Variation of Interface Compositions During Diffusion Controlled Precipitate Growth in Ternary Systems

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Isothermal diffusion controlled phase growth in ternary systems has been modeled using the Crank-Nicolson finite difference equations. Local equilibrium at phase boundaries and one dimensional growth are assumed. The model includes a method of determining phase growth velocity and interface compositions consistent with the diffusion rates of both elements. It also considers the effects of finite or overlapping diffusion fields (impingement). The growth of phosphide, $(FeNi)_3P$, in α ferrite in the Fe-Ni-P system was chosen for the simulation. Interface compositions are predicted to change with time, controlled by the necessity to balance the two solute (Ni and P) fluxes which cause the precipitate to grow. Diffusion controls the growth process although during initial growth interface structure may be important. The ratio of the major ternary coefficients $D_{PP}^{Fe}/D_{NiNi}^{Fe}$ controls the amount of shift of the precipitate interface composition from the tie line through the bulk composition. During the major period of growth the Ni interface compositions in phosphide and α remain constant and a square root of time, $t^{1/2}$, dependence for growth is predicted. The practical effect of impingement is to decrease phase growth and to allow the interface compositions to shift towards the tie line through the bulk composition.

ANALYTICAL solutions for the general case of isothermal ternary diffusion controlled growth have been developed by Kirkaldy[1] and Coates.[2,3] These solutions assume that interface compositions remain constant during growth and do not consider the effect of overlapping diffusion fields or impingement. Commonly, however, growing phases are a finite distance apart and diffusion fields in the matrix overlap or impinge. In these situations impingement can be important during the later stages of growth. Specifically, it may change the interface compositions and the growth rate of the precipitate phase. Impingement effects have been approximated in certain cases.[4]

Numerical models for diffusion controlled growth can accurately handle the problem of impingement in binary systems as demonstrated by Tanzilli and Heckel[5] and Hickl and Heckel.[6] Recently the same capability was demonstrated for ternary systems by Randich and Goldstein.[7] The ternary model uses a computer solution for nonisothermal ternary diffusion controlled phase growth. Both analytical and numerical models for ternary systems assume local equilibrium at the precipitate/matrix interface for the calculation of the interface velocity and the interface tie line compositions.

The purpose of this paper is: 1) to describe a numerical method for treating the isothermal two phase, diffusion controlled, moving interface problem in ternary systems and; 2) to investigate the variation of precipitate matrix interface compositions during the initial stages of growth and during the late stages of growth where impingement is important.

ASSUMPTIONS AND MATHEMATICAL FORMULATION

Diffusion in ternary or higher order systems may be determined with the aid of Onsager's extension of Fick's first law.[8] For a ternary system[9] the generalized Fick equations for the flux of elements 1 and 2 in terms of the concentration gradients in a given phase are:

$$J_1 = -D_{11}\frac{\partial C_1}{\partial X} - D_{12}\frac{\partial C_2}{\partial X} \qquad [1a]$$

$$J_2 = -D_{22}\frac{\partial C_2}{\partial X} - D_{21}\frac{\partial C_1}{\partial X}\,. \qquad [1b]$$

Separate sets of equations are necessary for each phase.

The flux balances at the matrix-precipitate (M/P) interface for components 1 and 2 are given by:

$$(C_1'' - C_1')\frac{d\xi_1}{dt} = -[J_{1,\xi^+}^{M} - J_{1,\xi^-}^{P}] \qquad [2a]$$

$$(C_2'' - C_2')\frac{d\xi_2}{dt} = -[J_{2,\xi^+}^{M} - J_{2,\xi^-}^{P}] \qquad [2b]$$

where ξ is the spatial position of the M/P interface, C_1', C_2' and C_1'', C_2'' are the tie line compositions in the matrix and precipitate phase respectively and J_{1,ξ^+}^{M}, J_{2,ξ^+}^{M} and J_{1,ξ^-}^{P}, J_{2,ξ^-}^{P} are the mass fluxes of elements 1 and 2 just at the M/P interface. The two flux balances are related to each other since the rate of movement of the interface, $d\xi/dt$, must be the same for each component; that is:

$$\frac{d\xi_1}{dt} = \frac{d\xi_2}{dt} = \frac{d\xi}{dt}\,. \qquad [3]$$

At any given time the two mass balances, Eqs. [2a] and [2b], can be simultaneously satisfied through Eq. [3] by selection of an appropriate tie line and interface velocity.[1,2,10]

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Kirkaldy[1] and Coates[2] have assumed the matrix phase to be infinite in extent and that the interface compositions C_1'', C_2'', C_1' and C_2' are constant during growth. However the interface compositions may vary if boundary conditions change, that is, if impingement of diffusion fields occurs. To explore this question of varying interface compositions in more detail and to calculate Eqs. [1] to [3] allowing for the effect of impingement, a numerical solution is employed.

A Crank-Nicolson finite difference method has been used to obtain numerical solutions for Eqs. [1] to [3]. The method is very similar to that employed by Randich and Goldstein[7] for nonisothermal ternary diffusion controlled growth and is described in detail in their paper. Fig. 1 is a schematic representation of the space concentration grid of the model. ΔX^M and ΔX^P are the grid spacings in the matrix and precipitate used for the finite difference method. There are N points in the space grid of which r-2 points are contained in the precipitate phase. The assumptions of the method are: 1) ternary coefficients independent of concentration; 2) one dimensional, planar front interface movement; and 3) local equilibrium at the two phase M/P interface during the diffusion process.

In the computer method, the interface tie line compositions are allowed to vary for each time step in the Crank-Nicolson finite difference treatment. Tie line compositions at the M/P interface are chosen to satisfy the mass balance equations for elements 1 and 2. The fluxes $J^M_{1,\xi^+}, J^M_{2,\xi^+}, J^P_{1,\xi^-}, J^P_{2,\xi^-}$ are calculated from the compositional gradients generated during the previous time step and the compatible interface tie line compositions and precipitate growth rate $d\xi/dt$ are calculated from a combination of Eqs. [2] and [3]. By this method the tie line can shift to satisfy Eqs. [2] and [3] and the growth rate $d\xi/dt$ is predicted directly. Compositional gradients which may develop in the precipitate phase due to changing tie line compositions are also calculated. The model is applied from the center of the precipitate phase to the center of the matrix phase. Within this diffusion distance, L, (see Fig. 1) a mass balance of elements 1 and 2 is preserved. Zero mass transfer boundary conditions, $\partial C_1/\partial X = \partial C_2/\partial X = 0$, are set at the center of the matrix phase and at the center of the growing precipitate.

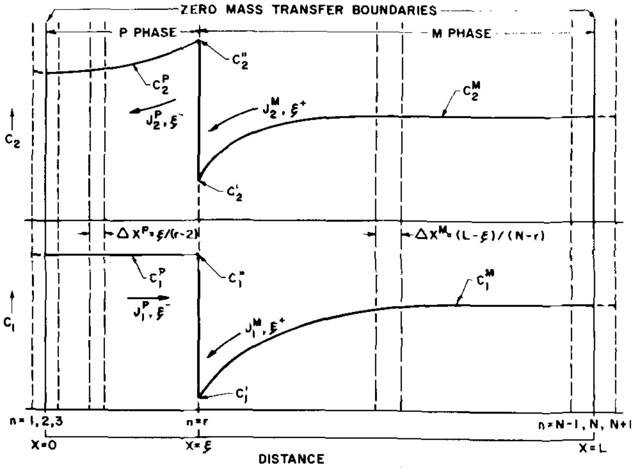

Fig. 1—Schematic representation of the space concentration grid used for the numerical analysis. The matrix M/precipitate P interface is positioned at the distance ξ from the center of the precipitate phase.

APPLICATION OF THE NUMERICAL METHOD—ISOTHERMAL GROWTH OF PHOSPHIDE IN THE Fe-Ni-P SYSTEM

The phase transformation $\alpha \rightarrow \alpha$ + Ph in the Fe-Ni-P system was chosen for the calculation. Components 1 and 2 may be taken as P and Ni respectively. The Ph or phosphide is the precipitate phase and has the chemical formula $(Fe,Ni)_3P$. The α is the matrix phase and is bcc Fe-Ni. This transformation was chosen for computer modeling because ternary diffusion coefficients in the Fe-Ni-P system have been measured as a function of temperature.[11,12] The faster diffusing element is P and the ratio of the diffusion coefficients D^α_{PP} to D^α_{NiNi} varies between 5 and 10. The cross coefficients D^α_{PNi} and D^α_{NiP} are essentially zero.[11] The value of the ratio D^{Ph}_{NiNi} to D^α_{NiNi} is approximately 0.05.[12] The transformation $\alpha \rightarrow \alpha$ + Ph was also chosen for computer modeling because the tie lines in the α + Ph phase field have been experimentally determined.[13] The phosphide phase is stoichiometric in P and the Fe and Ni are interchangeable. Since each α + Ph tie line is unique the variations in all four interface compositions, C_1', C_1'', C_2', C_2'', can be determined by calculating only the variation of one of these values. For simplicity we used C_2'' the Ni interface composition of the Ph to describe the variation of the interface composition.

Ph growth was simulated for a nominal 2 wt pct Ni, 2 wt pct P, 96 wt pct Fe alloy. The simulation started with a 0.01 μm nucleus of Ph in a homogeneous α phase and growth proceeded isothermally at 750°C. Fig. 2 shows the low Ni region of the Fe-Ni-P system at 750°C. The bulk composition of the alloy lies in the two-phase α + Ph region at 750°C and is

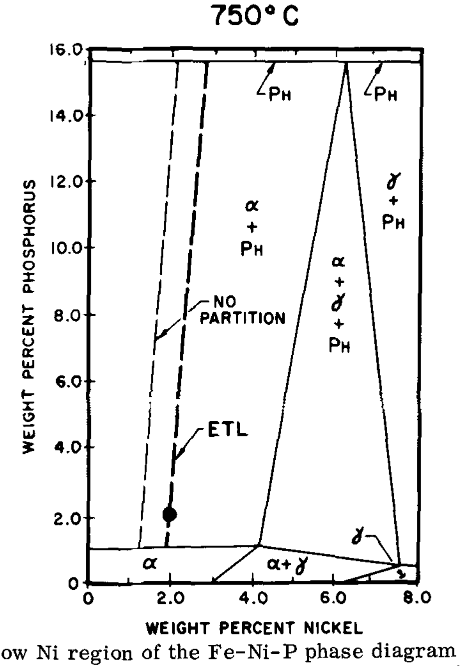

Fig. 2—Low Ni region of the Fe-Ni-P phase diagram at 750°C. The bulk composition of our test alloy 2P-2Ni-96Fe is identified by ● on the figure.

identified by the solid circle on the figure. At this temperature the alloy is supersaturated in P and the Ph phase will nucleate and grow. Fig. 3 shows the microstructure of a nominal 2P-2Ni-96Fe alloy after slow cooling from 875°C and an isothermal treatment for two weeks at 750°C (Ref. 12). Generally the Ph grows as a plate and the average impingement distance is ~50 μm.

The tie lines in the α + Ph phase field will define the local interface matrix/precipitate (α/Ph) compositions during growth. The tie line called the equilibrium tie line (ETL) goes through the bulk alloy composition (see Fig. 2). The α and Ph compositions given by the ETL will be observed in an equilibrated alloy. The no partition tie line represents the condition where the Ni content of the growing phosphide and the bulk composition of the alloy are the same. The no partition tie line gives the lowest permissible phosphide Ni content, when considering the bulk Ni content of the alloy. The no partition tie line still retains equilibrium between α and Ph at the two phase interface. The concept of the no partition tie line or pile up model was introduced by Hillert and others.[1,14,15]

Since $D_{\mathrm{PP}}^{\mathrm{Fe}} > D_{\mathrm{NiNi}}^{\mathrm{Fe}}$ in the matrix α, the P growth rate $d\xi_1/dt$ will in general be higher than that of the Ni, $d\xi_2/dt$. To satisfy Eq. [3], tie line shifts from the ETL towards the no partition tie line are predicted. This shift will decrease the Ni interface compositions C_2', C_2'' in the α and Ph (Fig. 1). Therefore the Ni flux J_{2,ξ^+}^{M} into the M/P interface will increase and J_{2,ξ^-}^{P} away from the M/P interface will decrease. In this manner, the growth rate $d\xi_2/dt$ will be increased, Eq. [2b], and the interface velocity relationship Eq. [3] will be satisfied.

The composition gradients of Ni and P predicted by the simulation are shown in Fig. 4. The length of the space grid, L, from the center of the phosphide to the center of the α phase was 50 μm and a grid spacing of approximately 0.5 μm in the matrix α phase was used. Ni and P gradients are shown for four growth times, 1 h, 1 day, 5 days and the total growth time of 80 days. In this example the interface compositions assumed for the first increment of growth were those given by the ETL (Fig. 1): 1.94 wt pct Ni in α, 2.76 wt pct Ni in Ph. At 1 h of growth, ξ = 0.35 μm and the P depletion in the matrix α is much more extensive than that of the Ni. This reflects the larger diffusion coefficient of the phosphorus. The value of the Ni interface compositions is less than that given by the ETL allowing the Ni interface fluxes to increase and the growth rate $d\xi_2/dt$, Eq. [2b] to increase to that due to the P flux. The P interface composition in α remains constant at 0.903 wt pct during the growth process since the P solubility limit in α is independent of Ni content (Fig. 2).

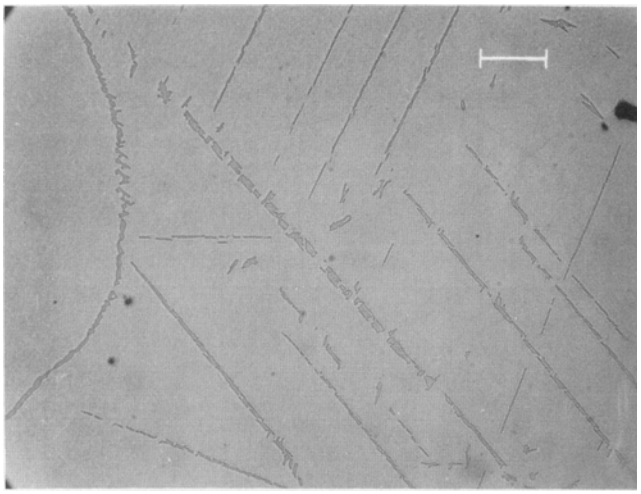

Fig. 3—Microstructure of a nominal 2P-2Ni-96Fe alloy after slow cooling from 875°C and an isothermal treatment for two weeks at 750°C. Ph generally precipitates as long plates in the α matrix. Grain boundary nucleated Ph is observed on the left side of the photomicrograph. Magnification marker 116.8 μm.

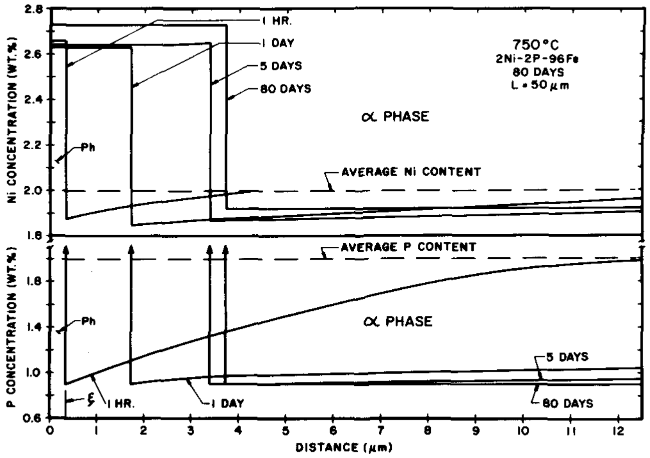

Fig. 4—Ni and P composition gradients predicted by the numerical model for a 2P-2Ni-96Fe alloy heat treated at 750°C. Diffusion gradients at several growth times, 1 h, 1 day, 5 days and 80 days are given.

Impingement of P occurs 50 μm from the nucleation point after only 3 h. Ni impingement occurs after about 2 days. When Ni impingement occurs the impingement of P has already depleted the α matrix by over half of the P which was originally available for Ph growth. Between 5 and 80 days little Ph growth occurs (ξ changes from 3.5 to 3.75 μm). However during this later period of impingement the Ni contents of the Ph and α at the α/Ph interface C_2'', C_2' rise to the value predicted by the ETL. This later effect occurs because the P flux in α has decreased due to impingement (see Fig. 3). This causes the growth rate $d\xi_1/dt$ to decrease. The Ni interface compositions can rise because the Ni interface fluxes need no longer support a large Ph growth rate. During the final growth period Ni and P gradients are readjusted so that a condition of chemical equilibrium throughout the alloy system is obtained.

The predicted variation of the phosphide Ni interface composition with time is shown in Fig. 5. To examine how initial conditions affect phosphide growth several tie lines, ETL, 2.3 wt pct Ni and no partition, were chosen as starting compositions for the phosphide phase. After about 1/2 h or about 0.25 μm of growth, a phosphide Ni interface composition of 2.62 ± 0.02 wt pct is chosen for further growth. This interface Ni concentration apparently balances the phosphide growth rate as predicted by the Ni and P mass balances as long as impingement is not severe. This result supports the method of Coates,[2] which

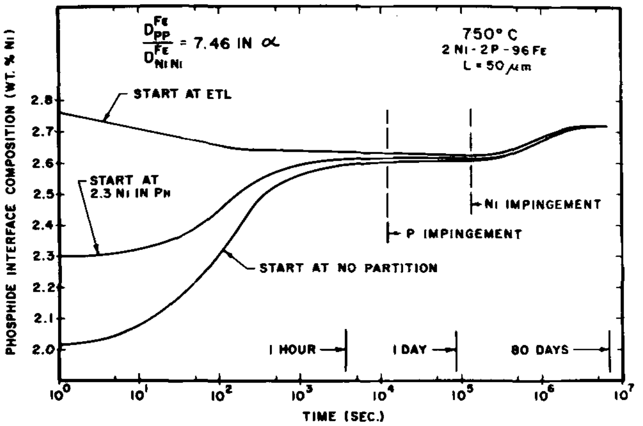

Fig. 5—Predicted variation of C_2'', the phosphide interface Ni content, with time for three different phosphide starting compositions.

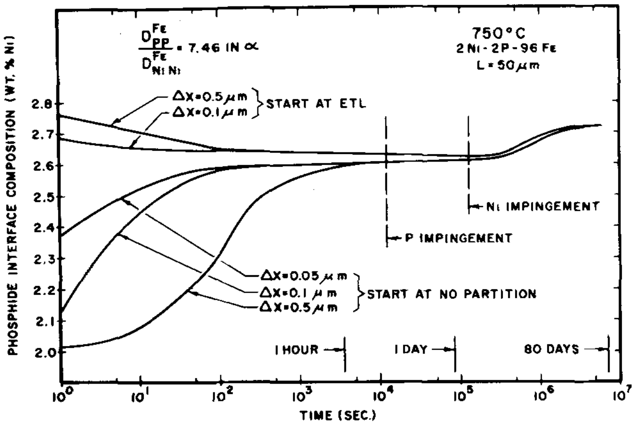

Fig. 6—Influence of matrix grid spacing size ΔX^M on the phosphide interface Ni content.

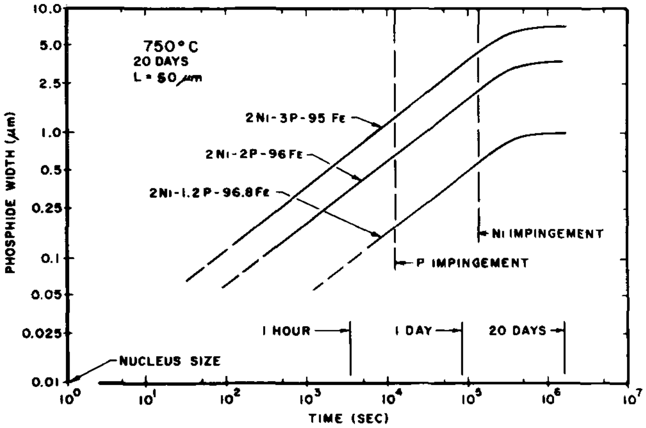

Fig. 7—Predicted variation of phosphide width with growth time at 750°C. Three alloy compositions 2Ni-1.2P-96.8Fe, 2Ni-2P-96Fe and 2Ni-3P-95Fe are investigated.

uses constant velocity or interface compositions determined by tie line compositions and relative diffusion coefficients. His method appears to be quite acceptable as long as impingement of the fast diffusing element is not significant. Once P impingement becomes severe, after 2 days of growth, and the P flux at the two phase interface approaches zero, the interface tie line moves back to higher Ni contents and approaches the ETL.

Three stages of growth are therefore observed in this example. 1) Initial growth stage. During this stage, which takes less than 0.1 pct of the time necessary to achieve bulk chemical equilibrium, the α/Ph interface Ni compositions cannot be uniquely specified. 2) Major growth stage. Growth occurs until impingement of the faster diffusing element becomes severe. In addition the Ni interface compositions in α and Ph do not vary during growth. 3) Final growth stage. Little growth occurs, Ni contents of the Ph and α are adjusted to the equilibrium values and gradients in the α and Ph phase disappear. The initial growth stage could possibly be an artifact of the numerical solution used in the model. Using finer grid spacings in the matrix α phase allows a more exact modeling of the diffusional process. As Fig. 6 shows, finer matrix grid spacings, ΔX shorten the initial growth stage by as much as an order of magnitude, *i.e.*, from greater than 1000 s to less than 100 s.

Fig. 7 shows the predicted variation of phosphide width with growth time for the 2Ni-2P-96Fe alloy at 750°C. Calculations of growth rates during the initial growth stage vary according to the starting composition and computer grid spacings in the matrix α. However the predictions of growth during Stage 2, the major growth period, are independent of the assumed starting composition. A square root of time, $t^{1/2}$, dependence for growth is predicted for Stage 2. This rate dependence is observed until P impingement becomes severe (~2 days). In Stage 3 growth slows and the Ni interface values increase. Ni impingement only becomes significant after 20 days of growth and total phase equilibrium is achieved in 80 days.

The time dependence of phosphide growth in two other alloys of similar Ni content are shown in Fig. 7. Although lesser or greater amounts of growth occur, a $t^{1/2}$ diffusion controlled dependence during Stage 2 is observed. In addition larger or smaller amounts of undercooling do not change the $t^{1/2}$ relationship for growth of the phosphide phase.

DISCUSSION

Three stages of growth are predicted by the computer model for phosphide growth in the α matrix phase. The initial growth stage is quite sensitive to the assumed starting composition and to the grid size in the α phase used for the Crank-Nicolson method. Reduction of matrix grid spacing below 0.05 μm might yield more accurate results. However, poor stability of the numerical solution under these conditions and extremely long computational times have not permitted us to reduce grid spacing below 0.05 μm. The calculation also starts with a phosphide nucleus of finite size (0.01 μm). This artificial nucleus size adds to the uncertainty of results during the initial growth stage. Finer grid spacings and a smaller nucleus size may shorten or eliminate the initial growth stage. At the present time the computer calculation is not of sufficient accuracy to determine the details of the initial growth stage (0 to 3000 s). It is possible that the initial growth stage, or a goodly portion of it is an artifact of the numerical solution.

The model assumes local equilibrium at the M/P interface and that diffusion is the rate controlling step. Structural effects at the interface are not considered. In the initial growth stage the interface structure could be most important.[16] At short times, the composition spike of Ni formed in α at the $\alpha/$Ph interface may be unrealistically small, of atomic dimensions. Interface controlled growth, perhaps by structural defects at the interface,[17] may occur. Coates[2] suggests that the composition spike at the interface must be >5 nm (50Å) in size to allow local equilibrium. The smallest computer grid spacing used in this study was 50 nm (500Å). Therefore we were not able to investigate this problem.

During the second stage of growth the growth rate shows a $t^{1/2}$ dependence. In addition the α and Ph interface compositions are essentially independent of any assumed starting composition for the phosphide nucleus. The computer model predicts constant interface compositions during this period of growth. Therefore the interface composition contours of Coates[2] or the iterative technique of Kirkaldy[1] will be applicable during this growth stage.

The faster moving element P begins to become depleted at the impingement distance L early in second stage growth. However this depletion does not appear to measurably change the time dependence of growth or the interface compositions. Apparently P depletion must be severe, >50 pct of the available supply, before the effect of impingement substantially changes the growth rate and interface compositions. The analytical calculation techniques[1,2] are therefore applicable even during initial impingement. During final stage growth, impingement effects become severe, growth decreases, and the interface compositions change significantly with time. The analytical calculation techniques are therefore not applicable in this growth region.

The calculation of ferrite or carbide growth in ternary Fe-C-X alloys, where X is a substitutional metallic element, must be considered as a special case. The diffusion rate of C is 10^4 to 10^6 times faster than the major substitutional element(s). To calculate precipitate growth, assumptions of paraequilibrium,[18,19,20] that is the lack of local equilibrium of component X at the 2 phase interface, have been invoked.[5,10,21] Unfortunately at the present time, the Randich-Goldstein computer model[4] cannot calculate phase growth in ternary systems when the diffusion rate of one solute is more than 10^2 times faster than the diffusion rate of the other solute element. This limitation is due to the fact that the grid size used in the computer model must be the same for both diffusing elements. If one of the solute elements diffuses much slower than the other, the grid size must be kept quite small in order to allow the details of the diffusion process to be calculated and to assure stability of the numerical technique. This situation leads to unreasonably long computation times.

Attempts can be made to generalize the Randich-Goldstein computer analysis for ternary systems in which the tie lines and diffusion coefficients have not been measured. We have attempted this generalization and in most cases we get unrealistic answers. Since diffusion coefficients are influenced greatly by the thermodynamics of a given system, arbitrary values of D's or two phase tie lines do not lead to satisfactory simulations of phase growth. The computer model can be applied more extensively as tie lines and diffusion coefficients are measured for more ternary systems.

SUMMARY AND CONCLUDING REMARKS

In summary we have been able to simulate the isothermal phase growth process in a ternary alloy using a diffusion theory. Interface compositions are predicted to change with time, controlled by the necessity to balance the two solute fluxes which cause the precipitate to grow. It is diffusion which actually controls the growth process although during initial growth interface structure may be important. The ratio of D_{11}/D_{22} controls the amount of movement of the precipitate interface composition from the ETL. The practical effect of impingement is to decrease phase growth and allow the interface compositions to move back towards the ETL. It should not be surprising therefore if precipitates in the same ternary alloy have different compositions. If there are different impingement distances in the alloy, precipitate compositions might very well be different for the same growth time.

The authors' numerical model considers planar interface geometry only. However the modification for cylindrical or spherical geometries are straightforward and methods to do this are readily available in the literature.[5] The approach presented should allow other investigators to apply the model to ternary systems which have well characterized phase diagrams and adequate diffusion coefficient data.

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