



MULTIPHASE LAYER GROWTH KINETICS IN FINITE GAS/SOLID DIFFUSION COUPLES

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Abstract—A model of the diffusion kinetics in multiphase finite one-dimensional binary diffusion couples is presented. The mathematical description of the diffusion process based on the analytical solution of Fick's laws allows the time evolution of the microstructure, i.e. the number of phases present in samples and their thickness, to be predicted from the known values of diffusion coefficients and the known homogeneity ranges. Conversely, the diffusion coefficients can be calculated in all phases of a finite sample from the movement of phase boundaries. As a first approach the Hf–N and Nb–C systems were treated.
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1. INTRODUCTION

Gas/solid diffusion couples offer an exceptional opportunity to study both diffusivities and the phase equilibrium in certain binary systems at high temperatures. Generally no problems exist in supplying an appropriate amount of diffusing species, in contrast to solid/solid diffusion couples where substantial problems may be encountered in contacting the two halves of the couple at high temperatures. In gas/solid couples the in-diffusing species need not necessarily be a gas in pure form. Thus (together with nitrides and oxides) carbides, borides and sulphides can be prepared by using carbon, boron and sulphur containing gases or media, which promote a transport reaction. The diffusion process is easier to perform and to describe if the surface concentration of the diffusing species is constant at a given temperature, i.e. if a constant gas pressure is applied.

Upon in-diffusion of non-metals, all phase boundaries move to the centre of the sample during the diffusion process. Consequently, the thickness of the outer phases (i.e. the phases located outside the core) increases, whereas the core phase (i.e. the phase with the lowest concentration of diffusing atoms) becomes narrow. After a certain time the phase currently in the centre of the sample disappears. Layer growth and disappearance of central phases continue successively until only the phase having the highest possible concentration remains in the specimen. The concentration in the single phase rises and the concentration profile consequently becomes flat. When the concentration is equal to the maximum

concentration given by the gas/solid equilibrium conditions, the diffusion process is finished.

The diffusion-controlled phase boundary movement is usually described by the well-known parabolic law as long as the diffusion geometry can be regarded as semi-infinite. If, however, the diffusion process is performed in plane-sheet samples, the proportionality between the layer thickness and the square root of time is no longer constant. The layer thicknesses also increase with decreasing size of the diffusion couple [1]. It has been observed in a recent study [2] that this effect can prevail for sample thicknesses that would be estimated to be safely quasi-infinite. An influence on the layer thickness was already observed when the sample thickness was 100 times larger than the sum of the layer thicknesses of all intermediate phases formed.

A model of the diffusion process based on the classical Boltzmann–Matano theory [3–6] cannot explain the observed layer growth enhancement. Similarly, it is not able to interpret the disappearance of central phases. Both phenomena were considered by Pawel [1, 7], but he solved the diffusion equations by using numerical methods that cannot accurately reproduce the behaviour of diffusion couples in extreme cases (disappearance of a phase, very narrow phases, etc.).

In the present study an analytical formalism is developed that describes the time evolution of phase band thicknesses in reaction diffusion couples with restricted plane-sheet diffusion geometry in which only the non-metal diffuses. This assumption is valid to a large extent for practically all transition metal–non-metal systems (an exception being Fe–O, for example). In contrast to the numerical solution, the analytical formalism allows the evolution of phase bands having a very narrow homogeneity range to be predicted. Advantages of the analytical

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solution of the diffusion equation were demonstrated by Kidson [5] and Crank [8], for instance.

2. DIFFUSION PROCESS IN FINITE SYSTEMS

In gas/solid diffusion couples, the diffusion flow of the non-metal decreases with increasing distance from the surface. If the diffusivity of the penetrating atoms can be characterized by a constant diffusion coefficient within every phase, the diffusion flow decreases as a Gaussian function. The diffusion flow would then be equal to zero very far away from the gas/solid interface. As an infinite diffusion couple, a sample in which the diffusion flow vanishes before its centre is usually considered. Behind the plane with zero diffusion flow, the spatial changes of the diffusion flow are also equal to zero. Consequently, according to the continuity equation, the time changes of the concentration are equal to zero as well.

Diffusion couples often cover narrow phases, which does not permit unambiguous detection of a phase band, or they may be too thin to be able to measure homogeneity ranges of phases. For techniques commonly used (metallography, electron probe microanalysis) it is useful if all phases are appropriately thick. In infinite samples, a sufficient thickness can only be achieved by using a very long diffusion time.

In real (finite) diffusion couples the diffusion flow does not usually vanish before the centre of the sample. Exactly the same case occurs in the second half of a symmetrical specimen. The atoms penetrating through opposite sample surfaces arrive at the centre of the sample in the same quantity (with the same diffusion flow). The process can be mathematically treated as a superposition of two opposite diffusion flows within the core, assuming formally that the diffusing atoms penetrate into the second half of the specimen. Another description is based on the assumption that the central phase is created by a non-permeable wall that prevents the penetration of atoms through the core. The returned atoms reduce the diffusion flow in the core. Both approximations give exactly the same result. Practically, the second description agrees more with reality, but the central plane cannot be regarded as an absolutely non-permeable wall. At the centre of the sample, random fluctuations of diffusing atoms can be observed. Nevertheless, as far as macroscopic diffusion flow is concerned, random fluctuations have no effect on the diffusion process.

The situation at the interface between the core and its adjacent phase is completely different. As this boundary is moveable (unlike the central plane), the atoms penetrating from the opposite sample surface (or the atoms returned from the centre) are consumed for layer growth and phase transformation.

The dependence of the diffusion flow on the distance from the surface calculated for finite one-dimensional gas/solid diffusion couples is pre-

sented in the Appendix and illustrated in Fig. 1. However, the diffusion flow is not a measurable quantity. Thus, we will discuss the influence of a finite sample geometry on the concentration profile and phase boundary movement.

At the beginning of the diffusion process, the diffusion couple behaves like an infinite sample (Fig. 1(a)). The concentration in the centre remains constant and equal to the starting concentration. The phase growth follows a parabolic law. After a certain time, the diffusing atoms reach the centre of the sample (Fig. 1(b)). The core is filled from both of the opposite sides, which leads to the steep increase in concentration in the core. The diffusing atoms that arrive at the next opposite phase boundary reduce the diffusion flow coming out from this interface. According to the continuity equation, the movement of the innermost phase boundary is accelerated. Physically speaking, the difference between the input and output diffusion flow, which is the factor

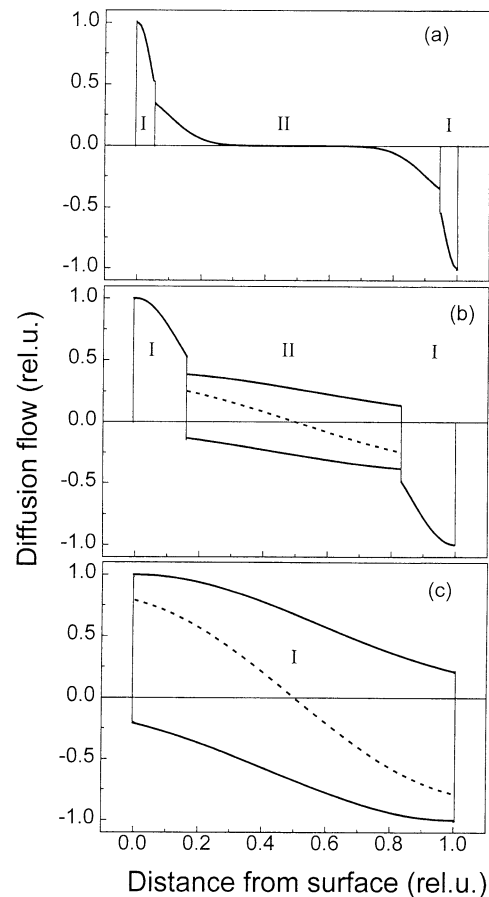


Fig. 1. Diffusion flow as a function of distance from the surface in a two-phase diffusion couple. (a) At the beginning of the diffusion process, the diffusion flows coming from both surfaces vanish before the centre. (b) The reduced diffusion flow in the core causes the accelerated phase growth. (c) After a long diffusion time, only one phase remains in the diffusion couple; the diffusion flow through the sample surface drops. The total diffusion flow is plotted with a dashed line.

determining the velocity of the phase boundary movement, becomes larger. Moreover, the accelerated growth of the outer layer close to the core causes all phase boundaries to move faster towards the centre, because the extension of one phase modifies the ratios of diffusion flows at every phase boundary in the sample. As a result, deviations in the layer growth from the parabolic law are observed.

Finally, if only one phase remains in the diffusion couple, the diffusing atoms reach the opposite sample surface (Fig. 1(c)). The concentration of diffusing atoms in the sample increases and the diffusion flow decreases. As soon as the concentration reaches its maximum value everywhere in the specimen, the macroscopic diffusion flow vanishes and the diffusion process is completed.

3. PHASE BOUNDARY MOVEMENT

Upon knowledge of the diffusion flow, it is possible to calculate the positions of phase boundaries as a function of diffusion time and sample thickness. According to Refs [3–5], the velocity of phase boundary movement follows directly from the continuity equation. It is proportional both to the difference in diffusion flow in neighbouring phases and to the difference in concentrations at the phase boundary. As the concentration differences at phase boundaries, Δc_i , remain constant (equal to the width of two-phase regions in the phase diagram at a given temperature), the partial derivatives in the continuity equation (equation (A3)) can be replaced by total derivatives and by differences, respectively:

$$\left(\frac{dx}{dt}\right)_i = \frac{J_i - J_{i+1}}{\Delta c_i} \quad (1)$$

where $(dx/dt)_i$ is the velocity of the movement of the i th phase boundary towards the core, Δc_i is the concentration difference (the concentration jump) at the i th phase boundary and J_i and J_{i+1} are the input and output diffusion flows at the i th phase boundary. The position of this phase boundary after the diffusion time t is given by integration of equation (1) over the diffusion time:

$$x_i(t) = \frac{1}{\Delta c_i} \int_0^t (J_i - J_{i+1}) dt' \quad (2)$$

$$x_n = \left[\frac{D_n(c_n^+ - c_n^-)}{\Delta c_n} \times \frac{\exp\left(-\frac{\xi_n^2}{D_n}\right)}{\int_{\xi_{n-1}}^{\xi_n} \exp\left(-\frac{y'^2}{D_n}\right) dy'} - \frac{D_{n+1}(c_{n+1}^+ - c_{n+1}^-)}{\Delta c_n} \times \frac{\exp\left(-\frac{\xi_n^2}{D_{n+1}}\right)}{\int_{\xi_n}^{\infty} \exp\left(-\frac{y'^2}{D_{n+1}}\right) dy'} \right] \times \sqrt{t} + \frac{D_{n+1}(c_{n+1}^+ - c_{n+1}^-)}{\Delta c_n} \times \frac{\exp\left(-\frac{\xi_n^2}{D_{n+1}}\right)}{\int_{\xi_n}^{\infty} \exp\left(-\frac{y'^2}{D_{n+1}}\right) dy'} l \int_{l/\sqrt{t}}^{\infty} \frac{1}{\tau^2} \exp\left(\frac{\xi_n \tau}{D_{n+1}}\right) \exp\left(-\frac{\tau^2}{4D_{n+1}}\right) d\tau \quad (5)$$

In all outer phases, the diffusion flow changes with diffusion time as $1/\sqrt{t}$, as follows from equation (A16). The movement of the outer phase boundaries is then given by

$$x_i = \left[\frac{D_i(c_i^+ - c_i^-)}{\Delta c_i} \times \frac{\exp\left(-\frac{\xi_i^2}{D_i}\right)}{\int_{\xi_{i-1}}^{\xi_i} \exp\left(-\frac{y'^2}{D_i}\right) dy'} - \frac{D_{i+1}(c_{i+1}^+ - c_{i+1}^-)}{\Delta c_i} \times \frac{\exp\left(-\frac{\xi_i^2}{D_{i+1}}\right)}{\int_{\xi_i}^{\xi_{i+1}} \exp\left(-\frac{y'^2}{D_{i+1}}\right) dy'} \right] \sqrt{t} \quad (3)$$

The symbols x_i and ξ_i denote the positions of phase boundaries in Cartesian coordinates and in Boltzmann variables, respectively; D_i is the diffusion coefficient in the i th phase, c_i^+ and c_i^- are the maximum and minimum concentrations within the phase i according to the phase diagram; and Δc_i is the concentration jump at the i th phase boundary. Phases are enumerated symmetrically from the sample surface towards the core, starting with 1 for the phase having the highest concentration of diffusing atoms. The innermost outer phase is labelled by n ; the core by $n+1$. Regarding phase boundaries, the first one separates the phases 1 and 2; the second one separates the phases 2 and 3 and so on.

Calculating the movement of the innermost phase boundary we must taken into account the discussed reduction of diffusion flow in the core. Compared to the outer phases, an additional term must be integrated over the diffusion time (see equation (A18)):

$$\int_0^t \frac{1}{2\sqrt{t'}} \exp\left(\frac{4l\xi_n\sqrt{t'} - t'^2}{4t'D_{n+1}}\right) dt' \quad (4)$$

This expression yields the last part of the sum in equation (5). Integral (4) was adjusted for numerical calculation by using the substitution $\tau = l/\sqrt{t'}$, where l is the sample thickness. The layer growth of the phase next to the core is then given by equation (5):

The lowest concentration in the central phase, c_{n+1}^- , is equal to the concentration of metalloids in the starting material, which is zero in pure metal.

If a diffusion couple is sufficiently thick or if the diffusion time is short enough, the diffusion flow vanishes before the centre of the sample. In such a case integral (4), and therefore the last expression in equation (5), goes to zero. Hence, the system of transcendental equations (3) and (5) can be written in the form of the frequently cited parabolic equation of layer growth in infinite diffusion couples [3–5]:

$$x_i = K_i \sqrt{t} \quad (6)$$

where K_i are the rate constants.

The last term in equation (5) characterizes the difference between finite and infinite diffusion couples. It can be considered as a correction factor for diffusion samples with finite geometry. Analogously to the parabolic layer growth that holds for infinite diffusion couples, we can also abbreviate the equations of layer growth in finite samples:

$$x_i = K_i(t, l) \sqrt{t} \quad (7)$$

where K_i is now a function of both the diffusion time and the sample thickness. The positions of phase boundaries in a one-dimensional diffusion couple are given by the solution of the system of transcendental equations (7).

4. ESTIMATION OF DIFFUSION COEFFICIENTS

For calculation of diffusion coefficients, the classical Boltzmann–Matano method is well established. This method works with derivatives of a measured concentration profile and can yield not only values of diffusion coefficients but also their dependence on concentration. However, the Boltzmann–Matano method is generally applied to single phase diffusion and not to reaction diffusion. Furthermore, a good quality of concentration data is needed. In phases having a narrow concentration range, the concentration profile has no significant shape, is difficult to measure and the concentration dependence of the diffusion coefficient can be neglected. Thus the use of the Boltzmann–Matano method is limited to phases having large homogeneity regions, which are identical with mono-carbides and mono-nitrides. For other phases, such as for sub-carbide and nitride phases, methods for calculating diffusion coefficients based on the evaluation of phase boundary movement in reaction diffusion couples are preferred.

It has been well explained [3, 4] that it is impossible to calculate the diffusion coefficients from the phase boundary movement only. That has rigorously been

demonstrated by Kidson [5] for solid/solid diffusion couples. In an infinite diffusion couple containing n phases, we have $(n - 1)$ equations (one equation for every phase boundary) for n unknown diffusion coefficients. As the rate constants do not depend on the diffusion time, the sole investigation of the time-dependent layer growth does not give an additional constraint. On the other hand, if a sample has a finite geometry, for every diffusion time or for every sample thickness we obtain, according to equations (5) and (7), different values of the factor K_i . Different diffusion times or different sample thicknesses thus supply additional equations for estimating diffusion coefficients. If the experimental data consist of more than two series of measurements (more than two different sample thicknesses or more than two different diffusion times), the least-squares analysis of diffusion coefficients can be applied.

The estimation of diffusion coefficients is based on the following procedure. Diffusion coefficients in all outer phases can be calculated if the diffusion coefficient in the core is known [3]. However, an appropriate value of the diffusion coefficient in the core has to be found. This diffusion coefficient is the main determining factor for acceleration of layer growth against the parabolic law. The higher the ratio between the diffusion coefficient in the core and the diffusion coefficient in the adjacent phase, the larger the layer growth enhancement. Assuming that diffusion coefficients do not depend on composition, the computation should yield constant values of diffusivities within every respective phase, despite the sample thickness (or the diffusion time). If the calculation is started with a low diffusion coefficient in the core, the obtained phase boundary movement is not satisfactorily fast. On the other hand, a high value of the diffusion coefficient in the core yields extremely high acceleration of the layer growth.

An investigation of diffusion coefficients in gas/solid diffusion couples that uses simulation of the layer growth enhancement can be performed using two experimental procedures: (a) samples with different thickness are annealed for the same diffusion time and (b) samples of the same size are annealed for different diffusion times. In both cases, the measured phase boundary positions are compared with those obtained from the calculation. In the present study the first possibility was used by taking wedge-shaped specimens [2]. In this way, temperature, diffusion time and heating rate could be kept constant. This method of sample preparation allows a series of diffusion couples to be made with continuously increasing thicknesses. The wedge-shaped samples fulfil the assumption of one-dimensional geometry if the angle of the wedge is small (a typical wedge angle was 10–20°). This was confirmed by an experiment where a wedge together with several plane-sheet samples of different thicknesses were annealed. The differences in the phase boundary positions were comparable with the errors in the measurement; even the phases

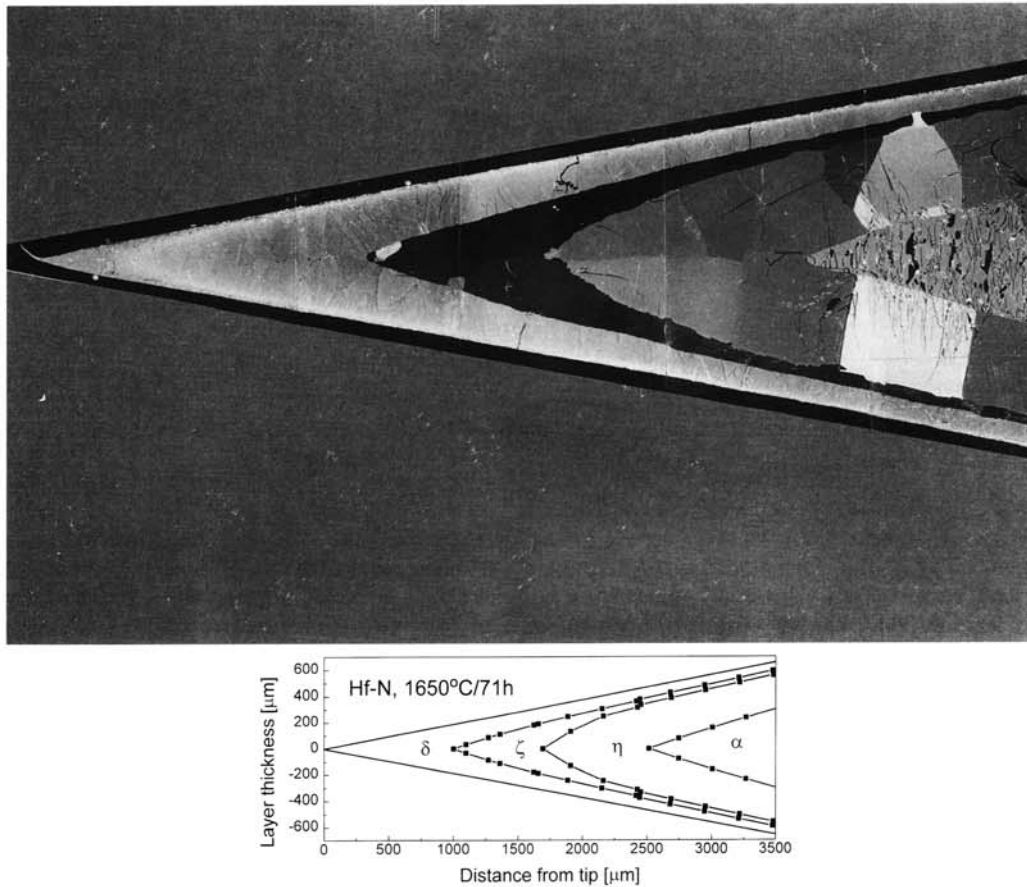


Fig. 2. (a) Phase band structure of wedge-shaped diffusion couple Hf-N prepared by annealing pure hafnium at 1650 °C for 71 h. (b) Positions of phase boundaries calculated with obtained diffusion coefficients.

disappeared at the same sample thickness in both cases.

To evaluate diffusion coefficients from the phase boundary positions in wedge-shaped samples, a FORTRAN computer code based on the procedure presented above was created.

5. RESULTS

As a first approach Hf-N and Nb-C were studied, because these systems show different behaviour regarding the layer thickness enhancement. The increase in layer thickness in the Hf-N system is striking, whereas in the Nb-C system only an insignificant acceleration of the layer growth with decreasing sample thickness was observed. The microstructure of a Hf-N wedge is shown in Fig. 2(a). The phase boundary structure that is given in Fig. 2(b) was calculated with the diffusion coefficients and limit concentrations listed in Table 1. The minimum and maximum concentrations were measured by electron probe microanalysis, recalculated to mole/cm³ in order to take into account the changes in molar volume [9, 10] and normalized to 1. Normalization of the surface concentrations to 1 is

optional and was used to visualize the different extent of concentration ranges in different materials. The normalization is connected solely to a multiplication constant that occurs in all terms containing concentrations. As the concentrations arise in fractions, the multiplication constant disappears in equations (3), (5), (6) and (7).

The large enhancement in layer growth in Hf-N is caused by the high diffusivity of nitrogen in pure hafnium. Consequently, the concentration of diffusing atoms in the core rises very quickly and the Hf-N system cannot be treated as a semi-infinite diffusion couple even if the sample thickness is large. When estimating the layer growth, restricted geometry must

Table 1. Diffusion data for Hf-N system at 1650 °C

Phase	c^+	c^-	D (cm ² /s)
δ -HfN _{1-x}	1	0.676	$(2.24 \pm 0.16) \times 10^{-9}$
ζ -Hf ₂ N ₃₋₄	0.619	0.590	$(1.38 \pm 0.24) \times 10^{-8}$
η -Hf ₃ N ₂₋₄	0.562	0.505	$(4.81 \pm 0.21) \times 10^{-8}$
α -Hf(N)	0.410	0	$(3-7) \times 10^{-4}$

c^+ and c^- : Highest and lowest nitrogen concentrations for the respective phase (in mol N/cm³ and normalized to the highest concentration) [2].

D : Nitrogen diffusion coefficients calculated from the positions of phase boundaries.

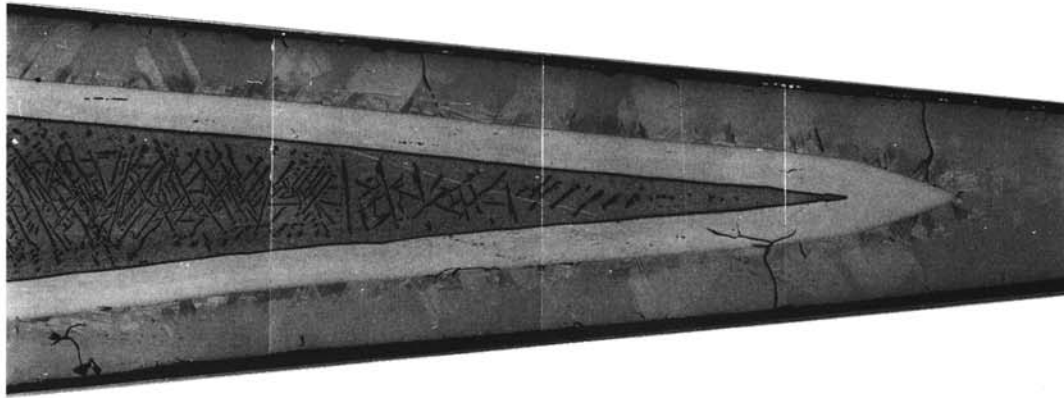


Fig. 3. Phase band structure of wedge-shaped diffusion couple Nb-C annealed at 2100°C for 6 h.

always be taken into account. Nevertheless, such systems are appropriate for calculation of diffusion coefficients from the phase boundary movements.

On the other hand, the Nb-C system shows only a small increase in the layer thickness with decreasing sample size. Changes in the layer thickness are visible only at the tip of the wedge (Fig. 3). The diffusion coefficients evaluated for Nb-C with the presented method are listed in Table 2.

The small observed variations in layer thickness are caused by the narrow homogeneity range of α -Nb(C) and by a very low maximum concentration in that phase. In such a phase, the concentration reaches its maximum value very quickly. The diffusion flow in the core is very low so that the diffusion flow within the α -phase cannot substantially influence the ratio between the diffusion flows at the phase boundaries. Therefore, variations in the sample thickness affect the layer growth only insignificantly. On the other hand, a large inaccuracy in the diffusion coefficient of the α -phase causes only small departures in the phase boundary positions.

Generally, the correctness of diffusion coefficients calculated from layer growth depends on the magnitude of the respective diffusion flows. The higher the diffusion flow, the more precise the estimated diffusion coefficient. This is the reason for the poor accuracy of the diffusion coefficient in α -Nb(C). However, the diffusion coefficients in the

next phases can be calculated with satisfactory accuracy, because the diffusion flow is much higher there. As a limit case, we can assume that no diffusion flow penetrates into the core. Then we can estimate the lowest value of the diffusion coefficients in all phases (excepting the core) that are necessary for the desired layer growth. The minimum diffusion coefficients that are listed in the last column of Table 2 agree with the diffusion coefficients calculated with a non-zero diffusion flow in α -Nb(C).

Finally, diffusion coefficients obtained in the Zr-O system are compared with values given by Pawel [7] (Fig. 4). Within the expected accuracy, our results agree with the diffusion coefficients presented in [7]. A slight difference was found only in the diffusion coefficients of the oxygen deficient β -Zr(O) phase that arises in the centre of samples.

We would like to emphasize that taking the finite diffusion geometry into account the diffusion coefficients can be obtained in all phases (according to the phase diagram at a given temperature). This is not possible in infinite samples [3, 4], where other methods have to be used.

Table 2. Diffusion data for Nb-C system at 2100°C

Phase	c^+	c^-	D (cm ² /s)	D (cm ² /s)
δ -NbC ₁₋₂	1	0.750	$(1.32 \pm 0.22) \times 10^{-7}$	1.20×10^{-7}
β -Nb ₂ C	0.632	0.578	$(2.87 \pm 0.10) \times 10^{-7}$	2.50×10^{-7}
α -Nb(C)	0.036	0	$< 2 \times 10^{-7}$	

Carbon diffusion coefficients listed in the fourth column were calculated using the presented method. Diffusion coefficients listed in the last column were also calculated from the positions of the phase boundaries, but assuming a zero diffusion flow in the central phase. In such a case the diffusion coefficient in the pure metal cannot be obtained. The highest and lowest carbon concentrations for the respective phases, c^+ and c^- (in mol C/cm³ and normalized to the highest concentration), were measured with EPMA/WDS [11].

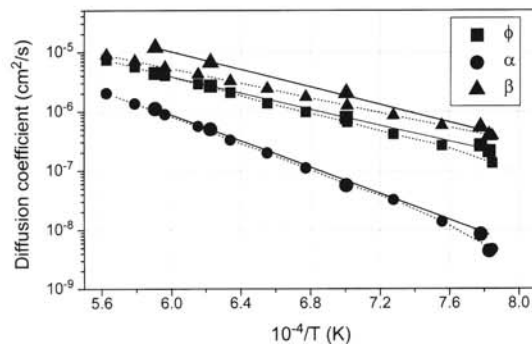


Fig. 4. Comparison of diffusion coefficients obtained for Zr-O. Large symbols show our data; the Arrhenius dependencies are plotted by solid lines. Data given in Ref. [7] are marked by small symbols and interconnected with dashed lines. Triangles correspond to β -Zr(O), circles to α -Zr(O) and boxes to ϕ -ZrO₂.

6. DISCUSSION

The main advantage of the presented method is that it can provide values of diffusion coefficients in all phases currently in the sample. However, diffusion coefficients do not have an identical precision in all phases. Their precision is highest in phases that are richest in diffusing atoms, and decreases with decreasing concentration of non-metals. Moreover, the precision as well as the accuracy of diffusion coefficients determined from the phase boundary movement generally increases if a large acceleration of layer growth is observed. As mentioned above, the accuracy of diffusion coefficients depends also on the value of the diffusion flow. Of course, the accuracy of diffusion coefficients is influenced by the accuracy in measuring both the layer thicknesses and the concentrations at the phase boundaries. From this point of view, diffusion coefficients are calculated with better precision in phases having a broader homogeneity range than in line-compounds—phases with a very narrow but non-zero homogeneity range.

Although the presented model of the diffusion process in finite one-dimensional reaction diffusion couples can characterize the evolution of the inter-phase boundary structure rather reliably, it has two principal limitations, which hold for the calculation of diffusion coefficients as well. In systems where the layer thickness enhancement with decreasing sample thickness is absent, the presented method cannot be applied *ab initio*. One of the diffusion coefficients has to be known. An exception is systems with a low concentration and a very narrow homogeneity range in the metalloid-poor phase discussed above. Second, by using this method, only diffusion coefficients independent of concentration can be obtained. If the diffusion coefficients depend strongly on composition, the method will fail. In such a case, it is helpful to calculate the concentration-dependent diffusion coefficients from the measured concentration profile and thereafter to obtain the diffusion coefficients in other phases from the phase boundary movements.

Finally, note that we assumed a non-restricted diffusion flow at the sample surface. Considering the time dependence of the diffusion flux (equations (A16), (A18)), we can see that at the beginning of the diffusion process ($t \rightarrow 0$) the diffusion flow should be infinite. However, the diffusion flow at the sample surface is restricted by the speed of penetration of the diffusing atoms through the diffusion interface, by the reaction of the diffusing atoms with the sample surface, by the decomposition of the gas molecules, etc., and therefore our assumption is not strictly correct. The restriction of the diffusion flow at the sample surface results in retardation of the layer growth during a certain diffusion time that is similar to the nucleation time [12]. After this diffusion time the desired diffusion flow given by equation (A18) falls below the threshold and the diffusion process

continues without restrictions. In addition, as the restriction of diffusion flow varies with both diffusion time and sample thickness, the acceleration of layer growth is enhanced again. If the differences in restriction of the diffusion flow along a wedge representing a set of samples with continuously decreasing thickness are large, the presented method can yield a slightly overestimated (higher) diffusion coefficient in the core.

7. CONCLUSIONS

A contribution to the phenomenology of phase band evolution in reaction diffusion couples has been made. The presented mathematical model of diffusion that has been supported by experiments in Hf–N, Nb–C and Zr–O systems yields the following differences between idealized (infinite) and the real (finite) samples.

In infinite one-dimensional diffusion couples, layer growth follows the well-known parabolic law. The distances of phase boundaries from the sample surface are directly proportional to the square root of the diffusion time. The proportionality constants depend on the maximum and minimum concentrations given by the phase diagram as well as on diffusion coefficients in all phases. As the proportionality constants of the parabolic layer growth do not depend on the diffusion time, a series of samples annealed for different diffusion times cannot be used for the calculation of diffusion coefficients.

In finite diffusion couples, the layer growth can be described by a modified parabolic law, where the rate 'constants' for phase boundary movements increase with diffusion time as well as with decreasing sample thickness. As a consequence, the layer growth in finite samples is accelerated in comparison with the layer growth in infinite samples. This acceleration causes a successive broadening of phase bands with decreasing sample thickness and/or with increasing diffusion time. The diffusion flow passing the surface of a finite sample sinks faster during the diffusion time than in infinite diffusion couples. During the diffusion process in finite samples, the phases with lowest concentrations disappear successively. Finally, only the phase having the highest concentration of non-metals remains in a finite diffusion couple. After the sample is homogenized, the macroscopic diffusion flow vanishes.

The acceleration of layer growth in finite one-dimensional diffusion couples can be used for the calculation of diffusion coefficients in all phases that exist in the system at a given temperature according to the phase diagram. This is not possible if the restricted diffusion geometry is not taken into account.

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APPENDIX

Calculation of the diffusion profile in multiphase diffusion couples

The diffusion process in systems with parallel geometry is described by the two one-dimensional Fick's laws:

$$J = -D \frac{\partial c}{\partial x} \quad (\text{A1})$$

and

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \quad (\text{A2})$$

where J is the diffusion flow, D is the diffusion coefficient, c is the concentration, x is the diffusion path and t is the diffusion time. Fick's second law [equation (A2)] has been derived from Fick's first law [equation (A1)] by using the one-dimensional continuity equation:

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x}. \quad (\text{A3})$$

Using the Boltzmann variable, $y = x/(2\sqrt{t})$, Fick's second law is usually transformed to the form of the total differential equation:

$$-2y \frac{dc}{dy} = \frac{d}{dy} \left(D \frac{dc}{dy} \right) \quad (\text{A4})$$

that can be solved analytically. Although equation (A4) is usually solved for concentrations (this means

that the solution has the form of a concentration profile), we will look for a solution in the form of a diffusion flow. Fick's second law, which was transformed to the Boltzmann variable:

$$-\frac{2y}{D} J = \frac{dJ}{dy} \quad (\text{A5})$$

has the solution

$$J(y) = J(y_0) \exp \left(- \int_{y_0}^y \frac{2y'}{D} dy' \right). \quad (\text{A6})$$

If the diffusion coefficient is independent of the composition, equation (A6) takes the form of a Gaussian function:

$$J(y) = J(y_0) \exp \left(- \frac{y^2 - y_0^2}{D} \right) \quad (\text{A7})$$

where $J(y_0)$ is the diffusion flow at the non-metal-rich phase boundary. The position of the phase boundary is denoted by y_0 . Analogously we can find a solution for the diffusion flow coming from the opposite sample surface:

$$J \left(\frac{l}{2\sqrt{t}} - y \right) = J(y_0) \times \exp \left\{ - \left[\left(\frac{l}{2\sqrt{t}} - y \right)^2 - y_0^2 \right] / D \right\} \quad (\text{A8})$$

where l is the sample thickness and t is the diffusion time. The ratio $l/2\sqrt{t}$ has the meaning of sample thickness in terms of the Boltzmann variable. The diffusion flow is a vector; thus the partial diffusion flows coming from the opposite directions are subtracted:

$$J(y) = J(y_0) \exp \left(- \frac{y^2 - y_0^2}{D} \right) \times \left[1 - \exp \left(\frac{4ly\sqrt{t} - l^2}{4tD} \right) \right]. \quad (\text{A9})$$

The macroscopic diffusion flow vanishes at the centre of the sample, i.e. at the plane $y = l/4\sqrt{t}$ (Fig. 1). According to Fick's first law (equation (A1)), no concentration gradient exists in the centre of a symmetrical sample and the concentration profile is usually very flat in the core. If the sample is very thick ($l \rightarrow \infty$), the diffusion time is very short ($t \rightarrow 0$) or the diffusivity is low ($D \rightarrow 0$), then the diffusion flow coming from the opposite side can be neglected, because the exponential function in the square brackets in equation (A9) is nearly equal to zero

and such a sample behaves like an infinite one (Fig. 1(a)).

To obtain the concentration profile, the equation of diffusion flow is further to be solved for concentrations. With the assistance of Fick's first law transformed, we can rewrite equation (A6) as follows:

$$\left(D \frac{dc}{dy}\right)_y = \left(D \frac{dc}{dy}\right)_{y_0} \exp\left(-\int_{y_0}^y \frac{2y'}{D} dy'\right). \quad (\text{A10})$$

The integration of equation (A10) yields the following dependence of concentration on the Boltzmann variable y within one phase:

$$c(y) = \left(D \frac{dc}{dy}\right)_{y_0} \int_{y_0}^y \frac{1}{D} \times \exp\left(-\int_{y_0}^{y'} \frac{2y''}{D} dy''\right) dy' + c_0 \quad (\text{A11})$$

where $(D dc/dy)_0$ is the first integration constant, which is proportional to the diffusion flow at the metalloid-rich phase boundary (at y_0), and c_0 is the second integration constant that is equal to the concentration at the plane y_0 . If the diffusion coefficient is independent of the composition, equation (A11) can be simplified:

$$c(y) = \left(\frac{dc}{dy}\right)_0 \int_{y_0}^y \exp\left(-\frac{y'^2 - y_0^2}{D}\right) dy' + c_0. \quad (\text{A12})$$

The integral in equation (A12) has the form of the well-known error function. Taking into account the limited thickness of sample that implicates penetration of diffusing atoms into the core from both sample surfaces, we obtain from equation (A9):

$$c(y) = \left(\frac{dc}{dy}\right)_0 \int_{y_0}^y \exp\left(-\frac{y'^2 - y_0^2}{D}\right) \times \left[1 - \exp\left(-\frac{4ly'\sqrt{t-l^2}}{4tD}\right)\right] dy' + c_0 \quad (\text{A13})$$

where D is the concentration-independent diffusion coefficient again. Inspecting equation (A13) we can see that the value of the integrand in a finite sample is less than in an infinite sample. Therefore the concentration profile becomes more flat in the central phase of a finite sample. Moreover, the value of the integrand in equation (A13) that corresponds to the

diffusion flow goes to zero if the diffusion time is very long or if the sample is narrow (Fig. 1(c)). Consequently, after a certain diffusion time, the concentration in the sample does not change any more and is equal to the maximum concentration c_0 , i.e. the sample is homogenised.

In the outer phases that do not reach to the centre of sample, the integration constants, $(dc/dy)_0$ and c_0 , follow from the boundary conditions. The latter (c^+) is equal to the maximum concentration of the non-metal at the given conditions. As the concentration at the non-metal-poor phase boundary is known and equal to the minimum concentration (c^-), the concentration gradient at the non-metal-rich phase boundary can be obtained from equation (A12) directly:

$$\left(\frac{dc}{dy}\right)_0 = \frac{c^- - c^+}{\int_{y_0}^{y_1} \exp\left(-\frac{y'^2 - y_0^2}{D}\right) dy'} \quad (\text{A14})$$

where y_0 and y_1 are the position of the non-metal-rich and the non-metal-poor phase boundary, respectively. The boundary conditions can only be applied if the respective phase appears in its entire concentration range given by the phase diagram. The concentration gradient at the border of the core has to be calculated from the starting condition. The concentration at the beginning of the diffusion process and/or very far away from the sample surface (at $y \rightarrow \infty$) is equal to the starting concentration of non-metal in the metal. According to equation (A12), the integration constant $(dc/dy)_0$ is given by

$$\left(\frac{dc}{dy}\right)_0 = \frac{c^- - c^+}{\int_{y_0}^{\infty} \exp\left(-\frac{y'^2 - y_0^2}{D}\right) dy'}. \quad (\text{A15})$$

In outer phases, the equation of diffusion flow takes the form

$$J(y) = \frac{D(c^+ - c^-)}{2\sqrt{t}} \frac{\exp\left(-\frac{y^2}{D}\right)}{\int_{y_0}^{y_1} \exp\left(-\frac{y'^2}{D}\right) dy'}. \quad (\text{A16})$$

The concentration profile in phases outside the core is given by

$$c(y) = c^+ - (c^+ - c^-) \frac{\int_{y_0}^y \exp\left(-\frac{y'^2}{D}\right) dy'}{\int_{y_0}^{y_1} \exp\left(-\frac{y'^2}{D}\right) dy'}. \quad (\text{A17})$$

The diffusion flow within the core is characterized by the equation

$$J(y) = \frac{D(c^+ - c^-)}{2\sqrt{t}} \frac{\exp\left(-\frac{y^2}{D}\right) \left[1 - \exp\left(\frac{4ly\sqrt{t-l^2}}{4tD}\right)\right]}{\int_{y_0}^{\infty} \exp\left(-\frac{y'^2}{D}\right) dy'}. \quad (\text{A18})$$

The concentration profile in the central phase follows the equation

$$c(y) = c^+ - (c^+ - c^-) \frac{\int_{y_0}^y \exp\left(-\frac{y'^2}{D}\right) \left[1 - \exp\left(\frac{4ly'\sqrt{t-l^2}}{4tD}\right)\right] dy'}{\int_{y_0}^{\infty} \exp\left(-\frac{y'^2}{D}\right) dy'}. \quad (\text{A19})$$