Transient Growth of Second Phases During Solution Treatment

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This study shows experimentally that, in the initial stages of a solution treatment process, an unstable phase may grow prior to dissolving if the diffusion flux in the unstable phase is larger than that in the stable matrix. The effect was demonstrated using diffusion couples fabricated from thin, multiple layers of α and β brass such that the mean compositions of the couples relative to the α-β phase equilibrium would result in solution of the β phase. Since at the diffusion temperature of 870°C the interdiffusion coefficient of the β phase is about twenty times that of the α phase, the initial β phase flux was much greater than that of the α phase. Metallographic observations of two sets of diffusion couples, each having a different mean composition, as a function of time of interdiffusion revealed that approximately 22 pct growth of the β phase preceded its ultimate dissolution. The analysis of this phenomenon was verified by reasonably good agreement between measured phase thickness values as a function of time and calculated values based upon a numerical solution of the appropriate multiphase diffusion problem.

The solution treatment process normally consists of heating a two-phase aggregate (α + β) to a temperature where only one of the phases (α) is stable, thereby effecting a time-dependent transformation to a single phase structure. It would, therefore, be expected that the content of unstable phase (β) would decrease continuously with time. In other words, for an initial structure of isolated β particles in an α matrix, it would be anticipated that the α:β interfaces would migrate in such a manner as to decrease the volumes of the β particles.*

Strictly speaking, the interface migration is controlled by the diffusional transport of mass in the vicinity of the interface; it is the difference in the fluxes in the two phases on opposite sides of the interface which determines the interface migration velocity. Ordinarily, the flux at the interface in the unstable phase (β) is negligible and the α-phase flux causes the β phase to decrease continuously in volume. If, however, a large flux in the β phase results from large variations in solubility with temperature and/or a large interdiffusion coefficient at the solution treatment temperature, it is possible for the α:β interface to move initially in the direction of increasing β-phase content. This situation is described in Fig. 1 in terms of the concentration-distance profile in the vicinity of the α:β interface. The initial condition is given by the dashed line:

\[
C = C_{β0} \quad X < 0
\]

\[
C = C_{α} \quad X > 0
\]

with the α:β interface position, \( \xi \), occurring at \( X = 0 \). The solid line represents the concentration-distance profile after the start of interdiffusion for the condition that the flux in the β phase at the interface, \( J^β_0 \), is greater than that for the α phase, \( J^α_0 \). Fig. 1 also shows the appropriate mass balance equation which controls the interface migration velocity, with \( D^α \) and \( D^β \) interdiffusion coefficients in the α and β phases, respectively.

\[
\left( C_{β0} - C_{αβ} \right) \frac{dξ}{dt} = J^β_0 - J^α_0
\]

or

\[
\left( C_{α} - C_{αβ} \right) \frac{dξ}{dt} = -D^β \frac{dc}{dx}_ξ + D^α \frac{dc}{dx}_ξ
\]

Fig. 1—Schematic concentration-distance profile at the α-β interface at the outset of the solution process under conditions where the flux in the unstable phase is greater than that in the stable phase.
This section of the text discusses the phase diagram of a one-phase (α) structure. It involves only compositional changes local to the interface and, therefore, adequately described in terms of the infinite boundary condition ($C = C_{α0}$, $X = -∞$; $C = C_{β0}$, $X = +∞$).

If the initial motion of the $α$-$β$ interface results in an increase in the amount of the $β$ phase, a second stage to the process must occur to allow the transformation to approach the endpoint defined by the equilibrium phase diagram (a one-phase (α) structure). This second stage results from the rapid loss of supersaturation in the $β$ phase due to the high fluxes which initially forced the interface to migrate toward the $α$ phase. This situation is shown in Fig. 2 as a series of concentration-distance profiles for a characteristic symmetry element of the microstructure. The zero gradient requirements result from the conservation of mass in the element and occur at positions in the $α$ and $β$ phases which are the midpoints of these phases. (For $β$ particles arranged regularly in an $α$ matrix, the position of $(dc/dx)_β = 0$ represents the centers of the $β$ particles and the position of $(dc/dx)_α = 0$ represents the midpoint between $β$ particles in the $α$ phase.) If large $β$-phase fluxes do occur, forcing the growth of the unstable phase, the effect will only be transitory, since these fluxes will decay rapidly and "normal" solutions due to only small amounts of growth being possible in many systems; the effect occurs at relatively short times compared to the times necessary for complete solution of the unstable phase, and generally less change in solid solubility with temperature and smaller interdiffusion coefficients in the unstable phase of most systems of interest.

The only experimental study which appears to be related to this subject was carried out by Clark, Aaronson, and Domian on interface migration in an $α$-$β$ brass diffusion couple. They studied the homogenization of compacts of tungsten and rhenium powders where the mean composition resided in the tungsten-rich terminal solid solution range. The rate of formation of the intermediate phase between the two terminal phases was greater than the rate of loss of the rhenium-rich phase. Therefore, the total volume fraction of unstable phases (rhenium-rich phase plus the intermediate phase) initially increased and then decreased as the system approached the equilibrium condition, the tungsten-rich phase. The same type of situation should occur in many other three-phase systems.

The purpose of the present investigation was to demonstrate experimentally the phenomenon of growth prior to solution in a two-phase system of constant solution kinetics, i.e., control by matrix fluxes, will set in for the final stage of the process. Another way of categorizing the transition between these two stages in the process is to note that the change in algebraic sign of the velocity is related to the transition from an infinite boundary condition situation to a finite boundary condition as shown in Fig. 2.

The factors which determine the extent of growth prior to solution have been studied previously using mathematical models defined for numerical methods and solved with computer techniques. This work has shown that large values of ($C_{α0} - C_{β0}$) and $D_β$, and small values of ($C_{αβ} - C_{α0}$) and $D_α$ promote large amounts of growth, in accord with the flux balance equation, Fig. 1. Although this growth phenomenon may be defined analytically and has been studied through mathematical modelling, direct experimental evidence of this phenomenon in two-phase systems of constant mean composition is lacking. This is surprising since the direction of motion of the interface at the onset of interdiffusion is determined by the initial phase concentrations, the interface concentrations, and the interdiffusion coefficients. The mean concentration of the system has no effect on the initial direction of motion of the interface, but determines only the ultimate direction of motion in accord with the phase solubilities. Since the factors which determine the initial direction of motion are independent of those which determine the ultimate direction of motion, growth prior to solution should be expected to occur in many systems. The lack of evidence of this phenomenon is probably due to only small amounts of growth being possible in many systems; the effect occurs at relatively short times compared to the times necessary for complete solution of the unstable phase, and generally less change in solid solubility with temperature and smaller interdiffusion coefficients in the unstable phase of most systems of interest.

Examples of the growth of unstable phases are available in three-phase systems. Smith and Hehemann studied the homogenization of compacts of tungsten and rhenium powders where the mean composition resided in the tungsten-rich terminal solid solution range. The rate of formation of the intermediate phase between the two terminal phases was greater than the rate of loss of the rhenium-rich phase. Therefore, the total volume fraction of unstable phases (rhenium-rich phase plus the intermediate phase) initially increased and then decreased as the system approached the equilibrium condition, the tungsten-rich phase. The same type of situation should occur in many other three-phase systems.

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