Diffusion-induced bending of thin sheet couples : theory and experiments in Ti-Zr system

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DIFFUSION-INDUCED BENDING OF THIN SHEET COUPLES: THEORY AND EXPERIMENTS IN Ti-Zr SYSTEM

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Abstract—Numerical and analytical calculations of concentration and stress distributions of thin-sheet diffusion couples have been carried out as well as the time dependence of the Kirkendall shift, x_K , and the curvature has also been determined. It is shown that the concentration distribution is not sensitive to the boundary conditions (bent and planar, constrained, samples) and is influenced mainly by the feeding back effects of stresses (described by the stress term in the generalized diffusion potential) only. The stress distributions obviously are different for bent and planar samples and the effect of cutting off, caused by the dislocation glide, is also illustrated. It is found that the Kirkendall shift follows the parabolic law only in high creep rate limit. For intermediate creep rates, as a function of the time, t , a change of the slope of the $x_K(t)$ function is expected due to the stress development and relaxation. It is shown that the curvature of samples, caused by the diffusion stresses, is proportional to the annealing time and the difference of the intrinsic diffusion coefficients in a wide range of input parameters. By the example of experiments on Ti-Zr thin-sheet diffusion couples it was illustrated that the theoretical results are in good agreement with the measurements. Copyright © 1996 Acta Metallurgica Inc.

1. INTRODUCTION

Interdiffusion, in general, because of the different partial molar volumes and mobilities of the diffusing species, can lead to an imbalance in the volume transport. This is equivalent to the creation of a non-uniform stress-free strain [1]: on one side of the diffusion couple there are contractions, while on the other side extensions will arise. The stress field related to this stress-free strain was not explicitly taken into account in the classical Darken analysis of interdiffusion [2], i.e. it was supposed that the relaxation of stresses are fast and complete and only the convective transport (the Kirkendall effect), as a result of this relaxation, was included into the theory [3]. Recently, Stephenson [1, 4, 5] gave an extended treatment of the complex interrelation of the diffusion transport, internal stresses and convective transport due to the induced deformation.

Figure 1 illustrates the scheme of the role of stress in interdiffusion for a binary diffusion couple. The internal stress developed during the process contributes to the thermodynamic potential for diffusion of atomic species and plastic deformation and gives rise to an elastic contribution as well. In the case of vacancy mechanism in solids the internal stress can also lead to a vacancy potential different from zero [1]. However, if the density and efficiency of vacancy sources and sinks are high, we can suppose that the net vacancy chemical potential is approximately zero

[1, 6]; this assumption (i.e. the local equilibrium of vacancies) will be used in our paper. The convective transport ... as a result of the plastic flow, realized either by creep or dislocation glide or by both of them ... obviously relaxes the internal stress and this will be a feeding-back effect in the coupled set of equations of the system (see below).

In his recent papers Stephenson has solved analytically [1] and numerically [5] the coupled equations of his general theory for a binary system and has shown that over relatively small distant scales the stress relaxation by plastic flow can be the rate limiting step of interdiffusion (crossover to Nernst–Planck limit instead of the Darken's limit), and the behaviour of the system will be non-Fickian in this case. The results of these calculations were in a good agreement with experimental results of [7] obtained in an NiZr amorphous system.

In our paper we will concentrate on another special case when the effect of stresses can be directly observed: thin crystalline diffusion couples will bend (not only in small distant scale limits) under the internal stress if they are not constrained. This effect was indeed observed experimentally. Stevens and Powell [8] performed a detailed study of bending and Kirkendall shift in a thin Ag-Au diffusion couple, while in [3] a strong bending of Ni-Cu and Ni-Mo couples was illustrated. It was also shown in [8] that this bending is caused primarily by diffusion-induced stresses and can be prevented by either mechanical

constraint during diffusion or mass constraint of the couple using thicker samples in the diffusion direction. The Kirkendall shift, x_k , was also different in bent and planar couples, but the difference was larger than the value estimated from the simple plastic geometrical deformation of the sample. (During bending the neutral fiber of the sample is shifted and this results in a reduction of x_k .) Furthermore, in the Ag-Au system a remarkable porosity formation was observed. This can be one of the reasons why in [8] a Kirkendall shift lower than would be expected from the pure geometrical correction was observed in bent samples.

The theoretical part of the present paper is the extension and completion of articles published elsewhere [9, 10] and is the first description of the diffusion bending on the basis of coupled equations of diffusion and plastic flow as given by Stephenson. The relation between the radius of the curvature and the annealing time will be analysed by a numerical simulation technique (finite element method) and some analytical results will be presented as well. The differences in the Kirkendall shift and the inter-diffusion coefficients between bent and non-bent (constrained) samples will also be treated.

In the light of our theoretical results for the time dependence of the bending radius, we decided to reanalyse the results of [8] and carry out new experiments in a system where the difference in the molar volumes and the intrinsic diffusion coefficients is so small that there is no porosity formation. Thus, Zr-Ti thin-sheet couples have been chosen and measurements between 1173 and 1273 K have been carried out.

2. BASIC EQUATIONS

2.1. Matter transport

In the classical treatment of Darken the continuity equation for species i , in the fixed laboratory frame of reference, was written in the form:

$$\frac{\partial \rho_i}{\partial t} + \text{div}(\mathbf{j}_i + \rho_i \mathbf{v}) = 0, \quad (1)$$

Fig. 1. Scheme of the role of the stress in interdiffusion for a binary diffusion couple (see also the text).

where ρ_i is the molar density, $\mathbf{v}$ is the Kirkendall velocity due to the convective transport and $\mathbf{j}_i$ is the atomic current in the lattice frame. As is usual in fluid mechanics the substantial derivative of ρ_i , $D\rho_i/Dt$ gives the rate of change of ρ_i seen at the actual (moving) lattice point. Then this derivative is related to the partial derivative of ρ_i by the following expression:

$$\frac{D\rho_i}{Dt} = \frac{\partial \rho_i}{\partial t} + \mathbf{v} \cdot \text{grad } \rho_i. \quad (2)$$

From equations (1) and (2) one can easily obtain:

$$\frac{D\rho_i}{Dt} + \text{div } \mathbf{j}_i + \rho_i \text{div } \mathbf{v} = 0. \quad (3)$$

The atomic currents of different chemical components relative to the lattice frame are proportional to the gradients of chemical potentials. Following [1], for the case of isotropic stress field, the diffusion potential (the generalized chemical potential) is the sum of the chemical potential in an unstressed system and the product $p\Omega_i$, where p and Ω_i are the pressure and the molar volume, respectively. Thus, we can write:

$$\mathbf{j}_i = -D_i \text{grad } \rho_i - L_i \rho_i \text{grad } p, \quad i = 1, 2, \quad (4)$$

where D_i is the intrinsic diffusion coefficient and L_i is the cross coefficient given by:

$$L_i = D_i \rho \Omega_i \Omega_2 / RT\theta. \quad (5)$$

Here R and T are the gas constant and temperature, respectively. θ is the Darken's thermodynamic factor and for binary system $\rho = \rho_1 + \rho_2$. This relation can be easily obtained from equation (7) of [5] if the diffusion coefficient is related to the mobility M_i by $D_i = M_i RT\theta / \rho \Omega_2$, and $c_i = \rho_i / \rho$.

2.2. Strains and stresses

The total strain tensor is taken to be the sum of elastic, plastic and stress-free strain tensors [1], i.e.

$$\epsilon_{ij}^T = \epsilon_{ij}^{SF} + \epsilon_{ij}^P + \epsilon_{ij}^E. \quad (6)$$

Here the stress-free strain is related to the volume transport and we will suppose that this deformation is isotropic. This means that on the length scales of interest there is a dense, isotropic distribution of sources and sinks of lattice sites. The rate of the stress-free deformation can be given by an expression equivalent to equation (29) in [1]:

$$\frac{De^{SF}}{Dt} = -\frac{1}{3}(\Omega_1 \text{div } \mathbf{j}_1 + \Omega_2 \text{div } \mathbf{j}_2), \quad (7)$$

where $e^{SF} = \text{trace}(\epsilon^{SF}/3)$.

Once stress developed it can relax by creep, which is connected to the local atomic currents between vacancy sources and sinks. The resultant macroscopic

deformation relaxes the stress level without changing the total volume. Accordingly we can use the simple viscous creep model (Newtonian flow; see also equation (24) in [1]):

$$\frac{D\epsilon_{ij}^p}{Dt} = \frac{1}{2\eta} (\sigma_{ij} - \sigma_{ij}\delta_{ij}/3), \quad (8)$$

where η is the shear viscosity.

The stress relaxation can also take place, if the stress exceeds the critical shear stress level, by dislocation gliding mechanism. This effect can be taken into account introducing a cut-off stress level using the Tresca-flow model; the value of the shear stress can not exceed this level. The effect of such cutting-off will also be illustrated in the discussion (Section 4).

The internal stresses can also be related to the elastic deformation. According to the Hook's law, one obtains:

$$\sigma_{ij} = \frac{E}{(1+\nu)(1-2\nu)} [(1-2\nu)\epsilon_{ij}^e + \nu\epsilon_{kk}^e\delta_{ij}] \quad (9a)$$

or

$$\epsilon_{ij}^e = \frac{1}{E} [(1+\nu)\sigma_{ij} - \nu\sigma_{kk}\delta_{ij}], \quad (9b)$$

where E is the Young modulus and ν is the Poisson ratio.

It is worth mentioning that there is a relation between the velocity field and strain rate:

$$\frac{De^T}{Dt} = \frac{1}{3} \operatorname{div} \mathbf{v}, \quad (10)$$

where $e^T = \operatorname{trace}(\epsilon^T/3)$ and $e^p = 0$. Furthermore for isotropic case (9b) will have a form:

$$e^e = -\frac{1-2\nu}{E} p \quad (11)$$

and

$$\operatorname{div} \mathbf{v} = -(\Omega_1 \operatorname{div} \mathbf{j}_1 + \Omega_2 \operatorname{div} \mathbf{j}_2) - \frac{3(1-2\nu)}{E} \frac{dp}{dt}. \quad (12)$$

Thus, from equations (3) and (12) we can write the continuity equation into the form:

$$\frac{D\rho_1}{Dt} = \Omega_2(\rho_1 \operatorname{div} \mathbf{j}_2 - \rho_2 \operatorname{div} \mathbf{j}_1) + \rho_1 \frac{3(1-2\nu)}{E} \frac{dp}{dt}, \quad (13)$$

where use has been made of the relation:

$$\Omega_1\rho_1 + \Omega_2\rho_2 = 1 \quad (14)$$

(Vegard-law).

The stress distribution will be governed by the condition of local mechanical equilibrium [1]

$$\operatorname{div} \sigma = 0 \quad (15)$$

and by nonlocal *boundary conditions and constraints*. One global constraint can be for example the shape of the sample, which obviously can be different for different geometry of the couple. This is a very important characteristic of the problem. The final

form of the coupled equations of the system and thus their solutions can be different for different boundary conditions.

For example, for one-dimensional diffusion in a semi-infinite amorphous system (supposing isotropic limit), Stephenson [5] arrived at:

$$\frac{Dp}{Dt} = -\frac{2E}{9(1-\nu)} (\Omega_1 \operatorname{div} \mathbf{j}_1 + \Omega_2 \operatorname{div} \mathbf{j}_2 + 3p/4\eta). \quad (16)$$

Coupled equations (12), (13) and (16) with (4) and (5) determine the evolution of deformation, composition and pressure of the system. For example, if the creep rate is large ($\eta \Rightarrow 0$) in equation (16) we will arrive at the Darken limit because the stress relaxation will be very fast and the process will be controlled by the diffusion of the fast component. For finite values of η the cross-over to the Nernst-Planck limit will depend on the relative magnitudes of the two terms on the right-hand side of equation (16). For very short times (small length scales) the atomic currents will be very large (because of the large gradients) and the plastic deformation can be the rate limiting step for interdiffusion. In the Nernst-Planck limit ($\eta \Rightarrow \infty$) the stress fields developed will make the difference in the atomic currents disappear and the interdiffusion coefficient will be determined by the diffusivity of the slower component [1].

In our paper the boundary conditions will be considerably different than in [5] and thus the results are obviously expected to be characteristically different as well.

3. CALCULATION PROCEDURE

The free boundary problem of an unconstrained thin diffusion couple would require a difficult three-dimensional calculation. The problem can be greatly simplified by prescribing purely cylindrical macroscopic deformation. This can be done because this shape has been spontaneously developed in experiments carried out by Stevens and Powell [8]. The cylindrical shape can also be achieved by keeping flat one end of the sample during the diffusion heat treatment (see also the experimental part of our paper). When the thickness of the sheet is much smaller than the other dimensions, we can assume that the stress inhomogeneity, arising from the outer constraints, is small. This is valid both for flat and cylindrically constrained samples.

The problem can be reduced to a one-dimensional calculation in a cylindrical coordinate system, fitted to the deforming sample as shown in Fig. 2. Both the deformation and the stress tensors are diagonal in this case. The macroscopic shape of the sample is given by the following parameters: R , the bending radius at the position of the neutral fiber, ϵ_{zz}^T and r_1 as well as r_2 the inner and outer radii of the sample, respectively.

Two diagonal elements of the total deformation

Fig. 2. Scheme of the deforming sample.

tensor are given by the shape parameters:

$$\epsilon_{\varphi\varphi}^T = (r - R)/R \text{ (a); } \epsilon_{zz}^T = \text{const. (b).} \quad (17)$$

The third diagonal, ϵ_{rr}^T , is free to change and actually its integral will give the Kirkendall displacement as

$$x_k(r) = \int_{r_1}^r \epsilon_{rr}^T dr'. \quad (18)$$

We will ignore the φ and z dependence of concentration, stress and deformations. The *condition of mechanical equilibrium* in equation (15) now has the form:

$$\frac{\partial(r\sigma_{rr})}{\partial r} = \sigma_{\varphi\varphi}, \text{ or } \sigma_{rr}(r) = \frac{1}{r} \int_{r_1}^r \sigma_{\varphi\varphi} dr'. \quad (19)$$

The *free boundary conditions* with respect to the cylindrical bending are expressed by requiring the disappearance of the total force and torque exerted across a plane perpendicular to the axis of the cylinder:

$$\int_{r_1}^{r_2} \sigma_{\varphi\varphi} dr' = 0 \text{ (a); } \int_{r_1}^{r_2} r' \sigma_{\varphi\varphi} dr' = 0 \text{ (b).} \quad (20)$$

The free dilation along the z axis requires the disappearance of the total force across a plane perpendicular to the z axis:

$$\int_{r_1}^{r_2} \sigma_{zz} dr' = 0. \quad (20c)$$

A set of coupled equations can be derived for the shape parameters in the following way. The elastic deformation is expressed from equation (6) with the help of the total deformation, for a given stress-free strain and plastic deformation. Stresses are calculated through equations (9a) and (b), keeping ϵ_{rr}^T , $\epsilon_{\varphi\varphi}^T$ and σ_{zz} as free variables. Now equations (20a)–(c) lead to the required set of equations for the shape parameters. These equations were solved at each time step during the numerical calculations using the $\sigma_{\varphi\varphi}$ value of the previous time step. Once the new shape parameters are determined, the new value of $\sigma_{\varphi\varphi}$ is calculated

from equation (9a). This approximate procedure is based on the smallness of the σ_{rr} stress component, which can also be seen from equation (19) if the sample radius is much larger than the thickness. The numerical simulation also supported this assumption.

We have also simulated planar samples for comparison. In this case a rectangular coordinate system was used, with the x direction parallel to the direction of diffusion. The z and y component of the stress satisfy equations similar to (17b) and (18c). The condition of mechanical equilibrium shows that σ_{xx} is zero in this case.

In some cases, in addition to the creep, we have considered plastic deformation by glide as well. Here the Tresca condition was monitored and when the glide conditions were satisfied, an ideal plastic behaviour was assumed according to the von Mises theory. The appropriate plastic deformations, reducing the stress level below the critical value, were calculated directly from the stress tensor using the condition that the relieved stress equals the critical stress level, σ_{crit} .

The finite element method was used during the numerical simulations. The diffusion couple was divided into about 30 thin sheets perpendicular to the diffusion direction in the lattice frame of reference. The calculations can be divided into three subsequent steps.

First the atomic currents and the composition of each element were calculated from the difference equations according to (4) and (13), respectively. [The second term in (13), similarly as in [5], was neglected compared with the first term.] Then the thickness and the cross sections of each element were modified according to equations (7) and (8) (second step). Finally, the new elastic deformations, stress and shape of the sample were calculated. In this process the cross-coupling of the difference equations was resolved by calculating the σ_{rr} stress component up to first order.

The above procedure was repeated and the concentration profile, stress distribution and shape was recorded from time to time during the calculations. The program was written in Turbo Pascal and run on an IBM compatible PC.

Taking into account that σ_{rr} is much smaller as compared with σ_{zz} or $\sigma_{\varphi\varphi}$ equations (17), (18), (19) and (9) can be linearized, i.e. the parameters determining the shape of the sample (ϵ , r_0 and R) can be determined from linear equations.

For the numerical work all equations were transformed into the form containing only dimensionless variables and parameters:

$$x' = x/l; \quad r' = r/l; \quad t' = tD/l^2; \quad \sigma'_i = \sigma_i/E;$$

$$\rho'_i = \rho_i\Omega;$$

$$D'_i = D_i/D; \quad \eta' = \eta D/EP; \quad \Omega'_i = \Omega_i/\Omega. \quad (21)$$

Here l is the thickness of the sample, E is the Young modulus and Ω is the average atomic volume. The

diffusion coefficient, D , determining the time scale, was chosen in a way that during unit time the diffusion zone would extend to about one fifth of the sample thickness.

We have simulated both bent and planar (constrained) samples.

The material parameters were supposed to be constant and composition independent. Furthermore, for simplicity, we assumed that $\Omega_2 = \Omega_1 = 1$. The viscosity was varied between zero (complete relaxation) and infinity (no stress relaxation). The ratio of the partial diffusion coefficients was varied between 1 and 1000. The factor $\beta' = 1/(RT)'$ was changed between 0 and 120 [$(RT)' = RT/E\Omega$]. The case where $\beta' = 0$, according to equation (5), corresponds to $L_i = 0$, i.e. when the cross effects are neglected, while $\beta' = 120$ corresponds to $T = (E\Omega/RT_m)T_m/120 \cong 0.75T_m$. (The ratio of $E\Omega/RT_m$, according to the law of corresponding states [11], is expected to be constant and indeed its value for metals is about 90.)

Stability problems were usually not encountered because the equations were of a relaxation type. The time step of the numerical simulation was chosen to keep the change of all parameters within a few per cent during each iteration.

The computer program was tested on a problem treated in the literature before [5]. We could well reproduce the initial stress development, the blocking of the further diffusion and the subsequent relaxation of stress by plastic deformation in the multilayer problem using the same parameters as the author of [5].

The parameters investigated during our calculations can be classified into two groups:

- local parameters (ρ_i, σ_{ii});
- global parameters (x_k, R , the maximum of $\sigma_{\varphi\varphi}$).

In the following we will analyse the position dependence of the local and the time dependence of the global parameters.

4. RESULTS OF NUMERICAL CALCULATIONS

As mentioned in Section 3, the coupling between the gradient of p and ρ_i is specified by the values of β and θ [equation (5)] if D_i, ρ, Ω and Ω_i are otherwise fixed. In fact, the coupling strength can be given by the parameter $\lambda' = \beta'/\theta'$, but in order to illustrate the effect of the temperature and the chemistry of the system the values of $\beta' = 1/(RT)'$ and $\theta' \equiv \theta$ will be varied independently. Calculations for $\lambda' = 0$ (no cross effects) are also enlightening and indeed they were carried out in [10]. Some of the results of [10] will be cited and shown in the discussion for comparison.

4.1. Concentration and stress distribution

Figure 3 shows the concentration profiles for three different times in a planar sample for two sets of

parameters $\theta'(\lambda')$ at $D_b/D_a = 0.8$, $v' = 0.3$, $\sigma'_{crit} = \infty$, $\eta' = 0.05$ and $\beta' = 120$ (which corresponds to $t = 0.75T_m$ and $\lambda' = 120$ as well as $\lambda' = 5$). Comparison of calculated profiles for planar and bent samples illustrated that the curves were the same, i.e. the bending process does not considerably effect the concentration profiles. This means that the interdiffusion coefficients calculated from the experiments in planar and bent samples are expected to be the same. On the other hand, although the difference between bent and planar samples is still not detectable, the effect of coupling is expressed in a suppressed diffusion zone [see especially the curves at $t' = 3.28$ in Figs 3(a) and (b)]. This is also an illustration of the deviation from Darken's limit, because in this limit the interdiffusion coefficient (which determines the evolution of the concentration profile) should be determined by the faster D' . Since in this example D'_a is the same in Figs 3(a) and (b) the thinner diffusion zone is an illustration of the stress effects. This is in accordance with the results obtained for the Kirkendall shift ($x'_k \cong 0$; see also later in Fig. 6).

Figure 4 shows the components of the stress tensor as a function of the diffusion distance for the same input parameters as in Fig. 3(b). Since there is a

Fig. 3. Concentration profiles at three different times and two different sets of parameters θ' (a and b, respectively) as well as at $v' = 0.3$, $\sigma'_{crit} = \infty$, $\eta' = 0.05$, $D_b/D_a = 0.8$ and $\beta' = 120$ for planar samples.

Fig. 4. Components of the stress tensor as a function of distance at three different times and for the same input parameters as in Fig. 3.

dislocation creep the stress components will decrease with time because of the relaxation. It can be seen that the planar and the bent sample differ only in a linear contribution [Figs 4(a) and (c)], which arises in the bent samples because of the torque compensation [equation (20b)]. Since there is no bending in the z direction, σ'_{zz} for bent sample is similar to Fig. 4(a). These results can also be well reproduced by

analytical calculations as shown in Section 5. The absolute values and also the gradients of σ'_{zz} are smaller by *ca* one–two orders of magnitude than for zero coupling [10] and there are relatively large values of σ'_{zz} far from the diffusion zone as well (e.g. at $x' > 0.7$ for $t' = 0.83$ or $t' = 3.28$), which indicates the flattening of the stress distribution.

The typical cutting-off effect of the dislocation glide is shown in Fig. 5. With increasing time this effect, because of the creep relaxation, can disappear. This phenomenon, because of its local character, cannot be treated analytically.

4.2. Time dependence

Figures 6(a) and (b) show the Kirkendall shifts for three different η' values and for the same input parameters as above, but at $\beta' = 120$ and $\theta' = 24$ ($\lambda' = 5$) as well as $\theta' = 1$ ($\lambda' = 120$), respectively. It can be seen for large η' and λ' values, x'_k is practically zero and from the comparison with values calculated in the limit of zero coupling [10] we can conclude that at the same creep rate x'_k is considerably smaller for $\lambda' \neq 0$. Furthermore, curves for different η' lie in the region limited by curves corresponding to $\eta' = 0$ and $\eta' = \infty$. This is in accordance with the results obtained for zero coupling [10]: for $\eta' = \infty$ (no stress relaxation) at the beginning only deformations parallel to the direction of diffusion will give a contribution to x'_k and the Kirkendall velocity will be decreased by a factor of 3 compared with the case of complete relaxation ($\eta' = 0$, Darken's limit), where stress free deformations perpendicular to x will be converted parallel to the direction of diffusion. Although the coupling effects can cause a very fast decrease of the Kirkendall velocity from $v = v_D/3$ (v_D corresponds to the Darken's limit) to zero, by compensating the difference of the atomic currents across the stress gradient terms [5], the curves still lie in the region limited by curves for $\eta' = 0$ and $\eta' = \infty$.

It is very interesting that for intermediate values of η' ($\eta' = 5 \times 10^{-3}$) the Kirkendall shift does not follow the law of parabolic growth even in planar

Fig. 5. Cutting-off effect of the dislocation glide.

Fig. 6. Kirkendall shift for different η' values for planar and bent samples at the same parameters as in Fig. 3(a), but with $\beta' = 120$ and $\theta' = 24$ as well as $\theta' = 1$, respectively.

samples. This can be understood if we take into account that at the beginning of the process the stress relaxation is negligible and we are in a regime corresponding to $\eta' = \infty$. For longer annealing times we will have a crossover to the regime of fast stress relaxation. Consequently, this process is related to the conversion of the stress-free deformations into the direction of diffusion. Since the rate of this conversion is determined by the intensity of the stress relaxation, the characteristic time of the crossover will be determined by the relaxation time proportional to $6\eta/E$ [see equation (16)].

The difference between the planar and bent samples is most expressed for $\eta' \cong 0$ (5×10^{-5}); this is a purely geometrical effect [10]. If the originally planar sample, say after the diffusion, is cylindrically deformed then the radial deformation (the neutral fiber will be shifted) reduces the value of x_K' [8]. This deformation is proportional to l/R [8] and, as we will see later, $1/R' \propto t'$. Thus, on the x_K' vs $(t')^{1/2}$ plot quadratic differences appear, i.e. deviations from the parabolic law arise. Obviously, for $\eta' = \infty$ (no creep) there is no difference between planar and bent samples.

The effect of critical stress level on the Kirkendall shift is not illustrated here because it is expected that it is similar to the case of zero coupling [10]. Stress level higher than σ_{crit}' can be present only for limited times; the creep relaxation will decrease the stress

level below the given limit. Nevertheless, in the time interval, where glide is an operating mechanism of relaxation, small deviations from the parabolic law are expected [10].

The maximal values of the $\sigma'_{\phi\phi}$ and σ'_{zz} are plotted on Fig. 7 for the same input parameters as above, but at $\beta' = 120$ and $\theta' = 24$ ($\lambda' = 5$) as well as $\theta' = 1$ ($\lambda' = 120$), respectively. In accordance with Fig. 4 the absolute values of the maximal stress components, compared with zero coupling, are smaller again and, which is remarkable, the curves for planar and bent samples are considerably different for large η' values: in the bent samples the stress level is lower. This is different from the results obtained for zero coupling [10]; there the differences caused by the macroscopic bending of the sample were smaller.

The time dependence of the bending radius is shown in Fig. 8(a) for two different D_b' at the same input parameters as above and for $\beta' = 120$ and $\theta' = 24$ ($\lambda' = 5$). Figures 8(b) and (c) illustrate the effect of the creep coefficient. The simulation also showed that the $\log(R')$ vs $\log t'$ function is almost independent of θ and σ_{crit}' and only its position is shifted at different D_a/D_b ratios. From the comparison of curves for $\lambda' = 5$ and $\lambda' = 120$ it was obtained

Fig. 7. Maximal values of σ'_{zz} and $\sigma'_{\phi\phi}$ for the same input parameters as in Fig. 3, but with $\beta' = 120$ and $\theta' = 24$ as well as $\theta' = 1$, respectively.

Fig. 8. Time dependence of R' for $\beta' = 120$ and $\theta' = 24$, as well as $\theta' = 1$, respectively. The effect of D_b' and η' is also illustrated.

that the effect of the coupling is only a small deviation from the $1/R' \propto t'$ law (the slope of the $\log R'$ vs $\log t'$ functions is less than 1) for $\lambda' = 120$.

Figures 8(b) and (c) show the effect of the creep coefficient on time dependence of R' for different coupling strengths. It can be seen that there is a considerable backward curvature for strong coupling if the creep rate is low. This probably can be observed experimentally as well and this is an effect of the plastic deformation caused by the global gradient of $\sigma'_{\phi\phi}$ [Fig. 4(d); it is a consequence of the torque compensation in bent samples]. This gradient causes

a mass flow resulting in a global deformation, the sign of which is opposite to the bending caused by the plastic deformation leading to the original curvature. This deformation explains also why the stress relaxation is more intensive in bent samples (see Fig. 7).

At first sight it is surprising that the slope of the $\log R'$ vs $\log t'$ function is almost constant and the relation $1/R' \propto t'$ is always valid for small η' values. The fact that the bending radius is not sensitive to the intensity of the stress relaxation (η' , σ'_{crit}) and depends practically on the $(D_a' - D_b')$ difference only can be understood from analytical calculations as well and we will turn to this question in the next section and in the experimental part of the paper.

5. ANALYTICAL CALCULATIONS

One of the interesting results of the numerical calculations is that the bending radius usually follows the $R' \propto 1/t'$ law and deviations from this can be observed only for relatively strong coupling and low creep (see Fig. 8). In this section we will show that this relation, using some simplifying assumptions, can be derived analytically as well.

Let us suppose that the material parameters are independent of concentration and they are the same for both materials of the couple: $E_1 = E_2$, $\nu_1 = \nu_2$, $\eta_1 = \eta_2$ and $\Omega_1 = \Omega_2$. For the determination of the time dependence of the curvature $\xi' = 1/R'$, let us take the time derivative of equation (6) and use the corresponding equations of deformations [equations (7), (8), (9b) and (17a)]:

$$\begin{aligned} \xi' r = (\Omega_1/3) \frac{\partial}{\partial r} \left([D_1 - D_2] \frac{\partial \rho_1}{\partial r} \right) \\ + (1/2\eta) [\sigma'_{\phi\phi} - (\sigma'_{\phi\phi} + \sigma'_{zz} + \sigma'_{rr})/3] \\ + (1/E) (\dot{\sigma}'_{\phi\phi} - \nu [\dot{\sigma}'_{rr} + \dot{\sigma}'_{zz}]). \quad (22) \end{aligned}$$

The effects of stress gradients were neglected rewriting the first term from equation (7). Taking the zeroth and first moment of equation (22), using $\sigma'_{rr} \ll \sigma'_{zz}$ and $\sigma'_{\phi\phi}$ and taking into account the boundary conditions (20), we have:

$$\begin{aligned} \xi' P/12 = -\nu \dot{M}_z/E - M_z/6\eta \\ - \Omega_1/3 \int_{\rho_1(r_1, t)}^{\rho_1(r_2, t)} (D_1 - D_2) d\rho_1, \quad (23) \end{aligned}$$

where

$$M'_z = \int_{r_1}^{r_2} \sigma'_{zz} r' dr'$$

and r_1 and r_2 are the coordinates of the edges of the sample (Fig. 2). Here it was also taken that $\partial \rho_1 / \partial r = 0$ at the boundaries.

Using equation (17b) we can take the zeroth and

first moment of ϵ_z^T [using again equations (7), (8), (9b) and (20)]:

$$M_z + EM_z/3\eta = E\Omega_1/3 \times \int_{\rho_1(r_1, t)}^{\rho_1(r_2, t)} (D_1 - D_2) d\rho_1 \equiv f(t). \quad (24)$$

The solution of this differential equation for the initial conditions:

$$M_z = 0, \quad t = 0$$

is as follows:

$$M_z(t) = \exp(-Et/3\eta) \int_0^t f(t) \exp(Et/3\eta) dt. \quad (25)$$

For the time interval during which the concentrations are unchanged at the boundaries of the sheet, i.e. $\rho_1(r_1, t) \cong \rho_1(r_1, 0)$ and $\rho_1(r_2, t) \cong \rho_1(r_2, 0)$, the value of the integral in equation (24) is constant and $f(t)$ as well as $M_z(t)$ can be given explicitly. Thus, after substitution into equation (23) and integration:

$$\xi = 6\Omega_1/l^3 \int_{\rho_1(r_1, t)}^{\rho_1(r_2, t)} (D_1 - D_2) d\rho_1 (t - (1 - 2\nu)\eta(1 - \exp\{-Et/3\eta\})/E). \quad (26)$$

From equation (26) we can easily obtain the curvature for low and high creep rate limits. If η is small the second term in the brackets will be negligible, while for large η values the Taylor series expansion of the exponential term can be made and the value in the brackets will be approximately $(1 - 2\nu)t/3$. Thus, the ratio of the slopes in these limits will be equal to $2(1 + \nu)/3$. Since the value of the Poisson ratio is typically between 0 and 0.5, this means that $\xi(\eta \rightarrow \infty)/\xi(\eta \rightarrow 0) < 0$, which is indeed the case in Figs 8(c) and (d). In the high creep rate limit equation (26) can be given as:

$$1/R = 6(\bar{D}_1 - \bar{D}_2)t/l^3, \quad (27)$$

where $(\bar{D}_1 - \bar{D}_2)$ denotes the concentration averaged value of the difference of the intrinsic diffusion coefficients.

It can be seen that equation (27) is just the $\xi = 1/R \propto t$ law and the slope is a measure of the concentration averaged value of $(D_1 - D_2)$, which is in accordance with the numerical results shown in Figs 8(a) and (b).

In the above calculations the effect of the cross terms was neglected. This can be taken into account by an extra term in equation (23):

$$\Delta = \frac{1}{3} \frac{\partial}{\partial r} \left((L_1 - L_2) \Omega_1 \frac{\partial}{\partial r} \{ \sigma_{rr} + \sigma_{zz} + \sigma_{\varphi\varphi} \} \right). \quad (28)$$

Supposing again that $\sigma'_{rr} \ll \sigma'_{zz}, \sigma'_{\varphi\varphi}$ and taking the first moment of equation (28) after integration one

obtains:

$$\begin{aligned} & \int_{r_1}^{r_2} \Delta r' dr' \\ &= \frac{1}{3} (L_1 - L_2) \left[\frac{\partial}{\partial r} \{ \sigma_{zz} + \sigma_{\varphi\varphi} \} r - \{ \sigma_{zz} + \sigma_{\varphi\varphi} \} \right]_{r_1}^{r_2} \\ &+ \frac{1}{3} \int_{r_1}^{r_2} \{ \sigma_{zz} + \sigma_{\varphi\varphi} \} \frac{\partial}{\partial r} (L_1 - L_2) dr'. \quad (29) \end{aligned}$$

Now, in the first stage of the diffusion annealing, since for short t stresses arising from the linear torque component will only be present at the boundaries of the sample, the following relation will be approximately valid:

$$(-1)^i \sigma_{\varphi\varphi}(r_i) = \frac{l}{2} \left| \frac{\partial}{\partial r} \{ \sigma_{\varphi\varphi} \} \right|_{r_i} \quad i = 1, 2. \quad (30)$$

Due to the coupling between z and φ directions a similar relation holds for σ_{zz} as well and thus the first term in equation (29) will be zero. Consequently, if $L_1 - L_2$ is constant the second term disappears and the correction Δ will also be zero. This result is in accordance with the results of numerical calculations.

6. EXPERIMENTS IN Ti-Zr SYSTEM

The Zr-Ti system possesses most of the important requirements necessary for a reliable theoretical prediction. First of all there is no porosity formation during interdiffusion in this mutually soluble system. It can be seen in the Ti-Zr phase diagram [12] that there is a $\beta \rightleftharpoons \alpha$ transition between 978 and 1055 K, which can disturb the interdiffusion and bending and thus should be avoided. On the other hand above 1273 K the diffusion process becomes so fast [13] that it makes difficult the *in situ* control of the bending process. For heat treatments of 2–3 h the thickness of the diffusion zone is expected in the order of a few hundred microns, which is comparable to the total thickness of the thin sheets used. The *in situ* observation of the bending was necessary to avoid the complicated problem of corrections of the bending caused by the difference in thermal expansion coefficients (see also later). Taking into account the above-mentioned conditions the optimum temperature lies between 1173 and 1273 K.

6.1. Experimental procedure

Diffusion couples were fabricated from 0.1 mm thick Ti and Zr foils of 99.8% purity. The sheets were cut by suitable scissors to form pieces of rectangular shapes of 10×5 mm size. The bulk samples, used for comparison, were cut from rods with a tungsten carbide blade saw. After ultrasound cleaning a welding procedure was carried out by heat treating the samples at 1073 or 1173 K for 10–60 min

under 5 kg load in an electron-gun furnace under a vacuum 5×10^{-6} mbar. The welding at the lower temperature and shorter times resulted in a contact not always homogeneous enough (*ca* 20–30% of the surface was welded as checked by microscopy after tearing the foils apart). For the majority of samples used we observed *ca* 60–70% welded area. The diffusion annealing of samples was performed in the same furnace at 1183, 1233 and 1273 K for 2–5 h (depending on the temperature). These times were long enough to produce a half roundly bent couple and to extend the diffusion zone to the ends of the sample.

Etching, necessary to obtain a reasonable morphological image and to find the Kirkendall plane, was carried out in the following solution: 20 cm³ nitric acid, 20 cm³ hydrofluoric acid and 40 cm³ glycerol.

Concentration profiles and the Kirkendall shifts were determined by a JEOL 840-A SEM microscope equipped with analytical facility.

Bending measurements were carried out with the help of a special clamping tool, made from MgO, which allows the sample (fixed at one end) to bend freely. The sketch of this tool is shown in Fig. 9. The sample had a horizontal position and it was shown (by using samples with downward or upward bending, as well as by pure Ti and Zr foils) that the effect of gravity can be neglected. The curvature was measured *in situ* using a katetometer through the window of the furnace and sometimes photographs were also taken and evaluated: the results of both measurements were consistent and the error of both was a few percent.

6.2. Results

The shape of the bent foils was not always completely cylindrical and some screwing (i.e. an additional curvature different from the cylindrical one) was also observed. In order to prevent this we deformed the free end of the foil before annealing to give an L-shape to the sample. This form resulted in a more pronounced cylindrical deformation, but even in this case the curvature of couples, heat treated under exactly the same conditions, was not the same. This problem is also illustrated in Fig. 10, where the results of annealing made at 1223 K for five different samples are shown. The lower curves in this figure correspond to samples where the curvature visibly was not completely cylindrical, while the upper curve

Fig. 9. Sketch of the sample holder used for the measurement of the bending.

Fig. 10. Curvature ($1/R$) vs annealing time, t , functions for five samples at $T = 1223$ K (see also text). The insert shows the $1/R$ vs t function as measured, i.e. before the correction for the thermal expansion.

can be termed “ideal” from this point of view. Figure 11 shows the photographs of these couples at the end of the heat treatment. It can also be seen in Fig. 10 that the scatter of the slopes of samples (the shapes of which seemed similar) is within a factor of three.

In the insert of Fig. 10 the original curvature–time function, taken directly, is drawn for one sample. From this the corrected curves can be obtained removing the first part up to *ca* 150 min, which is the warming-up time of the sample. This first part reflects the effect caused by the different thermal expansion

Fig. 11. Photographs of the bent samples for two samples at 1223 K. Sample (a) has ideal, cylindrical shape, while sample (b) has a screwing component as well.

Fig. 12. $1/R$ vs t functions at three different temperatures (the average of the curves shown in Fig. 10 is illustrated by a dashed line).

Fig. 13. Concentration profiles for planar and bent samples ($T = 1223$ K, 3 h) measured by EDAX in a SEM.

coefficients of materials of the couple. Since the elastic equations are linear this contribution can be simply extracted and the residual curvature related to the plastic deformations caused by thermal stresses leads to a second-order correction only.

Figure 12 shows the corrected $1/R$ vs t functions at 1273, 1223 and 1183 K. Table 1 contains the values of slopes, m , obtained at different temperatures. Since the slopes are proportional to the difference of the (averaged) intrinsic diffusion coefficients they are expected to have an Arrhenius-type temperature dependence; the tendency shown in Table 1 is in accordance with this. However, since at one temperature the scatter of m is considerable we cannot arrive at a definite conclusion on the activation energy.

Measurements for the concentration distribution and for the Kirkendall shift, at one temperature ($T = 1223$ K) for one annealing time ($t = 3$ h), in order to make a comparison between planar and bending samples were also carried out. Figure 13 shows the concentration profile for both planar and bent samples. It can be seen that they coincide within the limit of errors. The Kirkendall planes were situated at atomic fraction $c_{Zr} = 0.53$, after the same heat treatment in both planar and bent samples. It was easy to find the place of the Kirkendall plane, because the position of inclusions was revealed by etching. The value of x_k is (0.1042 ± 0.005) and (0.1035 ± 0.0005) mm for the planar and bent samples, respectively.

The values of the intrinsic diffusion coefficients at $c_{Zr} = 0.53$ were calculated in the bulk sample from the well-known Darken's relations (supposing $\Omega_{Zr} = \Omega_{Ti}$):

$$\tilde{D} = c_a D_b + c_b D_a \quad \text{and} \quad v_k = x_k/2t = (D_a - D_b)\text{grad } c \quad (31)$$

Table 1

T (K)	m (1/ms)
1183	0.01483
1223	0.0213 ± 0.008
1273	0.0244

and the following values were obtained: $D_{Ti} = 1.4 \times 10^{-13} \text{ m}^2/\text{s}$ and $D_{Zr} = 2 \times 10^{-13} \text{ m}^2/\text{s}$.

6.3. Discussion of experimental results

In order to compare our experimental results with the theory we have to make an estimation of the parameters used in the calculations there. From our experimental results $D_{Ti}/D_{Zr} = 0.7$, which is close to the ratio of values $D'_b = 0.008$ and $D'_a = 0.01$. Furthermore, we can take $v' = 0.3$ and $\sigma'_{crit} = \infty$ (since our calculations indicated that the results are not very sensitive to the choice of the critical shear stress σ'_{crit}). The Ti-Zr system is close to an ideal solid solution [12], thus $\theta' = \theta = 1$ and because the temperature interval investigated is around $T/T_m = 0.7$ the $\beta' = 120$ (corresponding to $T/T_m = 0.75$), used in Section 4, can also be accepted. The value of η' can be estimated from the well known relation [14]:

$$d\epsilon/dt = 14\sigma\Omega D \{1 + (\pi\delta D^{Gb}/Dd)\}/RTd^2, \quad (32)$$

taking into account that $\eta' = \eta D/EF$, where d is the grain size. The second term in the brackets represents the Coble-creep component (δ and D^{Gb} are the grain boundary thickness and diffusion coefficient, respectively). If this can be neglected (Nabarro-Herring creep) the comparison of equations (32) with (8) gives:

$$\eta' = (d/l)^2 (T/T_m) RT_m / 28E\Omega. \quad (33)$$

Now in Section 4 we have shown that $(T/T_m)RT_m/E\Omega \approx 120$ and supposing that d and l are in the same order of magnitude, $\eta' = 3 \times 10^{-4}$. If d/l would be less than 1 and the second term would not be neglected in equation (32), this ratio would be even smaller than the value estimated above. Thus, according to the results obtained in Section 4, metals $\eta' = 0.0005$ can be taken as the lowest value used in the calculations there (which corresponds to the high creep limit).

According to the estimation of the input parameters given above, we can compare our experimental results with Figs 3(a), 6(b) and 8(c) for the concentration profile, Kirkendall shift and curvature, respectively.

As discussed in Section 4 in our case, because the difference of the intrinsic diffusion coefficients is small, we are still in the Darken's limit and the difference between the concentration profiles obtained in the planar and bent samples should be negligible. The experimental results shown in Fig. 13 are in accordance with this prediction.

Calculations of the Kirkendall shift for our case [Fig. 6(b)] led to the conclusion that in the high creep limit (for small η' values) x_K should follow the parabolic law for planar sample and the difference between the Kirkendall shift for planar and bent samples should be equal to the geometrical effect caused by the shift of the neutral fibre of the bent sample: $2l^2/R$ (see also [8]). For our case $2l^2/R = 1.7 \times 10^{-3}$ mm ($l = 0.2$ mm, $R = 3$ mm) and this is in the same order of magnitude as the difference of x_K measured in planar and bent samples: 7×10^{-4} mm. Although this value is in the order of the experimental error (5×10^{-4} mm for each samples), the result is in accordance with the theory. This is remarkable, because in [8] Stevens and Powell observed a difference between the marker-shifts of planar and bent samples *one order of magnitude higher* than would be expected from the simple geometrical effect. In our opinion this effect was caused by the different porosity in their samples; the porosity was higher in bent samples (the constraint to keep the samples flat decreased the formation of pores as well) and, because of the well-known competition between the Kirkendall shift and the porosity formation [15–17], the value of x_K was considerably lower in bent samples.

According to Fig. 8(c) for high creep limit (small values of η') the $1/R$ vs t function is expected to be linear and the analytical results [equation (27)], presented in the introduction of this paper as well, should also be valid. Indeed, the linearity between $1/R$ and t is confirmed by Figs 10 and 12. Although the scatter of slopes of straight lines obtained at the same temperature (Fig. 10) is relatively large, and can be caused by the non-ideal bending and the not complete welding of the foils, their values are in the right order of magnitude. For example at 1223 K from equation (27) we obtain that $D_{Zr} - D_{Ti} = 5 \times 10^{-14}$ m²/s, which is in good agreement with the results obtained from our bulk sample at $c_{Zr} = 0.53$. Furthermore, our $\tilde{D}$ value ($\tilde{D} = 1.7 \times 10^{-13}$ m²/s) and our D_{Ti}/D_{Zr} ratio ($D_{Ti}/D_{Zr} = 0.7$) is also in good agreement with $\tilde{D} = 2.2 \times 10^{-13}$ m²/s and $D_{Ti}/D_{Zr} = 0.6$ obtained in [18].

It is also interesting to check whether the results of Stevens and Powell fulfil equation (27) or not. Figure 14 shows their (re-plotted) results on the log

Fig. 14. Log $1/R$ vs log t plot of data measured in [8] for Ag-Au system and straight lines with slope of unity [see equation (27)].

($1/R$) vs log t plot for two different l values ($l = 88$ and 132 μm, respectively). It can be seen that if we neglect two points measured at short times for $l = 88$ μm, straight lines, indicated in the figure and corresponding to equation (27), fit well to the data. Thus, the log $R \sim \log t$ relation is valid in this case too, but there is a deviation from the $R_1/R_2 (= l_2/l_1)^3$ ratio predicted by equation (27): if equation (27) is valid the shift between the two curves in Fig. 14 should be smaller.

7. CONCLUSIONS

It is shown that the concentration distribution, in the range investigated, is not sensitive to the boundary conditions, i.e. they are the same for bent and planar, constrained samples and influenced mainly by the feeding back effects of stresses (described by the stress term in the generalized diffusion potential) only.

The stress distributions obviously are different for bent and planar samples. The maximal values of stresses are about two orders of magnitude lower if we take into account the terms caused by stresses in the expression of atomic currents [effect of coupling; see equation (4)]. The effect of cutting off, caused by the dislocation glide, is also illustrated.

It is found that the Kirkendall shift follows the parabolic law only in low and high creep rate limits (with different slopes). For intermediate creep rates, as a function of the time, t , a crossover between these limits is expected which results in deviations from the parabolic law.

It is shown that the curvature of samples, caused by the diffusion stresses, is proportional to the annealing time in a wide range of input parameters. The slope of this straight line is proportional to the difference of the intrinsic diffusion coefficients. Deviations from this law are expected for strong coupling and low creep rates when a backward curvature of the sample at long annealing times can be observed.

It was shown, by the example of experiments on

Zr-Ti thin sheet diffusion couples, that the theoretical results obtained are in agreement with the measurements. It was illustrated that the concentration profiles for (constrained) planar and bent samples are the same within the resolution of the measurements. The Kirkendall shift differs in the planar and bent couples only by the simple geometrical effect related to the shift of the neutral fibre of the bending sample. It was shown that the results of Stevens and Powell [8] for the Kirkendall shift differ from this prediction, probably because of the strong porosity formation observed especially in their bent samples. The linear relation between the curvature, $1/R$, and the annealing time has been proven experimentally as well and the numerical values of the difference of the intrinsic diffusion coefficients (estimated from the slopes of the above straight lines) and their temperature dependence were in good agreement with the values published in the literature and obtained by us in a bulk sample.

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