phys. stat. sol. (b) **159**, 557 (1990)

Subject classification: 61.70 and 66.30

Departamento Materiales, Comisión Nacional de Energia Atómica, Buenos Aires[1])

Grain Boundary Sink Strength in Anisotropic Materials

By

A. SARCE and E. J. SAVINO

The grain boundary sink strengths for intrinsic point defects in an anisotropic lattice are calculated. It is shown that the sink strength depends on the grain size, its shape, its metallurgical state, and, for hexagonal symmetry, on the anisotropy factor for the diffusivity (D_c/D_a). It appears to be independent of the volume averaged diffusivity constant. For the grain shape dependence, the Holt and Ibrahim anisotropy factor is obtained only as a limit case.

Die Stärke der Korngrenzensenke für Eigen-Punktdefekte in einem anisotropen Gitter wird berechnet. Es wird gezeigt, daß die Senkenstärke von der Korngröße, deren Form, metallurgischer Zustand und für hexagonale Symmetrie, vom Anisotropiefaktor für das Diffusionsvermögen (D_cD_a) abhängt. Sie scheint von der volumengemittelten Diffusionskonstante unabhängig zu sein. Für die Abhängigkeit der Kornform wird der Anisotropiefaktor nach Holt und Ibrahim nur als Grenzfall erhalten.

1. Introduction

Intrinsic lattice defects, interstitials, and vacancies, migrate by thermal activation. Whenever one of those point defects reaches the capture cross section of a more stable and less mobile defects, either a linear, two-, or three-dimensional one, it may be trapped. This trapping process generally reduces the potential energy of the crystal. Also the otherwise random walk of point defects is biased by the long-range elastic field induced by the larger defects. The strength of those defects is therefore a function both of their capture cross section for point defects and the bias factor. Being the distortion field associated to the grain boundary weaker and of shorter range than the one of other crystal topological defects, like dislocations, point defects are presumably only weakly biased towards it. However, in fine-grained polycrystals, grain boundaries may be the main sink for determining the point defect fate. Also in not so fine grains, they may compete as sinks with other crystal imperfections. Under irradiation equal number of interstitials and vacancies, Frenkel pairs, are produced outside thermal equilibrium. When interstitials produced at a given grain are preferentially trapped at one of its grain boundaries, one may expect a net advance of that grain over neighbour ones (plus some residual compression field due to compatibility reasons) and therefore an extension of the specimen in a direction perpendicular to the boundary plane, conversely vacancies will introduce a contraction into that direction. This implies that selective defect absorption at grain boundaries may result in macroscopic straining. For spherical grains and isotropic crystals, where the diffusion rate does not depend on the defect migration direction, a preferential migration and trapping of interstitials at the boundary implies a positive contribution to the change in volume (negative one for

[1]) Avda. del. Libertador 8250, 1429 Buenos Aires, Argentina.

vacancies). As proved by Fainstein-Pedraza et al. [1], Savino and Laciana [2], and Holt and Ibrahim [3] for the case of parallelepiped grains the anisotropy in the shape of the grain implies the largest sink strength to be associated to the grain boundary faces perpendicular to the shortest grain axis. Even for pure metals, depending on the relation of orientation between grains, the boundary may have a restricted capacity as sink of point defects (i.e. to be a non ideal sink). This implies that once a point defect has reached the environment of the grain face its absorption depends both on the chemical species of the interstitial and vacancy defect and on a limited absorption rate [4, 5].

The dynamics of the point defects induced by irradiation determines the crystal permanent straining rate. This micro and the associated macro evolution of a crystal under irradiation are quantitatively calculated by means of the so-called "rate theory". This approach was first developed by Wiedersich [6] and later further developed by Brailsford and Bullough [5]. This theory generally assumes an average isotropic diffusivity and the differences between sinks for point defects are dumped into a sink strength parameter associated to each sink type. Therefore, the relevant parameters for this theory are the individual sink strengths which must be consistently calculated. At high irradiation flux and relatively high temperatures most materials swell by nucleation and growth of voids [7]. This phenomenon is mainly induced by the preferential attraction of interstitials towards dislocations with respect to vacancies. If so, more vacancies remain free to be trapped at impurities or other crystal defects (onset of void nucleation) or at already nucleated voids, allowing for their growing. In anisotropic materials, the network dislocations may have a preferential orientation of their Burgers vectors. The above-mentioned preferential attraction of interstitials and their subsequent trapping will induce the climbing of the dislocation and therefore a straining of the crystal in the case the corresponding vacancies can be trapped at alternative three-dimensional sinks, like grain boundaries. This is the basis of the irradiation growth theory for highly textured cold worked Zr [1, 8]. The whole subject of growth and creep under irradiation has been reviewed in a recent meeting at Hecla Island. There [9 to 14], the grain boundary appears as the relevant sink for calculating the evolution of the defect concentration in polycrystals under irradiation. However, a systematic calculation of the grain boundary sink strength has been relatively neglected in the literature, especially for the case of anisotropic crystals. Even for isotropic grains only a very few calculations have been reported, see for example Bullough et al. [15]. We also recently performed a calculation for several sink strengths including the grain boundary and considering the diffusivity constant to be anisotropic [16]

Generally for "rate theory" the approximation of a high density of sinks within the grain is adopted for calculating the grain boundary sink strength. This implies to consider that the boundary can only trap the point defects located in a narrow region neighbored to it where no alternative sinks are present. This approach was first proposed by Brailsford and Bullough [17] and, to the authors knowledge, only critically evaluated by the same authors in the above-mentioned work [15]. This high sink density approximation predicts the square of the grain boundary sink strength (k_{gb}^2) to be directly proportional to the strength of the other sinks (k_{sc}) within the grain and to the ratio of the boundary area with the grain volume. For a spherical grain of diameter d_g

$$k_{gb}^2 = 6k_{sc}/d_g . \tag{1}$$

As said above Bullough et al. [15] have shown in their work the relative validity of this limit, while Savino [18] performed a similar numerical work for the case of thin films. For

the case of parallelepiped grains, the strength for each face of the grain is 1/3 that in (1), where d_g is the distance between parallel faces. In those works only the isotropic case or one-dimensional diffusion was considered. Also Griffiths et al. [19] measured recently that the grain strength depends on the crystallographic orientation.

Recent explanations of the enhancement of creep under irradiation are based on the influence of the stress field on the sink strength [20 to 22]. The pioneer works of Savino [23] and Dederichs and Schroeder [24] showed that the symmetry of the point defect at its equilibrium and saddle point location influences its bias. Their approach for the diffusion under stress has been used previously for calculating the sink strengths of dislocations, voids, and grain boundaries under an external, homogeneous stress [16, 25, 26] and the effect of internal stresses [27, 28]. In this paper we shall calculate the grain boundary sink strength. Analytical and numerical calculations are performed within a mean cellular model [15]. The anisotropy on the diffusion, related to the crystal orientation, and on the grain shape is explicitly included in the calculations.

2. Grain Boundary Sink Strength

As said in the Introduction we shall calculate the grain boundary sink strength within a mean cellular model. This implies to model an isolated grain, with an internal distribution of sinks for point defects within it and a homogeneous damage density K. The internal sinks will be considered to be smeared out at an effective medium within the grain and their strength for point defects will be taken as a known parameter k_{sc}. This is related to their rate of absorption of point defects I_{sc} at a point $\boldsymbol{r}$ by the definition

$$I_{sc}(\boldsymbol{r}) = k_{sc}^2 \langle D \rangle \, c(\boldsymbol{r}) \,,$$

where $\langle D \rangle$ is the volume averaged diffusivity and $c(\boldsymbol{r})$ the point defect concentration averaged in a representative volume element (RVE) at the point $\boldsymbol{r}$ within the grain (for a definition of RVE see [29]).

The point defect density will vary within the grain, that is, c is a function with a slow space variation with respect to the distance between the defect sinks at the crystal. At steady state and when only a single point defect type is present at the crystal this density will satisfy the equation

$$\nabla \cdot \boldsymbol{J} + I_{sc} = K \,, \tag{2}$$

where $\boldsymbol{J}$ is the defect current at a point r and its dependence on c is a function of the crystal and defect symmetry which we discuss below for h.c.p. structures.

The average diffusivity is chosen hereafter as the invariant of the diffusivity tensor [30],

$$\langle D \rangle = [D_{(1)}^0 D_{(2)}^0 D_{(3)}^0]^{1/3} \,,$$

where $D_{(i)}^0$ is the i-th eigenvalue of the diffusivity tensor in an unstrained crystal.

The grain boundary sink strength k_{gb}^2 can be calculated from the total defect flow at the grain boundary,

$$I_{gb} = \int_A \boldsymbol{J} \cdot \mathrm{d}\boldsymbol{A} \,, \tag{3}$$

which, in turn, for an effective medium satisfies the equation

$$I_{gb} = k_{gb}^2 \langle D \rangle \langle c \rangle \,, \tag{4}$$

where $\langle c \rangle$ is the space-averaged point defect concentration within the grain; A is the grain boundary area.

Equation (2) can solved with the ideal sink strength condition at the boundary of the grain; for a parallelepiped grain of dimension $d_1 \times d_2 \times d_3$,

$$c(x_j = 0) = c_0\,, \qquad c(x_j = d_j) = c_0\,, \tag{5}$$

this implies that a constant concentration c_0 (which may be zero) is always maintained at the grain boundary. Also a rate limited approach may be adopted,

$$\begin{aligned} -\mathbf{D}\nabla c(x_j = 0) &= \hat{K} c(x_j = 0)\,, \\ -\mathbf{D}\nabla c(x_j = d_j) &= \hat{K} c(x_j = d_j)\,, \end{aligned} \tag{6}$$

where d_j is at the grain boundary perpendicular to the j direction, and $\hat{K}$ is the point defect transfer velocity. $\mathbf{D}$ is the diffusivity tensor; for the unstrained crystal, it agrees with $\mathbf{D}^0$ used before.

3. Grain Boundary Sink Strength Calculation

In the initial work [23] and the following [20, 22, 24], the dependence of the defect current $\boldsymbol{J}$ on the crystal and defect symmetry is thoroughly discussed. For the sake of illustration and simplicity, in this paper we shall reduce the general expression to the case of hexagonal symmetry. For this particular case, (33) in [23] reduces to

$$\boldsymbol{J}(\boldsymbol{r}_i) = \sum_{j=1}^{N} \frac{\nu_0}{2} \exp\left(-\frac{Q^{ij}}{kT}\right)\left[c(\boldsymbol{r}_i)\exp\left(\frac{E(\boldsymbol{r}_i)}{kT}\right) - c(\boldsymbol{r}_j)\exp\left(\frac{E(\boldsymbol{r}_j)}{kT}\right)\right]\boldsymbol{s}_{ij}\,, \tag{7}$$

where $c(\boldsymbol{r}_i)$ and $c(\boldsymbol{r}_j)$ ($E(\boldsymbol{r}_i)$ and $E(\boldsymbol{r}_j)$) are the point defect density (formation energy) at neighbor sites i and j, respectively, being N the number of sites j that the defect can occupy through a single jump from i in a direction $\boldsymbol{s}_{ij}$ passing a saddle point site with an energy Q^{ij}. The defect current reduces in the continuum limit to the well-known expression

$$\boldsymbol{J}(\boldsymbol{r}) = -\mathbf{D}(\boldsymbol{r})\left[\nabla c(\boldsymbol{r}) + \frac{c(\boldsymbol{r})}{kT}\nabla E(\boldsymbol{r})\right], \tag{8}$$

where

$$D_{\alpha\beta}(\boldsymbol{r}) = \sum_{j=1}^{N} \frac{\nu_0}{2} \exp\left[-(Q^{ij}(\boldsymbol{r}) - E(\boldsymbol{r}))/kT\right](s_{ij})_\alpha\,(s_{ij})_\beta \tag{9}$$

is the anisotropic diffusivity tensor at the continuum limit we already used in Section 2.

In case of a crystal being strained by a field $\boldsymbol{\varepsilon}$ the formation and saddle point defect energies for the undistorted crystal (E_0 and E_M) change in first order [23] to

$$E(\boldsymbol{r}_i) = E_0 - \mathbf{p}^{\mathrm{c}} \times \boldsymbol{\varepsilon}(\boldsymbol{r}_i)\,, \qquad Q^{ij}(\boldsymbol{r}_s) = E_M - \mathbf{p}^{\mathrm{s}} \times \boldsymbol{\varepsilon}(\boldsymbol{r}_s)\,, \tag{10}$$

where $\mathbf{p}^{\mathrm{c}}$ and $\mathbf{p}^{\mathrm{s}}$ are the respective defect dipole tensor as defined by Tomé et al. [31] at the equilibrium and at the saddle point location. The strain dependence of the energies in (10) implies, in turn, a strain dependence of the defect current in (7), (8) and of the diffusivity $\mathbf{D}$ in (9).

Equation (2) in the continuum limit of (8), has been solved by Bullough et al. [15] for the case of isotropic diffusion within a spherical grain. For the general three-dimensional case with non-isotropic diffusivity constant or a grain shape different from the spherical

one no simple analytical solution is available [32]. An approximate analytical solution is discussed below. As proposed by us in a previous paper [16] (2) can be solved numerically for the case of a parallelepiped shape grain including anisotropic diffusion and the effect of stress on the defect current. This solution is based on a finite difference scheme and it will be used in what follows for solving some applications to hexagonal anisotropic diffusion.

In the case of one-dimensional diffusion, (2) can be easily solved for the defect concentration. Imposing the *ideal sink* boundary condition (5) of zero concentration at two points (0 and d), the defect concentration on the line segment ($0d$) results as [21]

$$c(x) = \frac{K}{Dk_{sc}} \left[1 - \frac{\cosh k_{sc}(x - d/2)}{\cosh k_{sc} d/2} \right]. \tag{11}$$

In the three-dimensional case, if the flow current of defects to a grain face in a parallelepiped grain were independent of the effect of the other faces, this flow current could be taken as constant over the whole face. This approach provides an approximate solution to the three-dimensional problem based on the one-dimensional solution (11). The validity of this approximation, for a general case, must depend not only on the size and shape of the grain boundary, but also on the density of the single crystal sink strength (see Introduction). For the three-dimensional case the defect average concentration can be consistently taken at steady state as

$$K = (k_{sc}^2 + k_{gb}^2) \langle D \rangle \langle c \rangle . \tag{12}$$

This implies that the total number of defects being produced under irradiation are absorbed at the available sinks and no recombination is included. If one defines the sink strength for the grain face normal to the direction j by

$$k_j^2 = \frac{\varphi_j}{\langle D \rangle \langle c \rangle V} , \tag{13}$$

where $j = x, y, z$ identifies the direction of the normal to the grain face, V is the grain volume, and φ_j is the defect flux integrated over the area of the face, it results

$$k_x^2 = \frac{(2k_{sc}/d_x) \tanh \dfrac{k_{sc} d_x}{2}}{1 - \dfrac{2}{k_{sc}} \left(\dfrac{1}{d_x} \tanh \dfrac{k_{sc} d_x}{2} + \dfrac{1}{d_y} \tanh \dfrac{k_{sc} d_y}{2} + \dfrac{1}{d_z} \tanh \dfrac{k_{sc} d_z}{2} \right)} , \tag{14}$$

where d_x, d_y, and d_z are the main dimensions of the parallelepiped shaped grain. For a parallelepiped grain, one can assume under this simplified approximation and in obvious notation

$$k_{gb}^2 = k_x^2 + k_y^2 + k_z^2 . \tag{15}$$

In the case of a cubic grain, and in the limit of large single crystal sink strength, for constant grain size d_g,

$$k_{sc} d_g \to \infty ,$$

the grain boundary sink strength converges to

$$k_{gb}^2 = k_{sc} S , \tag{16}$$

where $S = A/V$ is the ratio between grain boundary area to grain volume. While, on the opposite limit of large grain boundary density,

$$k_{sc} d_g \to 0 ,$$

it converges to

$$k_{gb}^2 = S^2 . \tag{17}$$

The above-deduced approximate sink strengths for an ideal sink, cubic grain, can be compared with the ones deduced by Bullough et al. [15] for an spherical grain, where now d_g is the grain diameter. For the first limit, the limiting strength is

$$k_{gb}^2 = k_{sc} S . \tag{18}$$

It can be seen that (18) agrees with (16). For the other limit, the strength is

$$k_{gb}^2 = \tfrac{5}{3} S^2 . \tag{19}$$

However, one must be aware that the difference between (17) and (19) may be partly due to the approximate nature of the analytical solution (17) for the parallelepiped grain. For a set of numerical calculations of the cubic grain case, and assuming the same boundary condition (5), we obtained (see Fig. 1)

$$k_{gb}^2 = 1.3 S^2 . \tag{20}$$

For the case of boundary conditions (6), with a limited defect rate at the grain surface, and within the same approximation of extending the one-dimensional solution to a three-dimensional parallelepiped grain used above, the sink strength of the grain boundary normal to an axis x in the grain is

$$k_x^2(\hat{K}) = \frac{S}{3M} \frac{\left[T + \dfrac{T^2}{k_{sc} R \sinh (k_{sc} d_x)} \right]}{\left\{ 1 - \dfrac{S}{3 k_{sc} M} \left[T + \dfrac{T^2}{k_{sc} R \sinh (k_{sc} d_x)} \right] \right\}} , \tag{21}$$

where $T = \hat{K}/D$,

$$R = 1 - \frac{T}{k_{sc}} \coth (k_{sc} d_x) ,$$

and

$$M = 1 + \frac{T}{k_{sc}} \coth (k_{sc} d_x) + \frac{T^2}{k_{sc}^2 R (\sinh (k_{sc} d_x))^2} .$$

In the limit of very large rate $\hat{K} \to \infty$, the strength (21) agrees with the ideal sink one, (14); while for very small rate, (21) converges to $k_x^2 = ST/3$.

3.1. Stress free, ideal sink, grain boundaries

In all this section we shall assume the boundary condition (5), ideal sink, to be valid at the grain boundary. We shall first test the validity of the approximate analytical solution deduced above, (15), for the grain boundary sink strength. This will be compared with

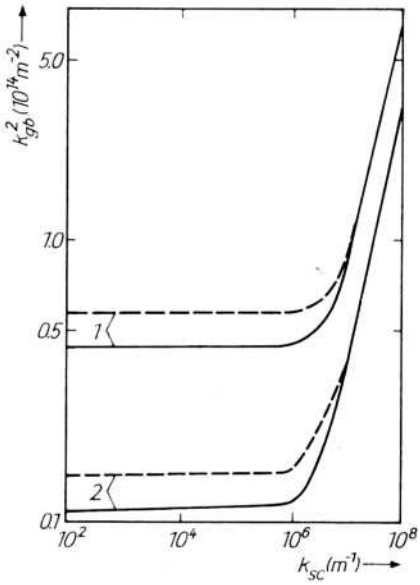

Fig. 1. Isotropic grain boundary sink strength k_{gb}^2 as a function of single crystal sink strength k_{sc} for different grain sizes: (1) 1×10^{-6} and (2) 2×10^{-6} m. ——— approximate analytical solution, – – – – numerical solution

the numerical solution [16] obtained by solving the case of isotropic diffusivity. We plot in Fig. 1 the grain boundary sink strength versus the strength of the sinks inside the grain (single crystal sinks). It can be seen that for the two approximations the predictions for the grain boundary sink strength have the same trend. While for a relatively large density of single crystal sinks the calculations predict a linear dependence of the grain boundary sink strength with the single crystal sink strength, for this strength smaller than $10^{12}\ m^{-2}$ the grain boundary strength converges to the constant value of (17).

With the purpose of studying the influence of the anisotropy on the numerical solution, we shall first assume a cubic grain but anisotropic hexagonal symmetry in the defect diffusivity. In Fig. 2 we plot the ratio between the anisotropic grain boundary sink strength to the isotropic grain boundary sink strength (k_{gb}^2/k_{gbis}^2) for point defects against the ratio $D_c/D_a(D_c(D_a))$ is the diffusivity parallel (perpendicular) to the c-crystal axis and, for the sake

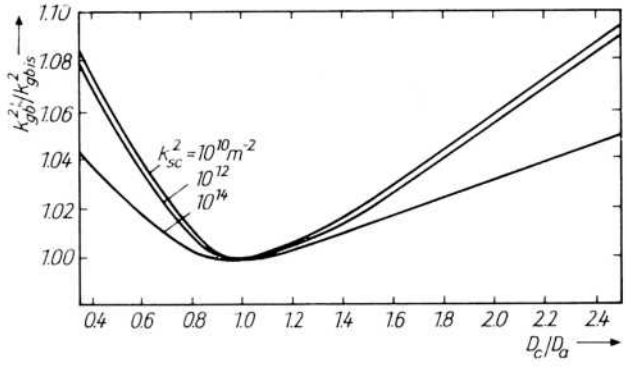

Fig. 2. Anisotropic/isotropic grain boundary sink strengths ratio (k_{gb}^2/k_{gbis}^2) vs. anisotropy factor (D_c/D_a) for different single crystal sink strengths (k_{sc}^2)

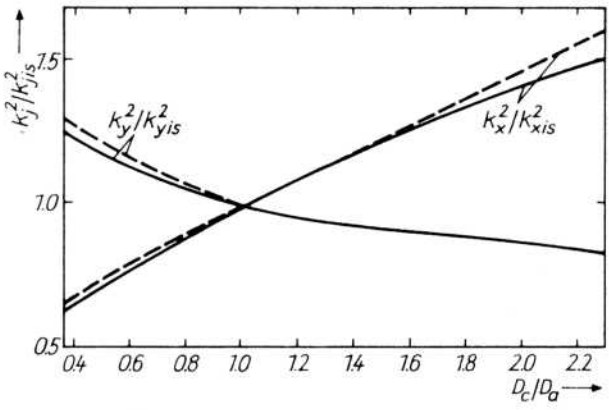

Fig. 3. Anisotropic/isotropic partial grain boundary sink strengths ratio (k_j^2/k_{jis}^2) vs. anisotropy factor (D_c/D_a). X-grain axis parallel to c-crystal axis. – – – – $k_{sc}^2 = 10^{12}$ and ——— 10^{14} m^{-2}

of illustration, in the Appendix we summarize a set of measured values of this ratio D_c/D_a for point defects in different h.c.p. metals. Three different single crystal strength values are used. It can be seen that for small anisotropy values ($D_c/D_a \approx 1$), the isotropic solution for the total sink strength is approximately correct and even for relatively different D_c/D_a values the ratio between strengths is near one. However, the anisotropy in the diffusivity determines the existence of a differential sink strength to different faces of the grain. This effect is shown in Fig. 3, where we plot the sink strength for different faces of the cubic grain against the ratio D_c/D_a. For the plot we have considered the direction x in the cube to agree with the crystal direction c. The results are independent of the area to volume ratio.

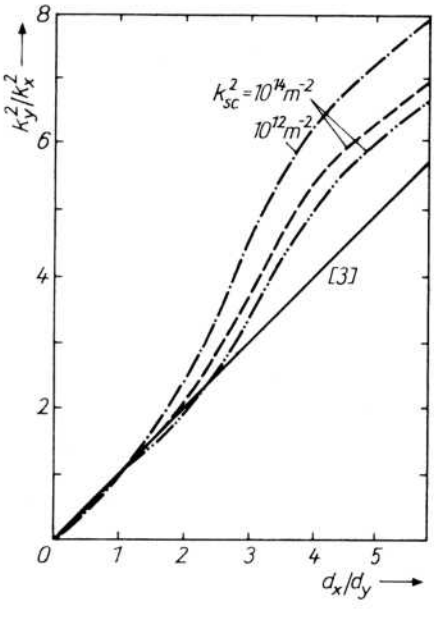

Fig. 4. Partial grain boundary sink strengths ratio vs. anisotropy shape factor (d_x/d_y). $D_c/D_a = 1.13$. – – – – and $- \cdot - \cdot - k_y^2(y \perp c)/k_x^2(x \perp c)$, $- \cdot\cdot - k_y^2(y \perp c)/k_x^2(x \parallel c)$

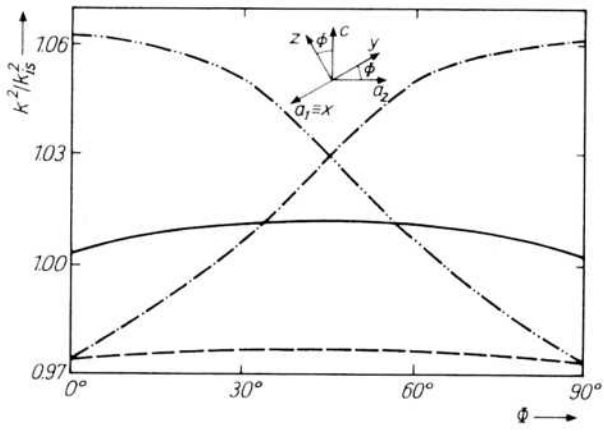

Fig. 5. Ratio between the anisotropic to isotropic total and partial grain boundary sink strength (k^2/k_{is}^2) vs. angle between crystal and grain axes. $k_{sc}^2 = 10^{12}\ m^{-2}$, ——— k_{gb}^2/k_{gbis}^2, - - - - k_x^2/k_{xis}^2, — · — · k_y^2/k_{yis}^2, — ·· — k_z^2/k_{zis}^2

Holt and Ibrahim proposed in [3], for parallelepiped grain shape, a sink strength for the grain face perpendicular to the x-axis,

$$k_x^2 = A_{xg} k_{gb}^2 , \tag{22}$$

where the anisotropy factor A_{xg} is

$$A_{xg} = \frac{1}{d_x} \Big/ \left(\frac{1}{d_x} + \frac{1}{d_y} + \frac{1}{d_z} \right). \tag{23}$$

In turn, the total strength for the grain boundary is

$$k_{gb}^2 = k_x^2 + k_y^2 + k_z^2 . \tag{24}$$

An equivalent cubic grain of side $1/d_g = 1/3(1/d_x + 1/d_y + 1/d_z)$ has, within that approach, the same total strength k_{gb}^2 as the parallelepiped one; also, it results $k_i^2/k_j^2 = d_j/d_i$ for $i, j = x, y, z$. However, in general the anisotropy factor is itself affected by the anisotropy in the diffusivity and the single crystal sink strength (k_{sc}). For illustration purposes we plot in Fig. 4 the calculated ratio k_i^2/k_j^2 for a hexagonal crystal and a ratio $D_c/D_a = 1.13$. We see how this ratio for different single crystal sink strengths differs from the expressions above, (22) and (23), proposed by Holt and Ibrahim.

In all the examples above, Fig. 1 to 4, we have considered either isotropic diffusivity or anisotropic one with hexagonal symmetry and the crystal axes parallel to the grain parallelepiped axes; for discussing the effects of the crystal orientation within the grain it is interesting to relax this latter condition. For the sake of illustration we shall assume a cubic grain with hexagonal symmetry and one of the basal plane axes to agree with a cube axis and $D_c/D_a = 1.13$. We plot in Fig. 5 the total grain sink strength and the one corresponding to each face for different rotations of the grain around the common axis.

3.2 Stress free, non-ideal sink

We shall consider in this section the boundary condition (6) of the sink strength being rate controlled. For the calculation we assume a cubic grain and the absorption of point defects

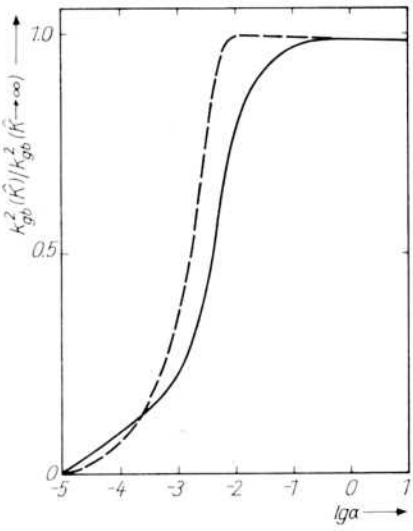

Fig. 6. Ratio between the rate limited sink strength to the ideal grain boundary one vs. α ((25)). $k_{sc}^2 = 10^{12}\ m^{-2}$, ——— approximate analytical solution, – – – – numerical solution

to be restricted by the last defect thermally activated jump [5, 29], that is

$$\hat{K} = \alpha\left(\frac{\langle D\rangle}{a}\right), \tag{25}$$

where α is a constant smaller than unity, and a is a distance of the order of the lattice parameter. We plot in Fig. 6 the sink strength for the grain as a function of the parameter α for the analytical equation (21) and numerical calculations.

3.3 Stressed grains

For an homogeneously strained crystal the diffusivity tensor can be expanded [33] as a function of the strain field ε as

$$D_{km} = D_{km}^0 + d_{kmrl}\varepsilon_{rl}\,, \tag{26}$$

where $\mathbf{D}^0$ is a second-order tensor and d_{kmrl} is a fourth-order one. Both tensors are related to the crystal symmetry and to the diffusing point defect at the equilibrium and saddle point configurations. For cubic crystals Dederichs and Schroeder [24] developed analytical expressions for these tensors, while Savino and Smetniansky-DeGrande [34] studied the self-defects in h.c.p. crystals. In the case of cubic crystals the diffusivity of vacancies and interstitials is isotropic. However, under the influence of a strain field it becomes anisotropic. For example, in the case of uniaxial stress of a cubic lattice that strains elastically the lattice by an amount

$$\varepsilon = \frac{\sigma}{E}\begin{bmatrix} 1 & 0 & 0 \\ 0 & -\nu & 0 \\ 0 & 0 & -\nu \end{bmatrix} \tag{27}$$

the diffusivity is anisotropic with hexagonal symmetry. For the sake of illustration we show in the Appendix the ratio of D_c/D_a resulting for some point defect dipole tensors for the interstitial and vacancy reported for cubic and h.c.p. lattices [35, 36] in case of a uniaxial stress applied in a symmetry axis direction. It can be shown that provided the correct average diffusivity $\langle D\rangle = (D_1D_2D_3)^{1/3}$ and the corresponding D_c/D_a ratio are used in (4) for

calculating the grain boundary sink strength, the calculated values coincide with those calculated in previous sections and one may conclude that the strength only depends on the above ratio. This result was somewhat obscure in own previous papers where we always calculated the sink strength by using the average $\langle D \rangle$ for the strain free crystal. However, one should keep in mind that the absorption of point defects at the grain boundary depends both on the sink strength and the average diffusivity (4).

4. Discussion and Conclusions

In this paper and in a previous one [16] we calculated the interstitial and vacancy sink strengths of grain boundaries. The calculations are based on a point defect diffusion model which includes the discrete character of the defect jump [23]. This model for a stress free crystal reduces in the continuum limit approach to a classical diffusion one, but it includes explicitly the anisotropy of the diffusion in a crystal lattice. The sink strengths are calculated assuming a cellular model for the grain boundary. The equations for this model are developed above and the numerical calculations are performed assuming hexagonal symmetry. The results show clearly that the grain boundary sink strength depends on the grain size (see Fig. 1), its shape (seeFig. 4), and the metallurgical state of the crystal. This one is simulated by assuming different strength values of the other sinks (single crystal sinks) within the grain besides the grain boundary (see Fig. 1). As expected, due to the anisotropy of the diffusion constant, we also found that grain boundary faces differently oriented with respect to the grain lattice, show different partial sink strengths (see Fig. 5).

The effect of applying stress to the crystal affects the diffusivity values as discussed by Savino et al. [23, 34]. In general this implies a change of the average diffusion value plus an added anisotropy depending on the lattice straining direction. On the other hand, we found that the sink strength for the grain boundary is independent of the average diffusivity value (see definition above in Sections 2 and 3.3 for anisotropic crystals). It can be said that for h.c.p. crystals or uniaxially strained cubic crystals in a given direction (call it c), D_c/D_a determines the values of the grain boundary sink strength for a given geometrical and crystallographic grain orientations. In strained crystals, the values D_c/D_a are dependent, at the same time, on the symmetry of the defect dipole tensor at equilibrium and at the saddle point configurations.

As said in the Introduction the partial sink strengths (the strength of each grain face) are important for calculating the strain rate when predicting radiation-induced creep and growth. We found a strong dependence of the partial sink strengths on the anisotropy factor (D_c/D_a) (see Fig. 3), the orientation of the grain axes (see Fig. 5), the anisotropy of the grain shape (see Fig. 4), and the rate of absorption of point defects at the grain (see Fig. 6). On the other hand, we found that the anisotropy shape factor may differ for anisotropic crystals from the one proposed by Holt and Ibrahim. This is clearly shown in Fig. 4. We conclude that only in the limiting case when the diffusivity tensor is isotropic and the defect flux is constant over the whole area of each grain face, the slope is unity, and we regain the Holt and Ibrahim anisotropy factor.

Acknowledgement

This work was partially supported by the "Proyecto Multinacional de Investigacion y Desarrollo en Materiales" OEA-CNEA (Organization of American States-National Atomic Energy Commision of Argentina).

Appendix

Anisotropy of diffusion constants

In this appendix we shall first review some experimental values of the anisotropy in vacancy and interstitial diffusivity reported in the literature for h.c.p. lattices. Our purpose is not to provide a complete data revision, but to determine the range of plausible values of that anisotropy in those crystals. In a second part we also review the values calculated for the change in the diffusivity of interstitials and vacancies in cubic and h.c.p. crystals when a homogeneous stress is applied to the specimen.

Diffusivity relationship

metal	vacancies			
	T/T_m	D_c/D_a	c/a	
Be	0.8	0.57	1.5847	[37]
$T_m = 1350$ °C	0.6	0.45		
Tl	0.8	0.72	1.6002	[37]
$T_m = 300$ °C	0.6	0.64		
Mg	0.8	0.89	1.6235	[38]
$T_m = 650$ °C	0.6	0.85		
Zn	0.8	1.96	1.8556	[37]
$T_m = 419$ °C	0.6	4.17		
Cd	0.8	1.50	1.8859	[39]
$T_m = 321$ °C				

"Interstitial" metal solutes

solvent	solute	D_c/D_a	T (°C)	
α-Zr	Co	6.79	840	[40]
	Cr	2.59	840	[40]
	Cu	2.94	840	[40]
	Fe	2.80	747 to 847	[41]
	Ni	3.75	747 to 847	[41]
α-Ti	Fe	2.6	800	[42]
	Co	3.6	800	[42]
	Ni	1.7	800	[42]
	P	0.66	800	[42]
	Mn	1.68	861	[42]
		2.00	800	[42]
		2.14	756	[42]
		3.68	652	[42]
		3.84	605	[42]
Cd	Cd	2.568	356	[39]
	Zn	1.532	356	[39]
	Ag	3.807	356	[39]
	In	0.549	356	[39]
	Au	1.726	356	[39]

Theoretical calculations in strained crystals

Mg vacancies $10^3\varepsilon$	$T = 427$ °C [35] D_c/D_a*)
	anis. $\mathbf{p}^c$ and $\mathbf{p}^s$
0	0.826
5	0.806

Mg $10^3\varepsilon$	self-interstitials D_c/D_a*)	$T = 427$ °C D_c/D_a*)	[35] D_c/D_a*)
	anis. $\mathbf{p}^c$ and $\mathbf{p}^s$	isotropic $\mathbf{p}^c$	isotropic $\mathbf{p}^s$
0	1.132	1.132	1.132
5	1.512	1.448	1.070

Cu vacancies $10^3\varepsilon$	$T = 427$ °C [36] D_c/D_a**)
	anis. $\mathbf{p}^c$ and $\mathbf{p}^s$
0	1.000
5	0.734

Cu self-interstitials $10^3\varepsilon$	$T = 427$ °C [36] D_c/D_a**)
	anis. $\mathbf{p}^c$ and $\mathbf{p}^s$
0	1.000
5	0.958

*) As calculated by using dipole tensor values reported in [43].
**) As calculated by using dipole tensor values reported in [25].

References

[1] D. Fainstein Pedraza, E. J. Savino, and A. J. Pedraza, J. nuclear Mater. **73**, 151 (1978).
[2] E. J. Savino and C. E. Laciana, J. nuclear Mater. **90**, 89 (1980).
[3] R. A. Holt and E. F. Ibrahim, Acta metall. **27**, 1319 (1979).
[4] L. K. Mansur, J. nuclear Mater. **83**, 109 (1979).
[5] A. D. Brailsford and R. Bullough, J. nuclear Mater. **44**, 121 (1972).
[6] H. Wiedersich, in: Physical Metallurgy of Reactor Fuel Elements. Ed. J. E. Harris and E. C. Sykes, Berkeley Nuclear Laboratories, 1973 (p. 142).
[7] F. A. Garner and D. L. Porter, J. nuclear Mater. **155/157**, 1006 (1988).
[8] C. C. Dollins, J. nuclear Mater. **59**, 61 (1975); **82**, 311 (1979).
[9] R. Dutton, J. nuclear Mater. **159**, 339 (1988).
[10] G. J. Field, J. nuclear Mater. **159**, 3 (1988).
[11] V. Fidleris, J. nuclear Mater. **159**, 22 (1988).
[12] M. Griffiths, J. nuclear Mater. **159**, 190 (1988).
[13] J. R. Matthews and M. W. Finnis, J. nuclear Mater. **159**, 257 (1988).
[14] R. A. Holt, J. nuclear Mater. **159**, 310 (1988).
[15] R. Bullough, M. R. Haynes, and C. H. Wood, J. nuclear Mater. **90**, 44 (1980).

[16] N. Smetniansky-De Grande, A. Sarce, E. J. Savino, and C. N. Tomé, J. nuclear Mater. **159**, 379 (1988).
[17] A. D. Brailsford and R. Bullough, J. nuclear Mater. **48**, 87 (1973).
[18] E. J. Savino, Radiat. Eff. **29**, 147 (1976).
[19] M. Griffiths, R. W. Gilbert, and C. E. Coleman, J. nuclear Mater. **159**, 405 (1988).
[20] C. N. Tomé, H. A. Cecatto, and E. J. Savino, Phys. Rev. B **25**, 7428 (1982).
[21] C. H. Woo, J. nuclear Mater. **159**, 237 (1988).
[22] C. H. Woo and E. J. Savino, J. nuclear Mater. **116**, 17 (1983).
[23] E. J. Savino, Phil. Mag. **36**, 323 (1977).
[24] H. Dederichs and K. Schroeder, Phys. Rev. B. **17**, 2524 (1978).
[25] E. J. Savino and C. N. Tomé, J. nuclear Mater. **108/109**, 405 (1982).
[26] N. Smetniansky-De Grande, E. J. Savino, and C. N. Tomé, phys. stat. sol. (b) **144**, 271 (1987).
[27] E. J. Savino and S. Harriague, Effects of Radiation on Materials, Proc. 12-th. Internat. Symp., ASTM STP 870, Ed. F. A. Garner and J. S. Perrin, American Society for Testing and Materials, Philadelphia 1985 (p. 667).
[28] C. H. Woo, J. nuclear Mater. **131**, 105 (1985).
[29] A. Sarce and E. J. Savino, phys. stat. sol. (b) **154**, 105 (1989).
[30] U. M. Gösele, Progr. Reaction Kinetics **13**, 63 (1984).
[31] C. N. Tomé, A. M. Monti, and E. J. Savino, phys. stat. sol. (b) **92**, 323 (1979).
[32] G. F. D. Duff and D. Naylor, Differential Equations of Applied Mathematics, Wiley, New York/London/Sydney 1966 (p. 264).
[33] C. P. Flynn, Points Defects and Diffusion, Clarendon Press, Oxford 1972.
[34] E. J. Savino and N. Smetniansky-De Grande, Phys. Rev. B **35**, 6064 (1987).
[35] N. Smetniansky-De Grande, Thesis, Universidad Nacional de la Plata, 1988.
[36] N. Smetniansky-De Grande, private communication.
[37] Y. Adda and J. Philibert, La diffusion dans les solides, Presses Universitaires de France, Paris 1966.
[38] J. Combronde and G. Brebec, Acta metall. **19**, 1393 (1971).
[39] Chih-Wen Mao, Phys. Rev. B. **5**, 4693 (1972).
[40] R. Tendler and J. P. Abriata, J. nuclear Mater. **150**, 251 (1987).
[41] G. M. Hood, J. nuclear Mater. **159**, 149 (1988).
[42] Y. Nakamura, H. Nakajima, S. Ishioka, and M. Koiwa, Acta metall. **36**, 2787 (1988).
[43] C. N. Tomé, Thesis, Universidad Nacional de La Plata 1982.

(Received January 18, 1990)