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G.W. Roper and D.P. Whittle

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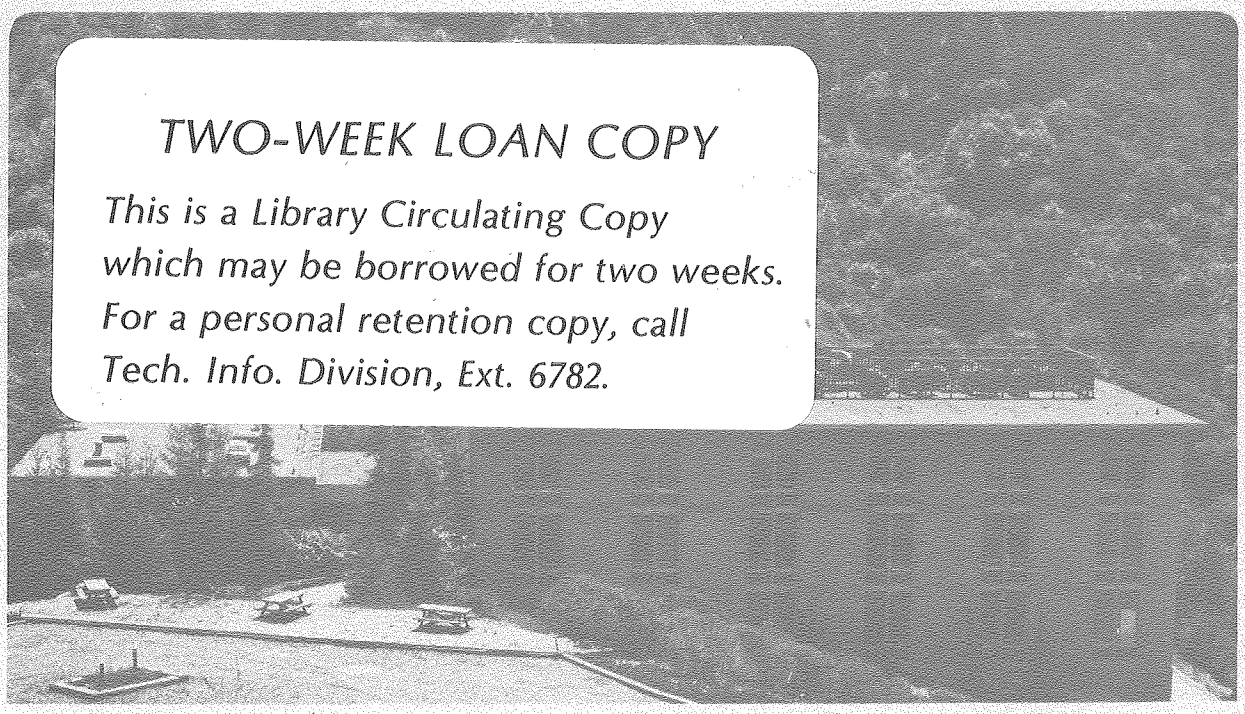

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INTERDIFFUSION IN TWO-PHASE TERNARY SOLID SYSTEMS

G. W. Roper[+] and D. P. Whittle[*]

Abstract

The pseudo-binary approach to diffusion in two phase ternary systems is discussed. In particular, the circumstances under which virtual diffusion paths arise are highlighted. Despite the imprecision inherent in virtual paths, it is recognised that they have an advantage over, so-called, real paths (which simply run along phase boundaries) in that they include information about the relative proportions of the phases present in two-phase regions. The term Composite Diffusion Path is introduced, which retains this advantage of a virtual path, but avoids its short-comings by not being based on the assumption of pseudo-binary behavior. The composite diffusion paths are derived from first principles for two model diffusion couples, each comprising a single phase (α) alloy annealed in contact with a two phase ($\alpha+\beta$) alloy.

Comments are also made on the interrelationship between diffusion coefficient data and the shapes of phase boundaries in ternary systems; results being presented which suggest that conclusions about one can be made on the basis of information about the other.

[+]Shell Research Center, Thornton, Near Chester, England
[*]Materials and Molecular Research Division Lawrence Berkeley Laboratory, and Department of Materials Science and Mineral Engineering, University of California, Berkeley, Calif. 94720, U.S.A.

1. INTRODUCTION

Many of the practical situations where diffusion is imporant involve systems of more than one phase and so an understanding of the nature of diffusion in such systems is important. Unfortunately, the theoretical complexities of diffusion in multiphase systems have so far prevented the attainment of complete elucidation.

Various authors have attempted to explain specific multiphase phenomena in terms of the pertinent diffusion data. For example, Shatynski, Hirth and Rapp [1] have attempted to interpret observations on the formation and growth of intermetallic compounds in binary systems in terms of the diffusion behaviour of the system, while various workers have discussed diffusion controlled precipitate growth in ternary systems including Coates [2,3] and Randich and Goldstein [4,5]. Another important phenomenon involving diffusional interactions between phases is the high temperature oxidation and hot corrosion of alloys. Important contributions in this field include those by Kirkaldy [6], Dalvi and Coates [7] and Whittle [8].

The following theoretical discussion of multiphase diffusion is intended as no more than a contribution to this extremely complex and relatively unexplored field. In particular, it highlights the close relationship between the phase diagram of a system and its diffusion behaviour.

2. PSEUDO-BINARY APPROACH

By making certain assumptions about the variation of diffusion coefficients with composition, it is possible to solve the diffusion equation for an infinite diffusion couple of a single phase ternary system [9]. This procedure reveals the solute concentration profiles across the couple after a particular diffusion anneal. Further, since the concentrations

of both solutes in such a system can be expressed as unique functions of a single parameter λ (equal to $x/t^{\frac{1}{2}}$, where x = distance and t = time), it is possible to eliminate λ between the two solute concentration profiles to generate a diffusion path, which shows the variation of composition across the couple. (The diffusion path, so defined, is a convenient way of presenting diffusion data since it is independent of distance and time, but the fact that diffusion paths are devoid of spatial and kinetic information can also be a weakness.)

For a system of more than one phase, however, things are much less straightforward because concentration profiles, and the diffusion equations defining them, are no longer smooth and continuous across the couple. Phase boundaries move as the diffusion process takes place and this compounds the difficulties of modelling such a system.

It is possible to cope with phase boundary movements in a binary system because the Phase Rule prohibits the development of composition gradients through two phase regions, with the result that phase boundaries remain stable and planar. Since phase boundary movements are diffusion controlled, changes of position of a planar boundary are confined to the dimension of diffusion and to a parabolic rate that can be simple defined.

In ternary systems, on the other hand, the additional component gives an additional degree of freedom, which means that α and β phases, for example, can co-exist at equilibrium over a range of compositions even when pressure and temperature are fixed. This means that non-planar interfaces and/or internal precipitates can arise. If this were to occur, concentration gradients in the vicinity of the interface would no longer be restricted to the single dimension of the macro-gradient of composition, which destroys

the condition for parabolic behaviour of the phase interface [10], i.e. its movement would no longer be a function of λ only. Precise determination of concentration profiles and diffusion paths from known diffusion data is impossible under such circumstances. In addition to this limitation, there is another consequence of the development of concentration gradients (and hence activity gradients) through two phase regions of ternary systems, namely the creation of a driving force for diffusion through such regions. Thus, when attempting to derive the concentration profiles across a multiphase ternary diffusion couple by solving the diffusion equation, allowance must be made for the possibility of diffusion through two-phase regions. This complication does not arise in binary system.

Consider, for example, an infinite diffusion couple comprising different single phase (α and β) of the same ternary system. An approximate approach to this problem is to treat the system as a pseudo-binary, by assuming that interphase boundaries remain planar and therefore parabolic in behaviour. It is then possible to match solutions to the diffusion equation on either side of the phase boundary by means of flux continuity relations. The diffusion path determined in this way is then plotted on the appropriate isotherm of the system's ternary phase diagram from which it is possible to see if the path runs through any two phase regions. If the only incursion to a two phase region is straight across a tie-line, as for example at the assumed planar junction between α and β phases, then the calculated diffusion path is a stable solution, i.e. the assumption of planar interfaces is valid. If, however, the calculated diffusion

path loops into two phase regions, cutting across tie-lines to create a finite region of supersaturation, then the solution is unstable because supersaturation is not usually tolerated in a real system.

When a calculated diffusion path turns out to be of this type it cannot be the same as that obtained in practice because the existence of a non-planar interface or precipitate was not taken into account in the original analysis. Kirkaldy and Brown [10] have called such unstable calculated diffusion paths Virtual Paths. Despite the fact that virtual paths frequently bear little resemblance to reality, they provide a useful means of determining whether or not phase boundaries in a system remain planar on annealing. An interesting feature of a virtual path is that, for any point in the two phase region, it contains information regarding both the compositions of the two phases present (given by the end points of the relevant tie-line) and also their relative proportions (by means of the lever rule). The so-called real diffusion path, on the other hand, lacks the latter feature because it does not cross the two phase region and merely runs along the phase boundaries. It is felt by the authors that a third type of diffusion path can be usefully defined for dealing with multiphase systems and the suggested title is Composite Path. The composite path has the same format as the virtual path and therefore contains information regarding the proportions of the two phases at any point in addition to their compositions. However, unlike the virtual path, the composite path describes the real situation and is not derived on the false assumption of pseudo-binary behaviour. In the following section, it is shown how composite diffusion paths through the two phase region of a ternary system may be obtained.

Consider the ternary system ABC and further consider a diffusion couple between two alloys of this system : X in the A rich solid solution (α) and Y in the adjacent phase field (β). Suppose now that the diffusion path for this couple is calculated on the bases of a planar boundary between the phases and that this calculated path is plotted on the appropriate isotherm of the ternary phase diagram to produce Figure 1 (in which the phase diagram isotherm is shown in rectangular co-ordinates for convenience).

Since this diffusion path is seen to loop into the two phase ($\alpha+\beta$) regime, it is in fact virtual. The section of the path shown as a broken line runs along a tie-line and corresponds to the assumed planar interface of the couple.

Kirkaldy and Brown have shown that, where a portion of a (composite) diffusion path passes into a two phase region from a single phase region at an angle to the tie-lines, the morphology of the resulting two phase zone is dependent on the way in which that path exists from the two phase region of the phase diagram. Exit to the same single phase region describes a zone of isolated precipitation in the diffusion couple, while exit into another phase represents a non-planar interface (possibly with associated isolated precipitation). If the shape of a calculated virtual diffusion path is broadly similar to the composite path which it represents, then this conclusion of Kirkaldy and Brown can probably be applied to the virtual path as well (in fact this was assumed without comment by Kirkaldy and Brown). Therefore, length PQ of the diffusion path in Figure 1 corresponds to a region of isolated precipitation while length RS is associated with a non-planar interface.

3. ALTERNATIVE TO THE PSEUDO-BINARY APPROACH

As described above, the pseudo-binary approximation for a ternary multiphase system (i.e. that no concentration gradient can occur at equilibrium through a two phase region) is a satisfactory expedient for describing a diffusion couple between two alloys of the system comprising different single phases, providing that phase interfaces all remain planar. If this proviso is not valid then a virtual path is the result.

Consider now an infinite diffusion couple between two alloys of the ternary system ABC, in which component A is the majority element, or solvent, and components B and C are the minority elements, or solutes; one of the alloys comprising single phase α and the other a mixture of α and β phases. Here a two phase region is in existence from the start and for any real ternary system concentration gradients through it are bound to occur. For such a system, therefore, it is more sensible to develop an analysis in which account is taken of concentration gradients through the two phase region rather than relying on the virtual path approach. The diffusion paths determined from such an analysis will be Composite Paths.

It is assumed that the $\alpha+\beta$ alloy lies on the α rich side of the two phase region such that α is the majority or matrix phase. Further it is assumed that all diffusion through the two phase region is via the α phase and none through the β. Equilibrium between the α and β in the two phase region is maintained by dissolution or growth (including precipitation) of β.

The diffusion equations for the distribution of components B and C throughout the two phase region may be obtained from the multicomponent version of Fick's 2nd Law:-

$$\frac{\partial Ci}{\partial t} = \sum_{j=1}^{n-1} \frac{\partial}{\partial x} \left[Di^{n}j \quad \frac{\partial Cj}{\partial x} \right], \; i = 1 \text{ to } (n-1) \qquad (1)$$

Where n = 3 for a ternary system.

Since no diffusion occurs through the β phase, the concentration gradients on the right hand side of equation (1) refer only to the α phase. The term on the left hand side, however, describes the nett accumulation or depletion of B or C, which must take account of the inert reservoir of components in the β phase since it maintains equilibrium with the α. On expansion, therefore, equation (1) becomes:-

$$\frac{\partial}{\partial t} \left[m_\alpha \cdot C_B{}^\alpha + (1-m_\alpha) \; C_B{}^\beta \right] = \frac{\partial}{\partial x} \left[D_{BB} \cdot \partial C_B{}^\alpha \right] + \frac{\partial}{\partial x} \left[D_{BC} \cdot \frac{\partial C_C}{\partial x} \right] \qquad (2)$$

$$\frac{\partial}{\partial t} \left[m_\alpha \cdot C_C{}^\alpha + (1-m_\alpha) \; C_C{}^\beta \right] = \frac{\partial}{\partial x} \left[D_{CB} \cdot \partial C_B{}^\alpha \right] + \frac{\partial}{\partial x} \left[D_{CC} \cdot \frac{\partial C_C{}^\alpha}{\partial x} \right] \qquad (3)$$

Where:-

m_α and m_β $(=1-m_\alpha)$ are the mass fractions of α and β phases respectively.

$C_B{}^\alpha$ and $C_B{}^\beta$ are the concentrations of B in α and β phases respectively.

$C_C{}^\alpha$ and $C_C{}^\beta$ are the concentrations of C in α and β phases respectively.

In the general case, the complexity of these equations defies solution. However, by considering a special case, simplification can be effected. The case to be considered is that described by Figure 2 with an α phase boundary parallel to the B axis.

The diffusion couple of interest is that between points X and Z. As will be described later, in the section on "Phase Boundaries and Diffusion Coefficients", a system whose phase diagram resembles Figure 2 might reasonably be expected to have a very low value of the cross diffusion coefficient D_{CB} in the α phase region. Therefore, consistent with this, it is assumed that D_{CB} for the system under consideration is zero, not only in the single phase α region, but also in the two phase region since diffusion is confined to the α phase therein.

Because of the orientation of the α phase boundary on the equilibrium diagram, the concentration of C in the α phase remains constant throughout the two phase region.

$$\text{i.e.} \quad \frac{\partial C_C^{\alpha}}{\partial x} = 0 \text{ and constant} \tag{4}$$

Taking this into consideration, together with the fact that D_{CB} is zero, equation (3) becomes:-

$$\frac{\partial}{\partial t} \left[m_\alpha \cdot C_C^{\alpha} + (1-m_\alpha) \cdot C_C^{\beta} \right] = 0 \tag{5}$$

As stated above, C_C^{α} is constant and therefore, if C_C^{β} is also constant, equation (5) becomes:-

$$C_C^{\alpha} \cdot \frac{\partial m_\alpha}{\partial t} = C_C^{\beta} \cdot \frac{\partial m_\alpha}{\partial t}$$

The solutions to this equation are

either : $C_C^{\alpha} = C_C^{\beta}$, i.e. no two phase region on the phase diagram.

or : $\frac{\partial m_{\alpha}}{\partial t} = 0$

$$m_{\alpha} = \text{constant} \qquad (6)$$

If the β phase boundary on the phase diagram is also parallel to the B axis then the condition of constancy for C_C^{β} is met and the above solution (6) is valid. Therefore, under these circumstances the proportions of α and β remain constant throughout the two phase region and the appearance of the composite diffusion path on the ternary isotherm of the phase diagram (assuming the tie-lines to be parallel to the C axis) is shown in Figure 3.

Since the C concentrations of α and β in equilibrium with each other are fixed, the constancy of m_{α} results in the overall concentration of C remaining invariant throughout the two phase region, as shown in Figure 3 (line ZH). The broken line HG runs along a tie-line and corresponds to a step change in concentration in the diffusion couple.

Figure 3 shows the diffusion path through the two phase region of the diffusion couple, but this gives no clue as to the nature of the B concentration profile. To determine this consider equation (2) taking account of equation (4) :-

$$\frac{\partial}{\partial t}\left[m_{\alpha} \cdot C_B^{\alpha} + (1-m_{\alpha}) \cdot C_B^{\beta}\right] = \frac{\partial}{\partial x}\left[D_{BB} \cdot \frac{\partial C_B^{\alpha}}{\partial x}\right] \qquad (7)$$

Because of the assumption that tie-lines are parallel to the C axis, α and β phases must have the same B concentration in order to co-exist in equilibrium. Therefore, since it was specified that local equilibrium be maintained between α and β throughout the two phase region, the conclusion is reached that at all points in the two phase region :-

$$C_B^{\alpha} = C_B^{\beta} = C_B \qquad (8)$$

Substitution in equation (7) gives :-

$$\frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x} D_{BB} \cdot \frac{\partial C_B}{\partial x} \qquad (9)$$

This is now the simple form of Fick's 2nd Law as for a binary single phase system. Therefore, it appears that, with respect to diffusion, component B sees no two phase structure at all. However, this is not strictly true since the presence of the β phase affects the kinetics of the system. For example, the β phase boundaries may act as fast diffusivity paths which may be important under certain circumstances. Also, the fact that no diffusion can occur through the β phase means that the β particles act as obstacles to the diffusion flux of B, effectively reducing the cross sectional area of the system with respect to diffusion.

The extent to which the flux through the two phase region is affected, by these and other kinetic effects of the β presence, depends on the volume fraction and morphology of the β phase and is difficult to quantify. However, account may be taken of these effects by incorporating an additional factor in the diffusion coefficient D_{BB} in equation (9). Thus, although diffusion in the two phase region is restricted to the α phase, the coefficient D_{BB} in equation (9) is not equal to that pertaining to single phase α of the same composition. Instead it equals D_{BB}^{α} multiplied by some factor to account for the kinetic influence of the β phase on the diffusion flux. Since this additional factor depends on the volume fraction of β, it is a function of m_{β}.

It is frequently a good approximation to assume that direct diffusion coefficients, like D_{BB}, are independent of composition (11). However, it is now seen that when dealing with a two phase system, such as the one described above, it is important to ensure that m_β is also constant with composition before making this approximation. For the model system described above, it was shown (equation 6) that m_α and hence m_β are in fact, constant across the two phase region. Therefore, it is probably reasonable to assume that D_{BB} is constant so that equation (9) can be written :-

$$\frac{\partial C_B}{\partial t} = D_{BB} \cdot \frac{\partial^2 C_B}{\partial x^2} \qquad (10)$$

Equation (10) has a simple error function solution.

To summarize, for an $\alpha/\alpha+\beta$ type diffusion couple of the ternary system ABC, for which : both α and β phase boundaries run parallel to the B axis, tie-lines run parallel to the C axis, D_{BB} equals zero and no diffusion occurs through the β phase, the concentrations of C in both α and β phases remain constant across the two phase region, while the concentration profile of component B is as defined by equation (10).

This, of course, only deals with the two phase region in isolation. To obtain the complete concentration profiles for the couple, and hence the diffusion path as shown in Figure 3, it is necessary to also consider solution to the B and C diffusion equations in the single phase α region according to, for example, one of the models discussed in (9). The solutions in the single and two phase regions must then be matched by considering the flux balance across the interface between the two. By this procedure, the whole diffusion path, i.e. XGHZ on Figure 3, would be determined.

So far, attention has focused on a single simplified ternary system. However, the potential exists for extension of this method of analysis to more complex systems. As an illustration, consider a ternary system ABC similar to the one considered above except that the stability range of the single phase β region on the pertinent isotherm of the ternary phase diagram is infinitessimally small, as shown in Figure 4.

All other assumptions about the system are as previously. Thus, the diffusion equation for component C in the two phase region can be reduced to equation (5) :-

$$\frac{\partial}{\partial t}\left[m_\alpha . C_C^\alpha + (1-m_\alpha)\, C_C^\beta\right] = 0 \qquad (5)$$

The vertical α phase boundary leads to the conclusion that C_C^α is constant. Further, since there is only one stable β composition (C_B^β, C_C^β) which must be maintained constant throughout the two phase region, equation (5) becomes :-

$$C_C^\alpha . \frac{\partial m_\alpha}{\partial t} = C_C^\alpha . \frac{\partial m_\alpha}{\partial t}$$

Hence, as before, providing that a real two phase system exists on the phase diagram, the result is :-

$$m_\alpha = \text{constant}$$

Thus, assuming that the tie-lines radiate regularly from the single phase β region, the diffusion path resembles that shown on Figure 4 i.e. JKLM. As before the C concentration of both α and β phases remain constant throughout the two phase region. To obtain the B concentration profile, consider the relevant diffusion equation (2) with m_α constant, C_C^α constant and C_B^β equal to zero :-

$$m_\alpha \cdot \frac{\partial C_B^\alpha}{\partial t} = \frac{\partial}{\partial x} D_{BB} \left[\cdot \frac{\partial C_B^\alpha}{\partial x} \right] \qquad (11)$$

Assuming that the diffusion coefficient D_{BB} is constant across the two phase region (taking account of the effect on the flux of the inert β phase) equation (11) becomes :-

$$\frac{\partial C_B^\alpha}{\partial t} = \frac{D_{BB}}{m_\alpha} \cdot \frac{\partial^2 C_B^\alpha}{\partial x^2} \qquad (12)$$

Thus the diffusion of B through the two phase region is like that through a binary single phase system, but with a modified diffusion coefficient.

In summary, it can be said that a two phase region of a ternary system, unlike that of a binary, can accommodate a composition gradient. To develop such a composition gradient, either the relative proportions of the two phases or their compositions or both must vary across the two phase region of the system. The concept of the composite diffusion path is very useful for such a system since it illustrates the variation of both proportions and compositions of the two phases.

It so happens that for the two simplified model systems discussed above it was found that the proportions of the two phases (as described by m_α and m_β) were constant throughout the two phase region. However, this result stems from the particular assumptions made in the analyses and is not generally true.

4. PHASE BOUNDARIES AND DIFFUSION COEFFICIENTS

In the determination of solute concentration profiles across a two-phase (e.g. α/β) ternary diffusion couple, solutions to the diffusion equation on each side of the phase boundary are matched by means of flux continuity relations. This procedure requires knowledge of the system's phase diagram, since it is necessary to be able to relate the solute concentrations to each other at the phase boundary. However, this presupposes that the position of the phase boundary is independent of the values of the diffusion coefficient matrix, which is not strictly true since they share a thermodynamic ancestry.

The thermodynamic element of the practical diffusion coefficients (i.e. D coefficient) of a multicomponent system is described elsewhere (see [12] for example). The important point to note here is that the cross diffusion coefficients contain information on the variation of the chemical potential of one element with the concentration of another. Thus, in the ternary single phase system ABC, with A as solvent, the coefficient D_{BC} is proportional to $\partial\mu_B/\partial C_C$, where μ_B is the chemical potential of component B, etc. A large value, then, of D_{BC} implies that the chemical potential of B changes rapidly as the concentration of C(C_C) varies. Therefore, since the value of μ_B contributes to the free energy of the system as a whole, this too must vary strongly with C_C. Now, in general, if the free energy of a given phase changes rapidly with any given parameter, then the range of that parameter over which the phase concerned is stable is likely to be small. Hence, a large value of D_{BC} for a phase implies that its stability range with C concentration is narrow.

The subject of phase equilibria is, of course, a complex field in itself and it would be wrong to assume from the above paragraph that it is possible to predict the positions of phase boundaries simply from a knowledge of diffusion coefficient data or vice versa. However, even this shallow understanding of the relationship between phase equilibria and diffusion data can be of some value in making general predictions about one on the basis of firm knowledge concerning the other for a particular system. It is likely that a deeper understanding of the link between these hitherto largely unconnected branches of scientific knowledge would be of great value and would therefore be a profitable field for future research.

Evidence has been obtained for the sort of interdependence described above between the values of diffusion coefficients and the shapes of phase boundaries. Measurements made on cobalt solid solution of the ternary substitutional alloy system cobalt -chromium - aluminum at 1100°C [13] have shown that the value of the cross diffusion coefficient $D_{Al}^{Co}{}_{Cr}$ is very low compared with the values of the other coefficients. This means that the chemical potential of aluminum shows very little dependence on chromium concentration, which suggests that there is little chemical interaction between chromium and the rest of the system. Following the arguments outlined earlier, this leads to the conclusion that the α phase boundary of the Co-Cr-Al system runs almost parallel to the chromium axis. Unfortunately, the complete phase diagram of the Co-Cr-Al system is not available, but some information was obtained by analysing (by EPMA) the α phase of the two phase alloy : Co 25.7 wt% 11.7 wt%Al. This alloy had previously been annealed in vacuo for 5 days at 1200°C and quenched, so that α and β phase compositions should have been at either end of a tie-line on the 1200°C isotherm of the phase diagram.

The α phase was found to have the composition : Co 27.2 wt%Cr 5.6 wt%Al, which may be compared with the positions of the α phase boundary at 1200°C in the binary system cobalt-aluminum [14], i.e. Co 6.5 wt%Al. Thus it is seen that at 1200°C (and therefore, probably at 1100°C also) the α phase boundary in the Co-Cr-Al system does in fact run almost parallel to the chromium axis over a wide range of chromium concentrations.

Kirkaldy and Brown [10] have discussed the possibility of making a diffusion couple of which both terminal alloys lie in the same single phase field, but whose diffusion path loops into adjacent two phase and and even single phase regions. Consideration was given to the possibility of observing this effect in the Co-Cr-Al system. In particular, the question of whether a region of the α phase (based on CoAl) could be "grown" in a diffusion couple made up of two alloys in the cobalt solid solution (α) was seriously investigated.

The reason for this interest lies in a problem that besets superalloy development, i.e. that optimisation of high temperature mechanical strength is incompatible with the maintenance of adequate environmental resistance. In order to circumnavigate this problem, attempts have been made to separate these conflicting requirements by designing an alloy with good mechanical properties and then applying a coating to resist oxidation and hot corrosion. One of the most important such coating procedures is aluminizing, whereby the surface of the superalloy is enriched in aluminum (to produce a layer of CoAl in the case of cobalt-based superalloy). Unfortunately, such coatings deteriorate in service as a result of (amongst other things) interdiffusion with the substrate. Thus, not only is the alloy's ability to maintain a protective oxide diminished, but also the mechanical properties of the substrate may be impaired by the influx of aluminum from the coating and by the loss of strengthening components to the surface.

Attempts to suppress the effect by the interposition of a physical diffusion barrier between the coating and the alloy substrate have up to now proved largely unsuccessful.

It was considered that a possible answer to this problem might have been to manipulate the metal chemistry of the superalloy surface so as to maintain a protective aluminide by the mechanism described above, i.e. growing a region of protective β phase by harnessing diffusional interactions in a otherwise single phase α system. However, it soon became apparent that in the case of the Co-Cr-Al system, at least, this would not be feasible because of the low value of the cross diffusion coefficient $D_{Al}^{Co_{Cr}}$ coupled with the fact that the α phase boundary is almost parallel to the chromium axis. As described earlier, these two features are probably manifestations of a single characteristic of the system.

To illustrate the reason why diffusion path looping out of the single phase α region is not possible, the assumption is made that the Co-Cr-Al system closely approximates to the model system ABC, in which D_{CB}^{A} is zero and the α phase boundary is parallel to the B axis, i.e. as shown in Figure 2.

Consider a couple between W and X. In order that any β phase be formed, the diffusion path must loop into a region of higher C concentration than that of alloy W. However, as described in [9], this is impossible if D_{CB} is zero because under these circumstances the B concentration gradient has no influence on the diffusion of C and so C is bound to diffuse down its own concentration gradient. This argument applies even in the case of a diffusion couple between alloy compositions W and Y, the diffusion path of which turns out to be simply a vertical line between the two terminal compositions.

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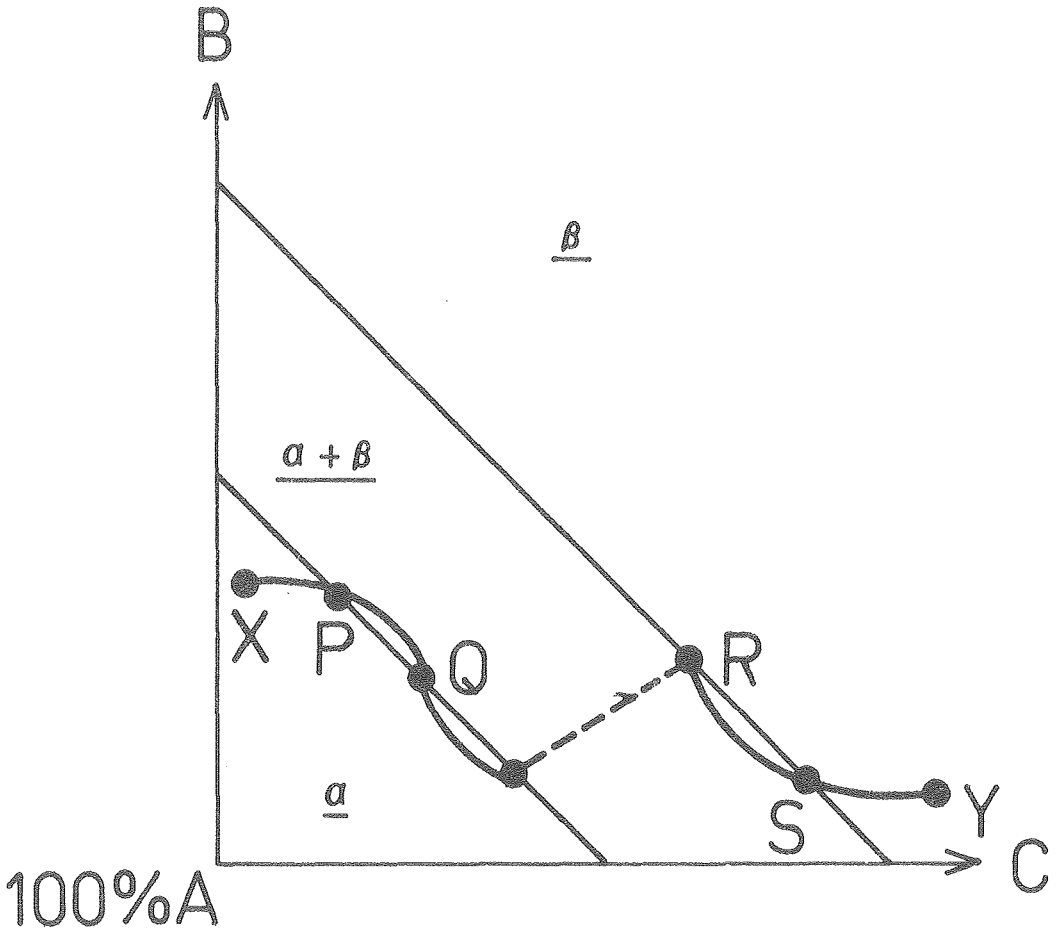

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Figure 1. Calculated Diffusion Path for Couple XY.

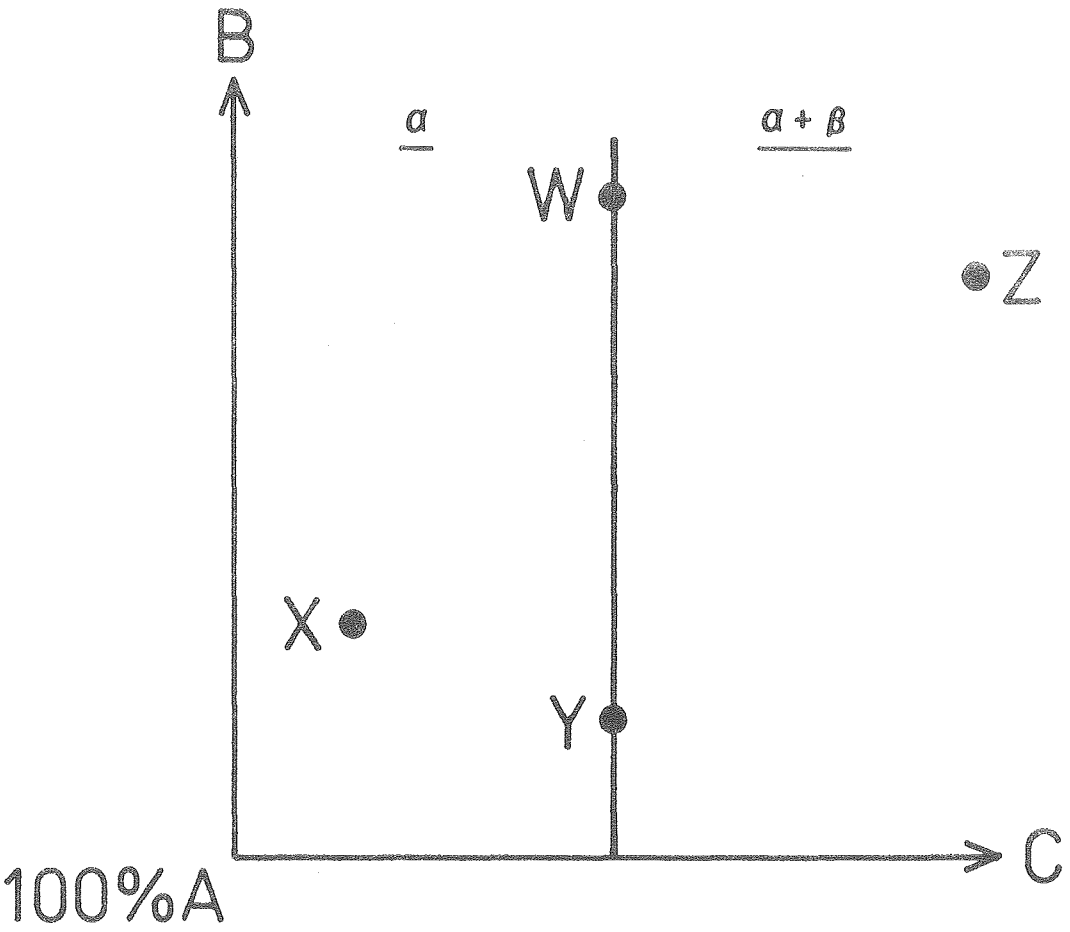

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Figure 2. Isothermal Section of ABC Phase Diagram.

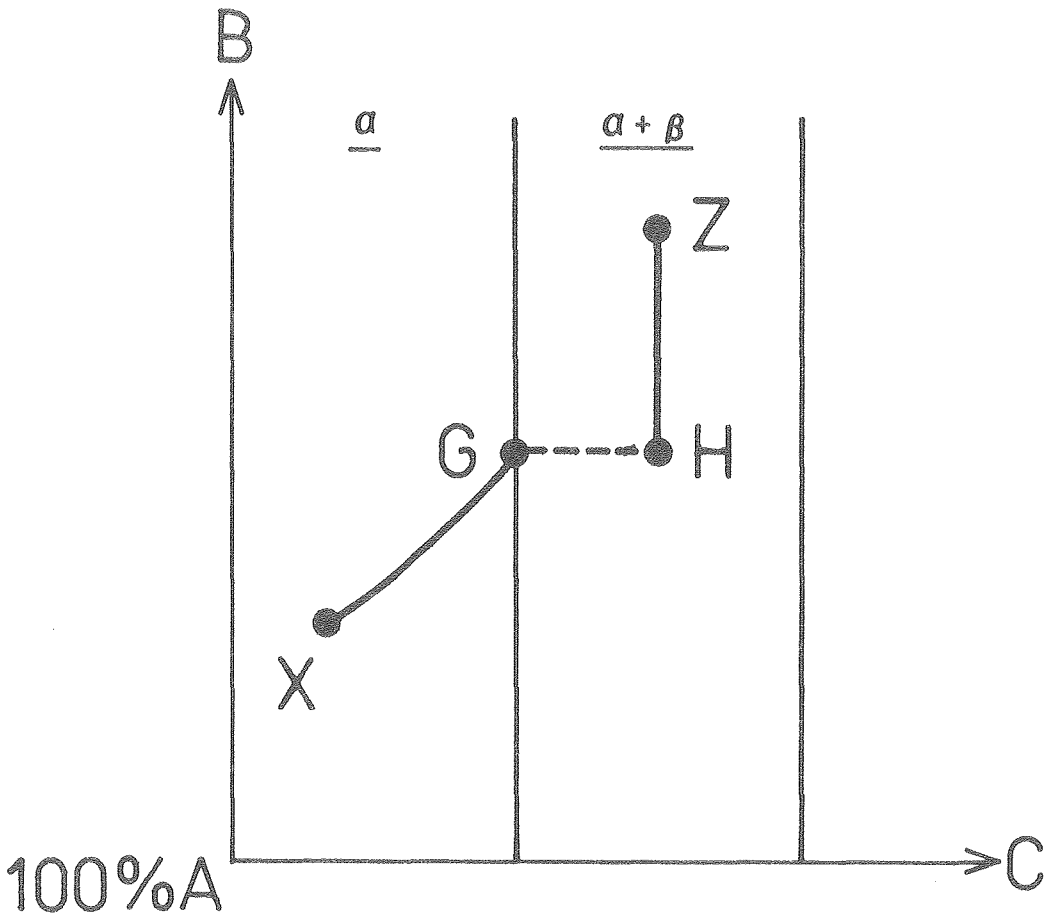

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Figure 3. Composite Diffusion Path of Couple XZ.

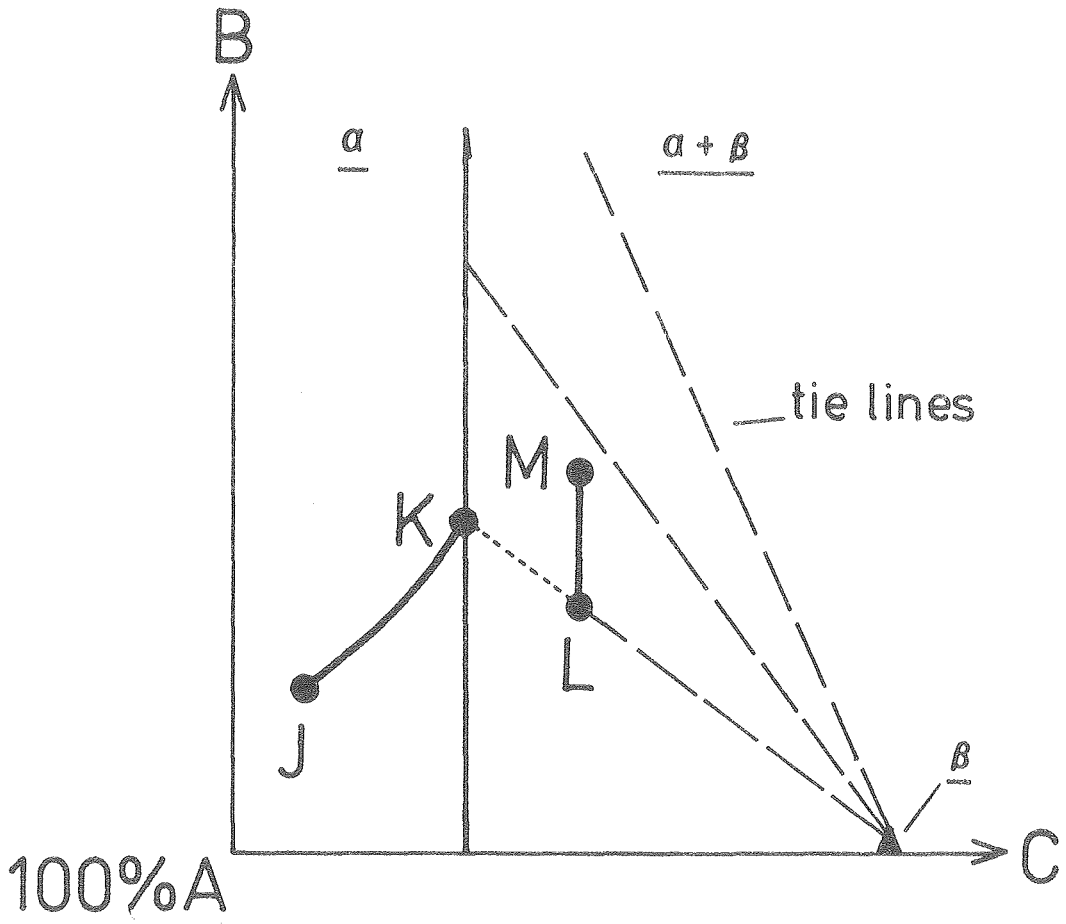

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Figure 4. Composite Diffusion Path of Couple JM.