

# AN ANALYSIS FOR ONE-PHASE DIFFUSION CONTROLLED DISSOLUTION IN PLANAR COMPOSITES

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**Abstract**—Approximate analytical solutions for one-phase diffusion controlled dissolution of uniformly sized and equispaced stacked plates in an infinite or finite matrix have been worked-out in a manner analogous to the momentum integral method in fluid mechanics. The analysis manifests remarkable agreement with the existing experimental data and rigorous numerical models. Comparison with the present model illustrates that for dissolution in an infinite geometry the linearized gradient assumption of Aaron [2] is more compatible than the stationary interface approximation of Whelan [5]. For the finite geometry cases rationalization of the effects of average composite composition  $C_A$  and solute concentration at the interface  $C_S$  on the starting time for diffusion field overlapping and the completion of dissolution has also been possible. When  $C_A < 0.75 C_S$ , a simple generalized plot can estimate the time for complete dissolution in many binary alloy systems. This generalization can also account for the size variation of second phase plates in the composites.

**Résumé**—Nous avons obtenu des solutions analytiques approchées pour la dissolution (contrôlée par la diffusion dans une phase) de plaquettes de taille uniforme régulièrement espacées, dans une matrice infinie ou finie, par une méthode analogue à celle de l'intégrale du moment en mécanique des fluides. Cette analyse est en accord remarquable avec les résultats expérimentaux et les modèles numériques rigoureux dont on dispose. Si l'on compare avec notre modèle, dans le cas d'une dissolution dans un milieu infini, on peut voir que l'hypothèse d'un gradient linéarisé d'Aaron [2] est meilleure que celle d'une interface stationnaire de Whelan [5]. Dans le cas d'une géométrie finie, nous avons pu rationaliser les effets de la composition moyenne  $C_A$  du composite et de la concentration de soluté  $C_S$  à l'interface sur le temps nécessaire à la superposition des champs de diffusion et à la complète dissolution. Lorsque  $C_A < 0.75 C_S$ , un simple graphique généralisé permet d'évaluer le temps nécessaire à une dissolution complète, dans de nombreux systèmes binaires. Cette généralisation permet aussi de rendre compte des variations de la taille des plaquettes de seconde phase, dans les composites.

**Zusammenfassung**—Für die diffusionskontrollierte Auflösung von gleichgroßen und gleichmäßig gestapelten Platten in einer unendlichen und einer endlichen Matrix werden analytische Näherungslösungen in einer Art analog der Momentenintegralmethode in der Fluidmechanik ausgearbeitet. Die Analyse ergibt eine bemerkenswerte Übereinstimmung mit den vorhandenen experimentellen Daten und den strengen numerischen Modellen. Der Vergleich mit gegenwärtigen Modellen zeigt, daß bei Auflösung in einer unendlichen Matrix die Annahme eines linearisierten Gradienten von Aaron [2] angemessener ist als die Näherung der stationären Grenzfläche von Whelan [5]. Bei Fällen abgegrenzter Geometrie war es möglich, den Einfluß der mittleren Konzentration  $C_A$  in der Legierung und der Konzentration  $C_S$  an der Grenzfläche auf den Beginn der Überlappung der Diffusionsfelder und den Abschluß der Auflösung zu beschreiben. Für  $C_A < 0,75 C_S$  kann mit einem verallgemeinerten Diagramm die Zeit bis zur vollständigen Auflösung in vielen binären Legierungssystemen berechnet werden. Diese Verallgemeinerung kann auch die Größenänderung der Platten der zweiten Phase in den Legierungen erklären.

## 1. INTRODUCTION

Diffusional dissolution of the second phase in solids is a problem of mass transfer with a mobile interface. When the process involves an array of particles, diffusion occurs in a finite geometry provoking impingement of the diffusion fields on adjacent particles. The present paper will focus attention on the simplified case of the dissolution of planar precipitate particles by diffusion in the matrix. A closed form exact solution of this problem is not yet available. Numerous

investigations have been directed to analyse the situation under various simplifying assumptions and these approximations often remain to be properly justified.

Thomas and Whelan [1] have proposed that dissolution is simply growth in reverse. Later, Aaron and coworkers [2, 3] pointed out that the salient features for the precipitate growth and dissolution are different and therefore, they cannot generally be considered as conjugate processes. In the estimation of the dissolution rate of an isolated precipitate in an infinite matrix Aaron [2] has adopted the linearized gradient

approximation of Zener [4], and Whelan [5] subsequently considers the interface location as time-invariant. Comparison between the models by Aaron and coworkers [3] shows that the stationary interface approximation is the best of the lot.

Closed form expressions for the approximate dissolution rate in the finite systems have been derived by Singh and Flemings [6] as well as Pasparakis and Brown [7]. These authors have presumed that the effect of interface movement is negligible. Singh *et al.* consider that the initial concentration profile slopes away from the precipitate particle, a situation typical to that for coring, and the concentration-distance profile is approximated by the sine function. Pasparakis and Brown on the other hand assume an overlapping diffusion field right from the inception of homogenization.

Rigorous treatment of the dissolution problem is possible by numerical analysis. Computer simulation techniques for the two-phase mobile interface cases have been formulated by Tanzilli and Heckel [8] by using the variable grid-space transformation of Murry and Landis [9], whereas Pabi [10] has introduced the isoconcentration contour migration technique in solving the same problem. These two-phase diffusion models have shown conspicuous agreement with the experimental data for homogenization [10-12], and naturally they are well suited to the single phase cases as well.

Present research attempts to work out a weak solution for the homogenization by one-phase diffusion and predict the solution kinetics with an accuracy comparable to intricate numerical models. The implication of the assumptions in some of the analytical methods and the effects of process variables in dissolution have been studied in the light of the present analysis. The current formulation at the onset assumes a uniform size and distribution of second phase particles, although deviation from uniformity is known [13] to substantially retard the rate of solution. In the subsequent development, an attempt has been made to include the effects of particle size variation.

2. ANALYSIS

2.1 Formulation of the problem

Uniformly sized and internally homogeneous plates of a solute rich second phase are supposed to be stacked at equal intervals in an isotropic matrix phase, as depicted in Fig. 1. The sketch illustrates the positions of the symmetry planes across which mass transfer is nil. *L* is the distance between two successive symmetry elements. The half-thickness of the precipitate plates is *R* (*R* = *l*/2) at time *t* = 0, and that at *t* > 0 is denoted by *S<sub>t</sub>*. The molar volume of both the phases is tentatively taken to be independent of concentration. Average solute content of the composite is *C<sub>A</sub>*. Initial composition of the solvent

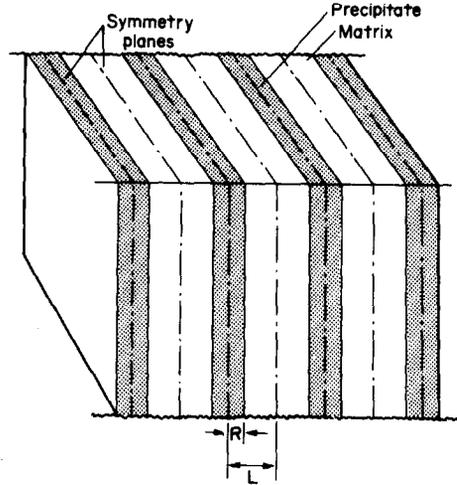


Fig. 1. Sectional view of the stacked plates illustrating the position of symmetry planes across which mass transfer is nil (schematic).

and second phase are *C<sub>M</sub>* and *C<sub>P</sub>*, respectively. As the homogenization starts, *C<sub>S</sub>*, the solute concentration in the matrix at the precipitate-matrix interface attains the equilibrium value given by the phase diagram. The compositions expressed in atomic fraction of solute have been rationalized such that *C<sub>M</sub>* is zero, *C<sub>P</sub>* is unity, and essentially *C<sub>S</sub>* and *C<sub>A</sub>* have the intermediate values.

The time-modulation of the concentration profile adjacent to a dissolving precipitate has been schematically displayed in Fig. 2. Diffusion occurs solely in the matrix phase and the field equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2}, \quad S_t \leq X \leq L, \quad t > 0, \quad (1)$$

is subjected to the initial conditions

$$C(X, t) = C_M = 0, \quad R \leq X \leq L, \quad t = 0, \quad (2)$$

$$C(S_t, t) = C_S, \quad t > 0, \quad (3)$$

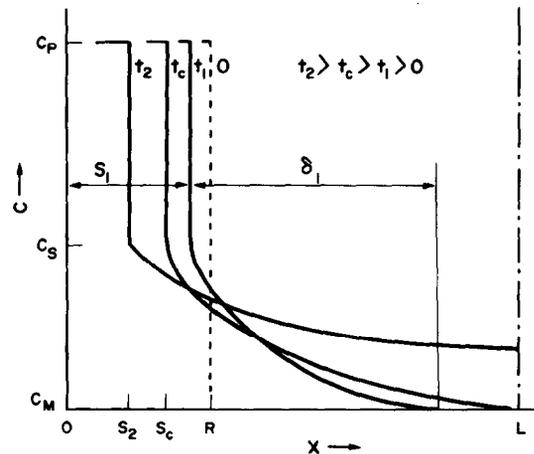


Fig. 2. Schematic time-modulation of solute concentration distribution at time 0, *t<sub>1</sub>*, *t<sub>c</sub>* and *t<sub>2</sub>*. *δ<sub>1</sub>* is the diffusion layer thickness at *t<sub>1</sub>*. *S<sub>1</sub>*, *S<sub>c</sub>* and *S<sub>2</sub>* are the half-thickness of second phase at time *t<sub>1</sub>*, *t<sub>c</sub>* and *t<sub>2</sub>*, respectively.

where  $D$  is the interdiffusion coefficient and  $C(X, t)$  is the composition at a distance  $X$  from the nearest second phase symmetry plane at time  $t$ .

The mass-balance condition at the interface can be expressed as

$$D \cdot \frac{\partial C}{\partial X}(S_t, t) = (C_p - C_s) \frac{dS_t}{dt} \quad (4)$$

It is often more convenient to eliminate  $S_t$  from (4) and derive an alternative expression. Differentiation of (3) with respect to  $t$  gives

$$\frac{\partial C}{\partial X} \cdot \frac{dS_t}{dt} + \frac{\partial C}{\partial t} = 0, \quad X = S_t \quad (5)$$

By eliminating  $dS_t/dt$  between (4) and (5), and substituting equation (1) it is readily found that

$$\left(\frac{\partial C}{\partial X}\right)^2 = -(C_p - C_s) \frac{\partial^2 C}{\partial X^2}, \quad X = S_t \quad (6)$$

The present analysis introduces the concept of a phenomenological diffusion layer thickness  $\delta_t$ , which is defined as the distance from the interface beyond which the initial solute distribution remains practically unperturbed by the applied diffusion field. This penetration distance is analogous to the boundary layer thickness in fluid mechanics [14] and thermal layer thickness in heat transfer [15].  $\delta_t$  increases with time and  $S_t$  diminishes. At the critical moment  $t = t_c$ , the diffusion layer extends up to the symmetry plane  $X = L$ , and Stage I of the dissolution process is considered to be complete. If  $S_t$  is positive and equal to  $S_c$  at  $t = t_c$ , then

$$S_c + \delta_t = L, \quad t = t_c \quad (7)$$

If dissolution continues beyond time  $t_c$ , Stage II of the process starts; the diffusion flux cannot cross the symmetry plane at  $X = L$ , and  $\delta_t$  would fail to have physical significance any further. The solution terminates at the equilibrium limit of the second phase.

The ensuing treatments are conceptually parallel to the momentum integral method [14] in fluid dynamics and heat-balance integral technique [15] in heat transfer. The theory is applicable to the cases where the second phase is completely soluble at the dissolution temperature. For homogenization in the two-phase region (i.e. when  $C_s < C_A$ ) the computation holds good till the equilibrium limit of  $S_t$  is reached; any further decrement of  $S_t$  in the formulation produces unrealistic results.

## 2.2 Mathematical treatment for Stage I

Since no mass is being transferred beyond  $X = \delta_t$

$$\frac{\partial C}{\partial X}(S_t + \delta_t, t) = 0 \quad (8)$$

Other stipulated boundary conditions can be expressed as

$$C(S_t + \delta_t, t) = C_M = 0, \quad (9)$$

$$\delta_t = 0, \quad t = 0, \quad (10)$$

$$S_t \rightarrow R, \quad t \rightarrow 0. \quad (11)$$

The concentration distribution in the matrix is assumed to be represented by a third-order polynomial of the form

$$C(X, t) = C_s + p_t \cdot (X - S_t) - q_t \cdot (X - S_t)^2 + r_t \cdot (X - S_t)^3, \quad (12)$$

which satisfies equation (3).  $p_t$ ,  $q_t$  and  $r_t$  can be functions of time and evaluated by substituting (6), (8) and (9) into equation (12). Thus, dropping subscript  $t$  everywhere one obtains

$$p = A/\delta, \quad (13)$$

where

$$A = -\left(\sqrt{4 + \frac{6C_s}{C_p - C_s}} - 2\right)(C_p - C_s), \quad (14)$$

and

$$q = \frac{p^2}{2(C_p - C_s)}, \quad (15)$$

$$r = (2C_s + p\delta)/\delta^3. \quad (16)$$

Differentiation of (12) with respect to  $X$  and the use of equation (13) gives

$$\frac{\partial C}{\partial X}(S, t) = A/\delta. \quad (17)$$

Substituting (17) into (4), it is seen that

$$\frac{dS}{dt} = \frac{AD}{(C_p - C_s)\delta}. \quad (18)$$

The mathematical solution employs a mass-balance integral method for determining  $S$  as a function of  $t$ . In order to obtain that integral, equation (1) is multiplied by  $dX$  and integrated from 0 to  $\delta$ . The concentration values would be made to satisfy the mass-balance integral but not the equation (1). Since in the present problem the extent of the interface shift rather than the exact nature of the concentration profile is of prime interest, the postulated averaging out of the diffusion equation is expected to be sufficiently accurate.

The mass-balance integral is given by

$$\begin{aligned} D \cdot \frac{\partial C}{\partial X}(S + \delta, t) - \frac{\partial C}{\partial X}(S, t) \\ = \frac{d}{dt} \int_S^{S+\delta} C \, dX - C(S + \delta, t) \cdot \frac{d}{dt}(S + \delta) \\ + C(S, t) \cdot \frac{dS}{dt}. \end{aligned} \quad (19)$$

Introducing (3), (4), (8), (9), (17) and (18) into (19) and rearranging it can be easily shown that

$$-\frac{ADC_p}{\delta(C_p - C_s)} = \frac{d}{dt} \int_S^{S+\delta} C \, dX. \quad (20)$$

Substitution of equation (12) along with equations (13-16) into (20) yields

$$\delta \frac{d\delta}{dt} = P, \quad (21)$$

where

$$P = - \frac{12ADC_P}{(C_P - C_S)(18C_S + 9A) - 2A^2}. \quad (22)$$

Equation (21) is integrated together with the initial condition (10). The result is

$$\delta = \sqrt{2Pt}. \quad (23)$$

The value of  $\delta$  from (23) is introduced into equation (18) and the solution of the resulting differential equation subjected to the condition (11) is given by

$$\frac{S}{R} = 1 - \frac{K}{R} t^{1/2}, \quad (24)$$

where

$$K = - \frac{\sqrt{2} AD}{(C_P - C_S)\sqrt{P}}. \quad (25)$$

Equation (24) specifies the precipitate-matrix interface position in Stage I. Using condition (7),  $t_c$  can now be readily evaluated from equation (24) and it follows that

$$t_c = \left( \frac{L - R}{\sqrt{2P} - K} \right)^2. \quad (26)$$

If  $S = S_c$  at the critical moment, then

$$S_c = R - Kt_c^{1/2}, \quad (27)$$

and hence

$$\frac{dS}{dt} = - \frac{K}{2} t_c^{-1/2}, \quad t = t_c. \quad (28)$$

Dissolution of the second phase would be completed in Stage I if  $R \leq Kt_c^{1/2}$ . However, when  $R > Kt_c^{1/2}$  Stage II is bound to be present at  $t > t_c$ .

### 2.3 Treatment for Stage II

In this period overlapping of the diffusion fields starts and, naturally, the boundary conditions (8) and (9) are replaced by the zero mass transfer condition across the plane  $X = L$ , i.e.

$$\frac{\partial C}{\partial X} = 0, \quad X = L, \quad t > t_c. \quad (29)$$

Once again a cubic profile of the form

$$C(X, t) = C_S - a \left( \frac{X - S}{L - S} \right) - b \left( \frac{X - S}{L - S} \right)^2 - c \left( \frac{X - S}{L - S} \right)^3, \quad (30)$$

is assumed and this also satisfies equation (3).  $a$ ,  $b$  and  $c$  can be functions of  $t$  and are expressed in terms of  $dS/dt$  by substituting equations (4), (6) and (29) into (30). The result is

$$a = - \frac{(C_P - C_S)(L - S)}{D} \cdot \frac{dS}{dt}, \quad (31)$$

$$b = \frac{a^2}{2(C_P - C_S)}, \quad (32)$$

and

$$c = - \frac{a}{3} - \frac{a^2}{3(C_P - C_S)}. \quad (33)$$

The diffusion zone extends from  $X = S$  to  $X = L$  and consequently, the mass-balance integral subject to the equations (3), (4) and (29) becomes

$$-C_P \frac{dS}{dt} = \frac{d}{dt} \int_S^L C dX. \quad (34)$$

$C$  in equation (34) is replaced in a manner analogous to that for Stage I. It follows that

$$\frac{d}{dt} \left[ (L - S) \left\{ -1 + \frac{5}{12} \left( \frac{L - S}{D} \right) \frac{dS}{dt} - \frac{1}{12} \left( \frac{L - S}{D} \right) \left( \frac{dS}{dt} \right)^2 \right\} \right] = 0. \quad (35)$$

Substituting

$$L - S = h, \quad (36)$$

and integrating, it is found that

$$h + \frac{5h^2}{12D} \frac{dh}{dt} + \frac{h^3}{12D^2} \left( \frac{dh}{dt} \right)^2 = Z. \quad (37)$$

$S$  is supposed to be a smooth continuous function of time and therefore, equations (27) and (28) represent the initial condition for Stage II.  $Z$  in equation (37) can readily be evaluated from these conditions in conjunction with equation (36). Solving equation (37), a quadratic in  $dh/dt$ , yields

$$\frac{dh}{dt} = \frac{D}{2h} \left( \sqrt{\frac{48Z}{h} - 23} - 5 \right). \quad (38)$$

Back substitution of (36) in (38) and integration together with the initial condition (27) gives

$$t = t_c + \frac{2}{D} \int_S^{S_c} \frac{L - S}{\sqrt{\frac{48Z}{L - S} - 23} - 5} dS, \quad (39)$$

which is the required solution for Stage II. The integral on the right hand side of equation (39) can easily be evaluated by Simpson's rule and for all possible cases merely six intervals give a very good convergent result.

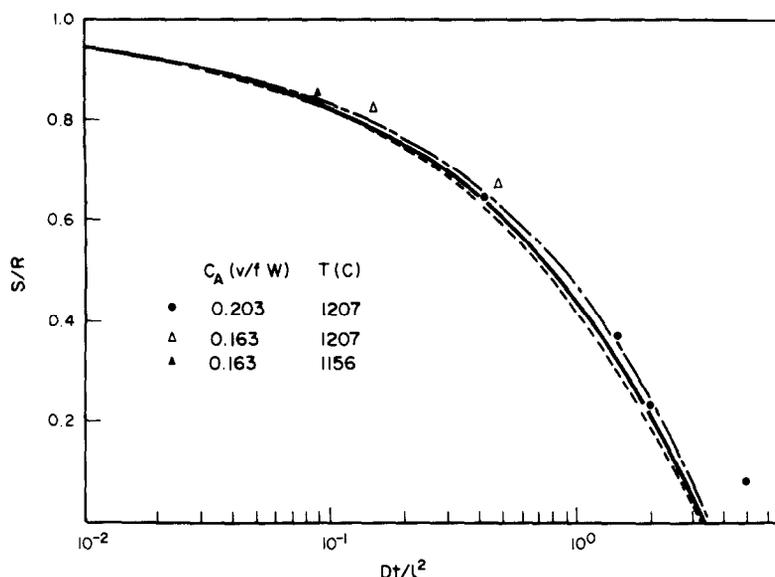


Fig. 3. Comparison of the experimental data (●, △ and ▲) of Tanzilli and Heckel [11] on the relative thickness variation of W-plates in Ni-W couples at two mean compositions and homogenization temperatures, with the predictions from Tanzilli and Heckel's [8] (—), Pabi's [10] (----) and present (— · —) models.

### 3. RESULTS AND DISCUSSION

#### 3.1 Validity of the analysis

The problem of dissolution is mathematically analogous to that of melting, and for a semi-infinite slab with constant surface temperature the cubic temperature profile approximation of Goodman [16] predicts the melting rates almost perfectly matching the output of an exact solution. For the present problem, however, no exact solution is available and hence, detailed numerical models of Tanzilli *et al.* [8] and Pabi [10] are taken as standards for comparison.

Figure 3 tests the predictions of the present method with the experimental data [11] for homogenization of multilayered Ni-rich Ni-W couples and compares its performance with the numerical models. The couples were solution treated at 1156 and 1207°C, and the interdiffusion coefficient for the Ni-rich solid solution at these temperatures is about two-orders of magnitude larger than that for W-rich phase [11]. Further, the volume fraction of the second phase is small, and hence the system is thought to be homogenized by diffusion in the Ni-rich matrix alone.

The present computation ignores any inequality in the atomic volume of the diffusing species and for the Ni-W system this difference is  $\approx 44\%$ . However,

the formulation in its present form can account for the diversity in molar volumes by assuming an ideal solution behaviour and defining concentrations in terms of volume fraction [10, 11, 17]. Compositions expressed in this manner were subsequently rationalized. Table 1 summarizes the values of the input variables used in the models and the data have been compiled from the paper of Tanzilli and Heckel [11]. Following these investigators, the time scale has been normalized as the dimensionless parameter  $Dt/l^2$ . The interface migration data for treatment number 1, 2 and 3 predicted by each of the models almost merge when plotted against this normalized scale; theoretical curves in Fig. 3 refer to treatment 3. The plot illustrates that the estimated variation in the relative thickness of second phase from the present formulation is in excellent agreement with the output of Tanzilli *et al.* [8] and Pabi's [10] models as well as with the experimental data [11] for homogenization of multilayered Ni-W couples. It may be pointed out that in all the three heat treatments impingement of the diffusion fields have taken place and therefore Stage I as well as Stage II becomes operative. Figure 3 illustrates that the present formulation for both the stages is sufficiently accurate and the model can be conveniently utilized for one-phase homogenization of planar composites.

Table 1. Input parameter values for Ni-W system. Compositions are expressed in rationalized volume fraction of W

Treatment number	Solution temperature (°C)	$C_P$	$C_S$	$C_M$	$C_A$	$D$ ( $\mu\text{m}^2 \text{s}^{-1}$ )	$l$ ( $\mu\text{m}$ )
1	1207	1.0	0.226	0.0	0.203	$3.47 \times 10^{-3}$	24.49
2	1207	1.0	0.226	0.0	0.163	$3.47 \times 10^{-3}$	24.56
3	1156	1.0	0.226	0.0	0.163	$1.60 \times 10^{-3}$	24.56

### 3.2 Comparison with other models

The analytical solutions of Aaron [2] and Whelan [5] mathematically correspond to the Stage I of the present model. Both of the former models predict a parabolic equation for interface motion, similar to equation (24) with values of  $K$  different. The linearized gradient approximation of Aaron yields

$$K = \frac{(C_S - C_M)D^{1/2}}{(C_P - C_M)^{1/2}(C_P - C_S)^{1/2}}, \quad (40)$$

whereas the stationary interface approximation of Whelan gives

$$K = \frac{2D^{1/2}(C_S - C_M)}{\sqrt{\pi}(C_P - C_S)}. \quad (41)$$

Following the proposed normalized concentration scale,  $C_S$  and  $D$  remain the only two process variables in Stage I. The present analysis as well as that due to Aaron and Whelan find  $K$  to be proportional to  $D^{1/2}$ .

The variation of  $K$  with  $C_S$  estimated by these models has been plotted in Fig. 4. At any level of  $C_S$ , the time-invariant interface location of Whelan predicts  $K$  values larger than those from the present model, the divergence being more at higher values of  $C_S$ . Migration of the interface can affect the solution kinetics principally by

- (i) changing the precipitate-matrix interface area;
- (ii) increasing the volume fraction of the matrix;
- (iii) causing distortion of the concentration gradient at the interface.

For dissolution of the planar second phase in an infinite matrix the first two factors are nonoperative; the third one is expected to diminish the precipitate decay rate. Comparison between Whelan's and the

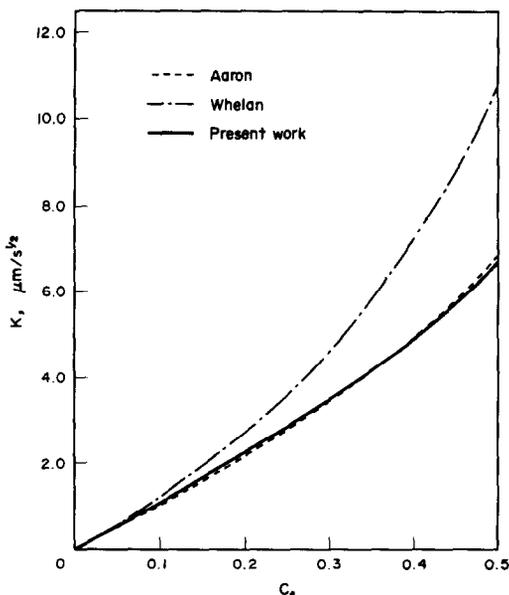


Fig. 4.  $K$  vs  $C_S$  from Aaron's, Whelan's and present models;  $D = 100 \mu\text{m}^2 \text{s}^{-1}$ .

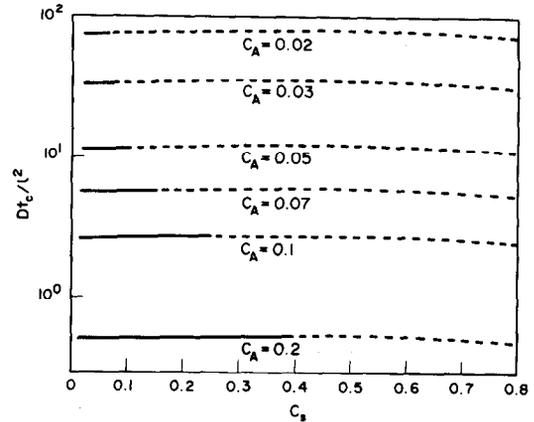


Fig. 5. Computed values of normalized critical moment vs rationalized interface composition of matrix.

present models in Fig. 4 indicates that the stationary interface approximation can largely overestimate the solution rate, primarily due to negligence to the third factor. A corollary follows that if dissolution by two-phase diffusion is assumed to occur by diffusion in the matrix alone, the interface diffusion flux within the precipitate would be neglected resulting in an overestimation of  $t_F$ , the time for complete solution.

The linear concentration profile of Aaron is really a first order simplification of the present model. This would lead to an average and hence shallower concentration gradient at the interface. The close agreement of Aaron's prediction with the present model (cf. Fig. 4) is somewhat incidental. Nevertheless, for homogenization in planar geometry the linearized gradient approximation seems to be superior to the stationary interface presumption.

### 3.3 Effect of the process variables in a finite geometry

Apart from  $C_S$  and  $D$ ,  $C_A$  is the third important process variable present in a finite geometry solution. The variation of  $t_c$ , plotted on a rationalized scale, with  $C_S$  at different values of  $C_A$  has been displayed in Fig. 5. The dotted lines in the plot indicate the completion of dissolution before reaching the critical moment.  $t_c$  is insensitive to the variation in  $C_S$ , up to  $C_S$  equal to 0.8. In contrast,  $Dt_c/l^2$  values manifest a strong dependence on  $C_A$ .

Figure 6 shows the calculated variation of  $t_F$  from the present model with  $C_A$  at different values of  $C_S$ . It is interesting to note that  $Dt_F/l^2$  varies scarcely with  $C_A$  for values of  $C_A < 0.75 C_S$ . Perhaps, overlapping of the diffusion fields hardly exerts any influence on the concentration gradient at the precipitate-matrix interface when  $C_A < 0.75 C_S$ . Increase of  $C_S$ , on the other hand, makes this gradient steeper which in turn reduces  $t_F$  (cf. Fig. 6).

It is now possible to generalize the effect of  $C_S$  on the average value of  $t_F$  for all  $C_A < 0.75 C_S$ . Figure 7 delineates the relation between  $\ln Dt_F/l^2$  and  $\ln C_S$  when  $C_A < 0.75 C_S$ . It is surprising to notice that the

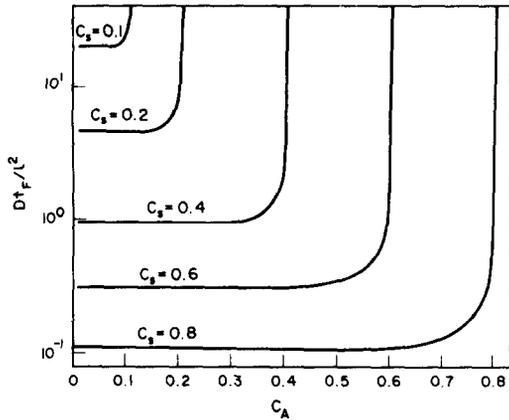


Fig. 6. Theoretical time for completion of dissolution vs rationalized composition of composite.

plot is linear for values of  $C_S$  between 0.01 to 0.3, the equation of the line being

$$\ln \frac{Dt_F}{l^2} = -2.073 \ln C_S - 1.816. \quad (42)$$

and for most practical systems  $C_S$  lies within this range. When  $C_S > 0.3$  the plot shows a negative deviation from linearity.

For a variety of systems it is possible to obtain a first order approximation of  $t_F$  from the plot in

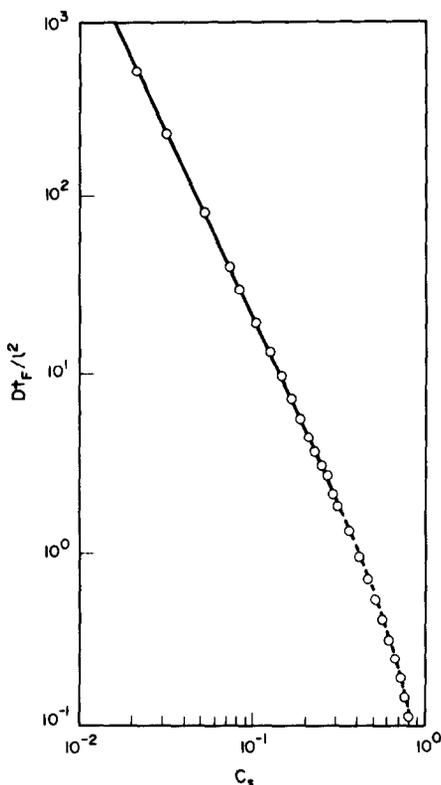


Fig. 7. Variation of  $Dt_F/l^2$  with normalized  $C_S$  for  $C_A < 0.75 C_S$ . Broken line indicates deviation from linearity (full line).

Fig. 7. Results for the Ni-W composites in Fig. 3 conform to this plot. In the case of the Ag-Cu multilayered couples of Tanzilli and Heckel [11] the concentration values (expressed in rationalized volume fraction) also permit the use of equation (42). Calculation in this manner gives  $Dt_F/l^2$  equal to 23.9 for Ag-rich sample and 48.5 for Cu-rich couples. These composites actually homogenize by two-phase diffusion and detailed numerical analyses predict [11]  $Dt_F/l^2$  values equal to 22.9 and 46.2 for Ag-rich or Cu-rich systems, respectively. The agreement between the generalized plot in Fig. 7 and the two-phase solution is really good, although  $t_F$  from the former source is slightly higher than that from later one, an observation anticipated in Section 3.2.

If  $0.75 C_S > C_A$ , it is also feasible to account for the effect of size variation of second phase from Fig. 7 (as well as from equation (42)) when  $0.01 < C_S < 0.3$ . If the dissolving particles are somewhat homogeneously distributed,  $t_F$  for each precipitate size can be estimated from the respective  $l$  value. Obviously, completion of solution treatment for the entire billet will be governed by the largest value of  $l$  present. If the distribution of second phase plates deviates strongly from uniformity, there can be small pockets where  $0.75 C_S < C_A$  (local, transient). In these cases, it is proposed to sum-up all the  $l$  values in that agglomerated region, and apply that total  $l$  in Fig. 7 [or equation (42)] to get a first-degree approximation of  $t_F$  for the entire set of particles present in that region. Perhaps, the possibility of forecasting the precipitate size distribution in the course of homogenization is not quite far off.

#### 4. CONCLUSIONS

Approximate analytical expressions have made it possible to derive equations for the one-phase diffusion controlled dissolution of multilayered couples by using an approach analogous to the momentum integral method in fluid dynamics. The equation for interface motion is parabolic as long as the matrix is virtually infinite. The predicted dissolution kinetics are well in tune with rigorous numerical solutions [8, 10] and experimental data [11].

For the dissolution of an isolated precipitate in an infinite matrix, the stationary interface approximation of Whelan [5] overestimates the second phase decay rate when compared with the present formulation. The error in the former analysis possibly originates from ignoring the distortion of the concentration profile adjacent to a receding interface. Incidentally, Aaron's linearized gradient approximation [2] seems to be quite satisfactory for the present situation.

For dissolution in a finite geometry, the dimensionless critical moment  $Dt_c/l^2$  depends markedly on  $C_A$  but is almost indifferent to any change in  $C_S$  (up to a rationalized  $C_S = 0.8$ ).  $Dt_F/l^2$  is, on the other hand, practically independent of  $C_A$  for values of  $C_A <$

$0.75 C_S$ . Perhaps, impingement of the diffusion fields does not affect the interface concentration gradient to any appreciable extent when  $C_A < 0.75 C_S$ . A simple and generalized plot for the theoretical variation of  $t_F$  with  $C_S$  (cf. Fig. 7) has been found to agree remarkably with the available experimental data [11] for several binary composites. The applicability of this curve can also be extended to account for particle size variation in the multilayered couples. When the distribution of second phase deviates strongly from homogeneity, a method has been proposed for obtaining a rough estimate of  $t_F$ .

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