon arrival of NX_A^β moles of A and NX_B^β moles of B from the matrix. The original atoms that comprised the α monolayer must all diffuse away or move away by fluid flow. Hence, $2N$ moles of atoms must be transported to form N moles of β.

A more-reasonable mechanism suggests itself from the observation that if supersaturations are small compared to p_i, the monolayer will contain NX_i^α moles of each element before transforming and NX_i^β afterward. Hence, the layer of α can transform to β by incorporating Np_B moles of B (assuming B is the majority component in β) and rejecting Np_A

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moles of A. By this mechanism, the same amount of β is formed with much less mass transport.

In addition, the fluxes of A and B produced by this mechanism are automatically opposite in sign and proportional to their respective supersaturations because both δX_i^α and J_i are proportional to p_i. Extending this argument to multicomponent solutions gives us

$$\frac{J_i}{J_k} = \frac{p_i}{p_k} . \tag{12}$$

The proportionality between supersaturations [Equation (10)] and the diffusive fluxes that result from them [Equation (12)] arises from conservation of matter, and is essential to self-consistency of the solution. This self-consistency lends credence to the approach used here.

Assumptions about Diffusivities

Reference [1] assumes that diffusion of the precipitate's majority component is rate-limiting. This rather restrictive requirement detracts from the usefulness of their idea, and is unnecessary because Reference [6] shows how to treat cases in which no single element's diffusivity controls coarsening. In such cases, each element contributes to an "effective" product of mobility and matrix concentration. Reference [6]'s treatment can be extended to alloys with substantial mutual solubility between matrix and precipitate, with the result that the effective product of concentration and mobility is [5]

$$(MC)_{eff} = \frac{C^\alpha}{\sum_i \dfrac{p_i^2}{M_i X_i^\alpha}} , \tag{13}$$

where C^α is the total number of atoms per unit volume in α, and M_i is the mobility of i. Using this "effective" value, the flux of element k is given by

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$$J_k = -p_k \big[(MC)_{\textit{eff}}\big]\sum_i p_i \nabla \mu_i^\alpha \ . \tag{14}$$

Because supersaturations are proportional to p_i, so too are the ∇X_i^α. Therefore, we can proceed as in [5] to write Equation (14) in terms of ∇X_k^α, with the result that

$$J_k = -\big[(MC)_{\textit{eff}}\big]RT\sum_i p_i\left[\frac{p_i}{X_i^\alpha} + \sum_{j \neq k} p_j\left(\frac{\partial \ln \gamma_i^\alpha}{\partial X_j^\alpha}\right)_{T,P,X_{m \neq j,k}^\alpha}\right]\nabla X_k^\alpha \ . \tag{15}$$

Net Effect of Non-Henrian Behavior Upon Coarsening

The net effect of non-Henrian behavior can be seen by writing the coarsening rate of an individual precipitate particle in terms of J_k. As shown earlier, one mole of α-phase atoms is converted to one mole of β-phase atoms for every p_k moles of element k transferred. Therefore, the coarsening rate of a particle of radius a is given by

$$\frac{\mathrm{d}a}{\mathrm{d}t} = -\frac{\Omega^\beta}{p_k}\big[(MC)_{\textit{eff}}\big]RT\sum_i p_i\left[\frac{p_i}{X_i^\alpha} + \sum_{j \neq k} p_j\left(\frac{\partial \ln \gamma_i^\alpha}{\partial X_j^\alpha}\right)_{T,P,X_{m \neq j,k}^\alpha}\right]\nabla X_k^\alpha \big|_{r=a} \ . \tag{16}$$

When $\mathrm{d}a/\mathrm{d}t$ is expressed in this form, the LSW rate constant K is equal to the product of $4/9\Omega^\beta$, the coefficient of $-\nabla X_k^\alpha$ in Equation (16), and the coefficient of $1/r$ in Equation (10). As a result, the thermodynamic terms in Equations (10) and (16) cancel, leaving

$$K = \frac{8}{9}\big[(MC)_{\textit{eff}}\big]\sigma\big(\Omega^\beta\big)^2 \ . \tag{17}$$

This result shows that when K is written in terms of mobilities, the change in supersaturation that accrues from non-Henrian behavior does not appear. This result is reasonable because the driving force for coarsening is the chemical-potential difference between precipitates of different radii, which difference is equal to $2\sigma\Omega^\beta[\Delta(1/r)]$ regardless of the resulting degree of supersaturation in the matrix.

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However, if we write K in terms of diffusivities, the non-Henrian behavior does enter the solution. For binary alloys, the effect is exactly as given by [1] because M_i in a binary alloy is given by $M_i = D_i/RT(1 + \mathrm{d}\ln\gamma_i^\alpha / \mathrm{d}\ln X_i^\alpha)$. In Reference [1]'s notation, $\mathrm{d}\ln\gamma_i^\alpha / \mathrm{d}\ln X_i^\alpha = -2X_A^\alpha X_B^\alpha l_{AB}$, where l_{AB} is a thermodynamic interaction parameter. $(MC)_{\mathit{eff}}$ then becomes

$$(MC)_{\mathit{eff}} = \frac{D_A D_B C^\alpha X_A^\alpha X_B^\alpha}{RT\left(p_A^2 D_B X_B^\alpha + p_B^2 D_A X_A^\alpha\right)\left(1 - 2X_A^\alpha X_B^\alpha l_{AB}\right)} . \tag{18}$$

Comparing Equation (18) with Reference [1]'s Equation (24) shows that Reference [1] is correct regarding the inverse relationship between coarsening rate and the factor $1 - 2X_A^\alpha X_B^\alpha l_{AB}$ in binary alloys.

Conclusions

Conceptual errors in Reference [1] and [2]'s treatment, particularly regarding flux ratios, invalidate much of it. However, Reference [1] and [2] are correct about the thermodynamic factor $1 - 2X_A^\alpha X_B^\alpha l_{AB}$ in binary alloys. Reference [1] and [2]'s treatment requires one element's diffusivity to "control" coarsening, but this unnecessarily restrictive requirement is readily avoided by using Reference [6]'s method to determine an "effective" product of concentration and mobility (or diffusivity). By doing so, the LSW equation can be extended to multicomponent alloys with large degrees of solubility between precipitate and matrix. The resulting formulas for show that both supersaturations and fluxes are proportionate to the degree of partitioning, p_i. This result is essential to self-consistency of the solution.

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