

M. H. Yoo¹

SUPPRESSION OF VOID FORMATION IN ZIRCONIUM²

ABSTRACT: An analysis is given of the effects of anisotropic thermal expansion coefficients and elastic constants on radiation-induced void formation in Zr and other hexagonal metals. Upper bound values of thermal stress in polycrystalline metals are estimated. A cyclic temperature fluctuation at high irradiation temperature causes changes in internal stresses that suppress nucleation and growth of voids as a result of the enhanced recombination of point defects at grain boundaries and also retard void growth due to the induced self stress field. Such effects are more pronounced in highly anisotropic Zr than in Mg. Effects of hydrostatic pressure on void formation are also investigated. Other metallurgical variables for void formation are discussed, and an experiment to test the current concept is suggested.

KEY WORDS: voids, irradiation, zirconium, hexagonal metals, thermal expansion, anisotropy, point defects, recombination, dislocations, grain boundaries

¹Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 37830.

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1. INTRODUCTION

Voids have been found in most irradiated metals and alloys of cubic structure [1,2]. In irradiated hexagonal close-packed metals, however, voids have been found in Mg [3-6], Co [7], Re [8,9] but not in α -Zr [9-12], Zircaloy-2 [11-13], and α -Ti [8-10]. In view of the swelling problem in reactor materials it is important to understand the causes of such seemingly unusual resistance of Zr and Ti to void formation.

Few suggestions have been offered to explain the absence of voids in Zr and Ti. Brimhall et al. [8] mentioned anomalous diffusion properties and very high solubilities of gas atoms, particularly oxygen, in Ti as possible causes. Wolfenden and Farrell [11,14] and Ferguson [15] comment on possible roles of common interstitial atoms (O, N, and H) in void formation in Zr. They [11] discount anomalous diffusion and stacking fault energy as the causes of void resistance in Zr but point out that an absence of radiation-induced dislocation structure and the small fission spectrum averaged (n,α) cross section of Zr may be contributory factors since helium may be required for void nucleation. Recently, Carpenter [16] has investigated the role of helium in void nucleation in Zr by use of a high voltage electron microscope, and he identifies voids in a specimen containing helium but not in specimens free from helium.

The physical and chemical properties of Zr and Ti are markedly similar, and they are notably anisotropic especially at elevated temperatures toward their respective α - β transformation temperatures. The purpose of this paper is to offer the explanation that highly anisotropic thermal expansion coefficients and elastic constants may, under small temperature fluctuations, give rise to appreciable internal stress in polycrystalline Zr and Ti at high temperature, and that such induced stress may suppress void development by causing stress-induced depletion of point defects to grain boundaries, by creating a dislocation

substructure, and by changing the stress field around a void. Effects of hydrostatic pressure, the complimentary effect to thermal expansion are also discussed. For the purpose of a general comparison several hexagonal metals are included in the analysis whenever their pertinent properties are known, but detailed comparisons of the calculated results for Zr are made directly with those for Mg.

2. INTERNAL STRESS AND STRAIN

2.1. Temperature Change

Consider a spherical grain surrounded by fine and randomly oriented grains at a reference temperature, $T_r = 0.4 T_m$, where T_m is the absolute melting point of the metal. When the temperature is changed by ΔT to $T_r + \Delta T$, an upper bound value of thermally induced stress in the grain may be estimated, e.g., as given by Piercy [17]. It follows that the internal stress in the grain, σ_{ij} , has the principal values along the a and c directions,

$$\sigma_a = \frac{1}{3} \Delta T (\alpha_c - \alpha_a) (C_{11} + C_{12} - 2C_{13}) \quad , \quad (1)$$

$$\sigma_c = -\frac{2}{3} \Delta T (\alpha_c - \alpha_a) (C_{33} - C_{13}) \quad , \quad (2)$$

and they are homogeneous within the grain. These stresses are directly proportional to the difference of thermal expansion coefficients, α_a and α_c , in the two crystallographic directions and the elastic stiffness constants, C_{ij} .

The calculated results of σ_a and σ_c are normalized by μ , the shear modulus based on Voigt's average, and they are listed in Table 1. The reference temperatures of Tl, Zr, Ti, and Ru are obtained from the effective melting temperatures [18]. The references for thermal expansion coefficients are given in the last column. When available, elastic constants at high temperature near T_r are used for the calculation [23], otherwise the constants at room temperature are used. With an assumption that the yield stress at T_r is $\tau_y = \mu \times 10^{-4}$ and with

only a small $\Delta T = 10^\circ\text{K}$ the maximum shear stresses are evaluated by $\tau = \frac{1}{2} |\sigma_a - \sigma_c|$, and they are listed in Table 1 in fraction of τ_y . The smaller the difference in α 's, the lower will be the value of τ . The temperature change of $\Delta T = 10^\circ\text{K}$ induces the maximum shear stress to be 65% of the yield stress in Zr, whereas it is only 15% of the yield stress in Mg.

2.2. Interstitial Gas Atoms

It has been established that nonmetal atoms such as oxygen and nitrogen occupy the octahedral holes of the hexagonal close-packed structure in a perfectly random manner, and these atoms cause a considerable lattice expansion along the c axis as compared to a moderate expansion along the a axis [24]. Differential strain components with respect to the change in atom ratio, x , in the range from zero up to the maximum ratio, x_m , are calculated based on the available x-ray data for Ti, Zr, and Hf [24-28], and they are listed in Table 2. Upper bound values of the internal stress are calculated by the same method as before, and they are also listed in Table 2. It is found that σ_c and σ_a induced by an increase of the O/Zr ratio by $\Delta x = 1.05 \times 10^{-3}$ at $T = 302^\circ\text{K}$ [24] are equal to those induced by a temperature change of $\Delta T = 1^\circ\text{K}$ at $T = 743^\circ\text{K}$ in Zr. This additional oxygen is equivalent to 184 ppm by weight. In other words, the resulting maximum shear stress in Zr is approximately 35% of the yield stress per 100 ppm of oxygen. Thus, in Zr and also in Hf, the internal stress induced by the increasing concentration of gas atoms in solution is additive to that induced by a temperature increase due to the anisotropic thermal expansion.

2.3. Hydrostatic Pressure

A problem complementary to the one discussed above is that internal deviatoric strain is induced in polycrystalline grains of a hexagonal metal when it is subjected to hydrostatic pressure, P . Upper bound values of the deviatoric

strain components are $\epsilon'_a = (S_{33} + S_{13} - S_{11} - S_{12})P/3$ and $\epsilon'_c = -2\epsilon'_a$, where S_{ij} are the elastic compliance constants. Numerical values of $\epsilon'_a \times 10^5$ induced by $P = 1$ kbar (14.5 ksi) are 1.5, 0.4, -0.02, -1.9, and 0.5 for Mg, Co, Re, Zr, and Ti, respectively. No deviatoric strain results when $S_{11} + S_{12} = S_{33} + S_{13}$ or the linear compressibility is isotropic. This condition is nearly met in the case of Re giving rise to a very small magnitude of the strain compared to Mg and Zr.

3. VOID FORMATION

How does internal stress or strain affect void formation? This is a difficult question. There have been several experiments and theoretical analyses to investigate the effects of stress on void formation [29-31], but considerable uncertainty still remains. Basic properties of point defect formation and migration are directly affected by the stress [32]. A complete understanding of such effects in Zr is not feasible because of our meager knowledge of point defect properties of the metal [33]. Several simplifying assumptions are made in the ensuing discussion. It is assumed that void embryos are available and only those associated with transmuted or implanted gas atoms survive to be stable nuclei. Moreover this nucleation stage is thought to be unaffected by the stress. If the point defect production rate is also independent of the stress, then a probable answer to the question may rest on the ways the stress influences the recombination rate and the migration of point defects to various types of sink. It is also assumed that at the reference temperature, T_r , interstitials migrate more easily than vacancies in hexagonal metals.

3.1. Point Defects in Stressed Crystals

The equilibrium concentration of non-interacting point defects in a stressed crystal is given by

$$c_d^e(\sigma) = c_d^e(0) \exp\left[-\frac{\delta G_d^f(\sigma)}{kT}\right], \quad (3)$$

where $c_d^e(0)$ is the defect equilibrium concentration in an unstressed crystal, k is the Boltzmann constant, and δG_d^f is the free energy of defect formation in the stressed crystal less the free energy of defect formation in the unstressed crystal [32]. When the internal stress or strain is homogeneous within a reference grain, the free energy change is essentially

$$\delta G_d^f = \delta E + \delta W, \quad (4)$$

where δE is the elastic interaction energy by the size effect and δW is the work done against the external force in removing or replacing an atom on the surface.¹ The size effect interaction is given by

$$\delta E = -\sigma_{ij} \epsilon_{ij}^d V_d, \quad (5)$$

where ϵ_{ij}^d and V_d are the strain tensor and the volume associated with the defect, respectively. The work term is simply

$$\delta W = \pm \frac{\Omega}{3} (\sigma_c \cos^2 \theta + \sigma_a \sin^2 \theta), \quad (6)$$

where Ω is the atomic volume, θ is the angle measured from the c axis of the reference grain, and the sign is positive for an interstitial and negative for a vacancy.

The size effect interaction of a vacancy with the internal stress was calculated by use of its local dilatation of $e_v = -0.1$ and $\Omega = a^2 c \sqrt{3}/4$ for V_d in Eq. (5), where a and c are the lattice parameters. It is found that the strength of δE in Zr is 32 times greater than that in Mg (see Table 3). Since δE is directly proportional to the defect strain, δE for an interstitial of dilatation strength, say $e_i = 0.3$, would be of opposite sign and three times the magnitude of those listed for a vacancy ($e_v = -0.1$) in Table 3. δE is independent of

¹Modulus effect interaction and indirect interaction via image fields of a point defect are neglected here.

position in the grain because of the uniform stress. The external stress in the neighboring grains directed normal to the grain boundary, the term inside the bracket of Eq. (6), is depicted schematically in Fig 1 for Zr. The amount of work involved in placing or removing an atom on the "surface" at C or A (see Fig. 1) is calculated and listed in Table 3. The difference between the two, δW_A and δW_C , gives a measure of the driving force on vacancies, $\Delta(\delta G)$. This in Zr is an order of magnitude greater than in Mg. The flow lines of vacancies are drawn schematically in Fig. 1. For an interstitial at a given site the strength of the driving force on it is the same as that on a vacancy but the flow will be in the opposite direction.

When a uniform hydrostatic pressure, P, is applied externally, it is convenient to express δG_d^f by $P\Omega_d^f$ where Ω_d^f is the activation volume of defect formation

$$\Omega_d^f = \left[\frac{\partial(\delta G_d^f)}{\partial P} \right]_T = -\frac{1}{\kappa} \left[\frac{\partial(\delta G_d^f)}{\partial \epsilon} \right]_T \quad (7)$$

where κ is the bulk modulus. Based on Eqs. (4), (5), and (6), one can derive the following relationship from Eq. (7):

$$\Omega_d^f = e_d V_d \left(\frac{3\kappa + 4\mu}{3\kappa} \right) \pm \Omega, \quad (8)$$

where the sign is positive for a vacancy and negative for an interstitial. For the assumed values of $e_v V_v = -0.1 \Omega$ and $e_i V_i = 0.3 \Omega$ one finds $\Omega_v^f/\Omega = 0.73, 0.83, 0.84, 0.88$ and $\Omega_i^f/\Omega = -0.18, -0.50, -0.52, -0.63$ for Be, Mg, Zr, and Tl, respectively.

A similar analysis for the jump frequency and the diffusivity of a point defect in a stressed crystal is possible but will not be attempted here.

3.2. Direct Recombination

Exactly equal numbers of interstitials and vacancies are produced by the irradiation at a certain production rate.¹ A good fraction of these defects will be annihilated by direct encounter during their random walk processes. In an unstrained crystal, the rate equation of such direct recombination for the case of uniform initial distribution of interstitials with respect to the vacancies is given by [34]

$$\frac{dc_i}{dt} = \frac{dc_v}{dt} = -4\pi r_c D \left[1 + \frac{r_c}{(\pi D t)^{1/2}} \right] c_i c_v, \quad (9)$$

where c_i and c_v are the average concentrations of interstitials and vacancies, r_c is the capture radius of a vacancy within which distance irreversible combination of an interstitial is assumed to occur, and $D = D_i + D_v$ where D_i and D_v are the isotropic diffusion coefficients of interstitials and vacancies. Equation (9) follows first-order kinetics after a long time, $t \gg r_c^2/D$. The greater the value of r_c^2/D , the longer the transient period would be.

It may be expected that at the reference temperature ($T_r = 0.4 T_m$) $D_i \gg D_v$ such that $D \doteq D_i$, and $c_v^e \gg c_i^e$ such that c_v^e contributes to the total c_v much more significantly than c_i^e to c_i . The numerical values of c_v^e at T_r are evaluated for five metals of which vacancy formation entropies, S_v^f , and enthalpies, H_v^f , are available [33] and they are listed in Table 4.

There are three possible sources of the stress effect on direct recombination. First, the $c_i c_v^e$ contribution to Eq. (9) will change under stress according to Eq. (3). The changes in the vacancy concentration, $\delta c_v^e(\sigma) [c_v^e(\sigma) - c_v^e(0)]/c_v^e(0)$, at sites C and A (see Fig. 1) are calculated to be rather small as shown in Table 4, being less than 2%. On the other hand, the concentration changes by

¹This production rate includes the probability factor of an interstitial escaping from spontaneous recombination with the correlated or close-pair vacancy within the damage cascade.

$P = 1$ kb calculated based on the value $e_v V_v = -0.1 \Omega$ in Eqs. (8) and (3) are $\delta c_v^e(P) = -7.4, -9.2, -14.6, -17.3,$ and -31.4% for Re, Co, Ti, Zr, and Mg at their respective T_r . As for the second source, namely the stress effect on D_i , no meaningful discussion is possible because the values of D_i even for unstressed crystals are not known. Lastly, the capture radius, r_c , of the vacancy for migrating interstitials may be changed by the stress to the extent that the elastic interaction between a vacancy and an interstitial is affected. This occurs by two effects, dia-elastic effect due to the additional volume change of a point defect caused by the stress and polarization effect of the point defect self stress induced by the stress. According to the continuum theory of lattice defects [35], the elastic interaction between point defects is realized only when a point defect is simulated by a set of unequal double forces and/or when anisotropic elastic properties of the continuum are taken into consideration. It is expected therefore that the stress effect on the capture radius would be greater in anisotropic Zr than in nearly isotropic Mg.

3.3. Defect Sinks

Sinks to which point defects migrate may be listed in the order of increasing self field qualitatively as follows: voids, grain boundaries, incoherent and coherent precipitates, incoherent and coherent twin boundaries, sub-boundaries, dislocation loops, and dislocation lines. Most of the sinks possessing the self field of either negligible or short-range strength will receive nearly equal fluxes of interstitials and vacancies, and they simply augment the recombination process indirectly. The role of grain boundary as defect sink is a case in point.

When the grain boundary is subjected to normal stress distributed as shown in Fig. 1, diffusional flow of interstitials and vacancies will occur to and from the boundary. The fluxes of point defects across the interface between the matrix and the narrow grain boundary region may be given by

$$J_d = -D_d \left[\nabla c_d + \frac{c_d}{kT} \nabla (\delta G_d^f) \right] , \quad (10)$$

where the lattice diffusion coefficient of either kind of defect, D_d , is assumed to be independent of concentration and stress. Once the grain boundary is reached, the point defects will diffuse along the boundary much more readily than in the matrix because of expectedly high grain boundary diffusivity, D_d^* , compared with D_d . The fluxes of the defects along the boundary may be given by

$$J_d^* = - \frac{D_d^* c_d}{kT} \nabla (\delta G_d^f) , \quad (11)$$

where c_d^* is the corresponding densities of defect sites in the boundary layer. Around the grain boundary (Fig. 1) δG_d^f varies directly proportional to the normal stress as discussed in Sec. 3.2. Consequently, the fluxes of interstitials and vacancies are opposed in a confined path all along the grain boundary giving rise to an enhanced recombination rate. This stress-induced indirect recombination at the grain boundary is more pronounced in Zr than in Mg by an order of magnitude (Table 3).

On the other hand, sinks with a long-range self field, such as dislocations, exert a stronger interaction potential for interstitials and give rise to a biased loss of interstitials leaving behind a slight excess concentration of vacancies. This is because in general the strength of dilatation associated with a self interstitial is believed to be large compared with that of relaxation associated with a vacancy. The presence of this bias for interstitials is the basic hypothesis common to all the current theories of void growth [1,2].

It is important therefore to investigate possible effects of an applied stress on the sink efficiency of dislocations, particularly in terms of dislocation structure. There are basically two kinds of microstructures of dislocations, one consisting of those dislocations generated by thermal and mechanical

means and the other consisting of dislocation loops and lines produced during irradiation. Under a stress of sufficient magnitude, say comparable to τ_y , the first kind of dislocation structure will evolve from a grown-in dislocation structure to one that results from active dislocation motion by stress induced glide and climb. In other words, a random distribution of more or less straight dislocations may be transformed into a cellular structure of tangled dislocations. This means effectively that during creep under irradiation the dislocations as a whole lose their long-range bias for interstitials over vacancies in some degree. Again, this effect would be much more pronounced in Zr than in Mg. As for the second kind of dislocation structure, the current knowledge of nucleation and growth of dislocation loops under an irradiation condition is too rudimentary to offer a clear answer to possible stress effects. As far as the effect of the thermal stress in a metal with $\alpha_c > \alpha_a$ is concerned, interstitial type loops will tend to form on prism planes and vacancy type loops will tend to form on the basal plane during a temperature increase. It is not immediately clear how such tendency of loop habit planes affect the overall effectiveness of the bias.

If the relaxation strain associated with a vacancy is small, say $|e_v| < 0.05$, then the inhomogeneity interaction with a dislocation stress field becomes as important a part of the elastic interaction as does the size effect [36]. In such a case, a uniform applied stress enhances the inhomogeneity interaction for the vacancy because of the quadratic dependencies on the stress components, while it does not alter for interstitials. Therefore, a certain degree of retardation on the bias could result from applied stress when the vacancy inhomogeneity interaction becomes of relative importance.

Formation of hydride precipitate in plate-like shapes is prominent in Zr. In the absence of twins the habit planes and the growth directions of coherent hydrides are $\{1\bar{1}00\}$ and $\langle 11\bar{2}0 \rangle$, respectively [37]. This is in conformity with the anisotropy of thermal expansion in Zr. The roles of the coherency strain

of a hydride on its sink efficiency are not understood. It is expected that incoherent hydride precipitates would also possess induced self stress fields under an applied stress.

3.4. Suppression of Void Growth

Let us consider a void of radius r_v and subject it to an axially symmetric stress system of principal values, $(\sigma_a, \sigma_a, \sigma_c)$. It can be shown that the local hydrostatic stress distribution around the void is [38]

$$\sigma = \bar{\sigma} - \frac{5(1+\nu)}{3(7-5\nu)} \left(\frac{r_v}{r}\right)^3 (\sigma_c - \sigma_a) (3 \cos^2\theta - 1) , \quad (12)$$

where $\bar{\sigma} = \frac{1}{3}(2\sigma_a + \sigma_c)$, r is the radial distance from the void center ($r \geq r_v$), and θ is the angle measured from the x axis. The elastic interaction energy by the size effect between the stress field and a point defect is obtained from Eq. (5),

$$E_d = e_d V_d \left[\frac{5(1+\nu)}{3(7-5\nu)} \left(\frac{r_v}{r}\right)^3 (\sigma_c - \sigma_a) (3 \cos^2\theta - 1) - \bar{\sigma} \right] , \quad (13)$$

where e_d is the local dilatation of the point defect within its associated volume V_d . For the case of $\sigma_c < 0$ (i.e., $\alpha_c > \alpha_a$) two zones of attractive interaction for interstitials are developed around a void as indicated in Fig. 2. These zones are of repulsive interaction for vacancies as far as the size effect interaction is concerned. Thus the interaction potential around a void is essentially the same in spatial form as that round a circular pure prismatic dislocation loop. The maximum strength of the interaction at the void surface, $r = r_v$, is calculated for an interstitial with $e_i = 0.3$. As shown in Fig. 3, the maximum strength in Zr and also in Re is an order of magnitude greater than that in Mg. Relatively high strengths developed in Tl, Cd, and Zn are due to their highly anisotropic α 's. When the second term in Eq. (13), $\bar{\sigma}$, is small compared with the first term, as in all the cases except Cd and Zn, it is found

that $E_d = 0$ at $\theta = 52^\circ \sim 55^\circ$. This condition occurs at $\theta = 54.7^\circ$ when $\bar{\sigma} = 0$ or $\sigma_c = -2\sigma_a$.

Substituting Eqs. (5) and (6) into Eq. (4), one can obtain the relative potential energy for each kind of point defect near a void and also at the grain boundary. The local dilatation strengths of $e_i = 0.3$ and $e_v = -0.1$ are used. The maximum interaction energy at the void surface, E_m is obtained as shown in Fig. 3, and this is averaged over the angle $\theta = 0 \sim 90^\circ$. Since the normal stress at the void surface is zero, this averaged E_m becomes the sole contribution to the total free energy change, δG . As discussed in Sec. 3.2. the only contribution to $\delta \bar{G}$ at the grain boundary is δW by Eq. (6). Thus an overall picture of the relative potential energies for the point defects may be given semi-quantitatively in Fig. 4 as far as a void and the grain boundary are concerned.

The flux of point defects across the void surface may be obtained by use of Eq. (10). A change in void radius will result from the net flux of point defects according to

$$\frac{dr_v}{dt} = \frac{\Omega}{4\pi} \int_S (J_{vi} - J_{vV}) \cdot dS_v, \quad (14)$$

where dS_v is a unit surface area of the void. In a relatively short time period in which the concentration gradient, the first term in Eq. (10), is negligible compared with the second term, the sign of dr_v/dt is directly related to the difference in the product of $c_d D_d$, and the gradient of $\delta \bar{G}$ between the two types of point defect, viz. $c_v D_v \nabla(\delta \bar{G}_v) - c_i D_i \nabla(\delta \bar{G}_i)$. If the condition $c_v D_v = c_i D_i$ is met near the void, then one finds from Fig. 4 that dr_v/dt is positive for Re, whereas it is negative for Zr and Zn. In other words, under the thermal stress induced by $\Delta T = 10^\circ K$ an existing void in Zr will shrink because of a net flux of interstitials diffusing in. The exact opposite is true for Re in which a

void will grow because of a net flux of vacancies. An interesting situation arises in Zn that a void will shrink due to a net influx of interstitials developed from a region between the void and the grain boundary thus creating a depleted zone of point defects around the shrinking void.

4. Discussion

Effects of the internal stress on the direct recombination rate are not understood adequately because of the lack of information on the diffusivities of point defects and the capture radius of a vacancy for interstitials. The calculation given in the preceding section shows that an increase in the rate of indirect recombination at the grain boundary in Zr is ten times greater than that in Mg. Consequently, the vacancy supersaturation is low and nucleation and growth of voids in Zr is more difficult than in Mg. The sink efficiency (Sec. 3.3) of dislocations for the biased loss of interstitials is lowered under an irradiation creep condition as the dislocation substructure evolves from a randomly dispersed kind to a kind of recovered structure, e.g., a cellular structure of tangled arrays. Since the maximum shear stress possible in Zr is more than four times that in Mg, such stress effect on dislocation sink efficiency would be more pronounced in Zr. Shrinkage of an existing void (Sec. 3.4) occurs in Zr because of a net flux of interstitials toward the void resulting from the induced void stress field. The stress induced void shrinkage in Mg is substantially smaller since the void stress field in Mg is smaller than that in Zr by an order of magnitude. Therefore, in view of all the three aspects considered above, it may be concluded that the thermal stress is likely to suppress void formation in polycrystalline Zr but not in Mg.

Dissolved interstitial oxygen in Ti, Zr, and Hf and nitrogen in Ti make additional contributions to the induced stress (Table 2). Thus, high solubilities of interstitial gas atoms in Zr compared to Mg augment the preceding argument based on thermal stress effects.

The effect of hydrostatic pressure on the equilibrium concentration of vacancies can be much more pronounced than that of the thermal stress (Sec. 3.2.). The rate of direct recombination will decrease with increasing pressure. Since both the pressure and the induced strain are homogeneous within a grain, the both terms in Eq. (4) are independent of position. Therefore the rate of indirect recombination at a grain boundary is not altered by the hydrostatic pressure. Since it is the deviatoric component of the stress that causes dislocations to glide and climb, no change in the dislocation bias for interstitials will result directly from the pressure itself. Whether or not the pressure would affect the efficiencies of other types of defect sinks significantly is not known, but around an existing void the relative potential energies for point defects would be similar to those given for Zr in Fig. 4. This means that void growth is inhibited by the hydrostatic pressure.

Both the enhanced recombination of point defects and the suppression of void growth have been based on the boundary values of the defect interaction potential fields during the transient stage of a stress-induced kinetic process. For a steady state case Eq. (10) must be solved for $\nabla \cdot \mathbf{J}_d = 0$ for either kind of point defect. The diffusivity of a point defect, D_d , is a second rank tensor with two principal values in a hexagonal crystal, and it is a function of stress since the formation and migration energies are dependent upon stress. Information on such properties for both vacancies and interstitials is therefore the important prerequisite to the solution of a steady state problem, which is entirely lacking at present. However, a steady state condition of defect fluxes may not be reached in an actual irradiation condition. If specimen temperature was to fluctuate within $\Delta T = \pm 10^\circ\text{K}$ at an average frequency that is shorter than the relaxation time at which the concentration gradient term in Eq. (10) begins to compensate the potential gradient term appreciably, then the present conclusion of enhanced depletion of point defects to the grain boundary is valid. It

is noted that the enhanced depletion during a temperature decrease is equally effective as that during a temperature increase. On the other hand, existing voids may grow or shrink depending on the sign of ΔT . If a cyclic temperature fluctuation is symmetric with respect to the reference temperature, T_r , then a net flux of point defects to a void will be alternately that of vacancies and interstitials thus giving rise to an increased rate of recombination. It may be concluded that temperature fluctuation with a short cycle will enhance the recombination rate suppressing nucleation and growth of voids and also retarding further growth of existing voids as their size becomes sufficiently large to induce the self stress field.

The present discussion has been based mainly on the upper bound values of internal stress calculated in Sec. 2.1. It is expected that in an actual case the internal stress would approach such upper bound value as the grain size decreases or specimen size decreases toward single crystal conditions, and as texture becomes strongly preferred. Thus the present theory allows the probability of void formation in a single crystal of Zr but not in randomly oriented fine grain polycrystalline Zr when both samples from the same stock are subjected to the same irradiation conditions suitable for introducing stable void nuclei.

There are other possibly important metallurgical factors for void resistance in Zr that are not based on the internal stress. Some of these were already mentioned in Sec. 1. Coherent and incoherent hydride precipitates may act as recombination sites. Suitable interaction between free vacancies and certain solute atoms may cause suppression of void formation [39,40]. Regular alignment of prismatic loops, due to the anisotropy of point defects migrating near the loops [41], could reduce their effectiveness as biased sinks for interstitials. As suggested earlier, an irradiation experiment with a single crystal and polycrystalline Zr would be a critical test for the present concept as to whether or not the absence of voids in Zr is due to the thermally induced internal stress.

5. Summary

A temperature change of only 10°K could induce a shear stress of 65% of the yield stress in polycrystalline Zr and of 15% of the yield stress in Mg. The maximum differential of drift interaction potential for point defects in a stressed grain is calculated based on a temperature increase of 10°K to be 30% of thermal energy change in Zr and only 3% in Mg. A cyclic temperature fluctuation will cause enhanced rate of recombination at grain boundaries. Consequently, the vacancy supersaturation is low and nucleation and growth of voids is more difficult in Zr than in Mg. During a temperature increase the stress concentration around an existing void in Zr creates a stronger interaction potential for an interstitial than for a vacancy thus resulting in suppression of void growth, but has the reverse effect causing enhanced growth in Re. A cyclic temperature fluctuation would make existing voids stress-induced recombination centers thus retarding void growth in both Zr and Re.

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Table 1. Upper Bound Values of Thermal Stress

| | Tr (°K) | α_c ($10^{-6}/^{\circ}\text{K}$) | α_a ($10^{-6}/^{\circ}\text{K}$) | $(10^{-6}/^{\circ}\text{K})$ | | τ/τ_y | Ref. |
|----|------------|--|--|------------------------------|------------------------|---------------|------|
| | | | | $\sigma_c/\mu\Delta T$ | $\sigma_a/\mu\Delta T$ | | |
| Cd | 238 | 48.7 | 17.3 | -8.77 | 29.71 | 1.92 | (19) |
| Zn | 277 | 64.5 | 10.8 | -8.37 | 37.59 | 2.30 | (19) |
| Mg | 369 | 29.1 | 27.8 | -2.00 | 1.05 | 0.15 | (19) |
| Co | 707 | 16.1 | 12.6 | -7.21 | 3.81 | 0.55 | (19) |
| Re | 1365 | 4.96 | 7.03 | 3.65 | -1.81 | 0.27 | (20) |
| Tl | 228 | 72.0 | 9.0 | -161.82 | 61.87 | 11.18 | (19) |
| Zr | 743 | 11.84 | 5.19 | -9.06 | 3.85 | 0.65 | (21) |
| Ti | 692 | 13.37 | 11.03 | -4.42 | 2.31 | 0.34 | (19) |
| | | 5.6 | 9.5 | 7.36 | -3.84 | 0.56 | (22) |
| Ku | 1040 | 16.1 | 12.6 | -6.55 | 3.03 | 0.48 | (19) |
| Be | 620 | 9.4 | 11.7 | 3.31 | -1.49 | 0.24 | (19) |

Table 2. Upper Bound Values of Stress Induced by Interstitial Gas Atoms

| Gas Atoms | x_m | (10^{-2}) | | (10^{-2}) | | Ref. | |
|-----------|-------|----------------------|----------------------|------------------------|------------------------|-------|------|
| | | $\Delta c/c\Delta x$ | $\Delta a/a\Delta x$ | $\sigma_c/\mu\Delta x$ | $\sigma_a/\mu\Delta x$ | | |
| Ti | 0 | 0.1 | 1.27 | 1.70 | 0.80 | -0.42 | (24) |
| | 0 | 0.1 | 8.55 | 2.37 | -11.65 | 6.09 | (25) |
| | N | 0.07 | 18.38 | 4.07 | -27.02 | 14.11 | (26) |
| Zr | 0 | 0.05 | 4.03 | 3.40 | -0.86 | 0.37 | (27) |
| Hf | 0 | 0.1 | 4.47 | 2.36 | -3.28 | 1.58 | (28) |

Table 3. Change in the Free Energy of Vacancy ($e_v = -0.1$)
 Formation at Sites C and A in units of Thermal
 Energy Change ($k\Delta T = 8.6 \times 10^{-4}$ eV)

| | δE | δW_C | δW_A | $\Delta(\delta G)$ |
|----|------------|--------------|--------------|--------------------|
| Cd | 0.2071 | 0.12 | -0.40 | 0.52 |
| Zn | 0.3298 | 0.14 | -0.62 | 0.76 |
| Mg | 0.0003 | 0.02 | -0.01 | 0.03 |
| Co | 0.0003 | 0.15 | -0.08 | 0.23 |
| Re | 0.0005 | -0.20 | 0.10 | -0.30 |
| Zr | -0.0096 | 0.21 | -0.09 | 0.30 |
| Ti | -0.0014 | -0.11 | 0.05 | -0.16 |
| Be | 0.0028 | -0.10 | 0.04 | -0.14 |

Table 4. Equilibrium Concentration of Vacancies at T_r
and Its Change due to Stress at Sites C and A

| | $\frac{S_v^f}{k}$ | H_v^f (eV) | $c_v^e(0)$ | $\delta c_v^e(\sigma)$ (%) | |
|----|-------------------|-----------------|-----------------------|----------------------------|-------|
| | | | | C | A |
| Cd | 1.19 | 0.44 | 1.6×10^{-8} | -1.37 | 0.83 |
| Zn | 1.65 | 0.44 | 5.1×10^{-8} | -1.67 | 1.05 |
| Mg | 2.37 | 0.81 | 1.2×10^{-10} | -0.05 | 0.03 |
| Zr | 4.61 | 1.75 | 1.4×10^{-10} | -0.27 | 0.13 |
| Ti | 5.14 | 1.55 | 8.7×10^{-10} | 0.16 | -0.08 |

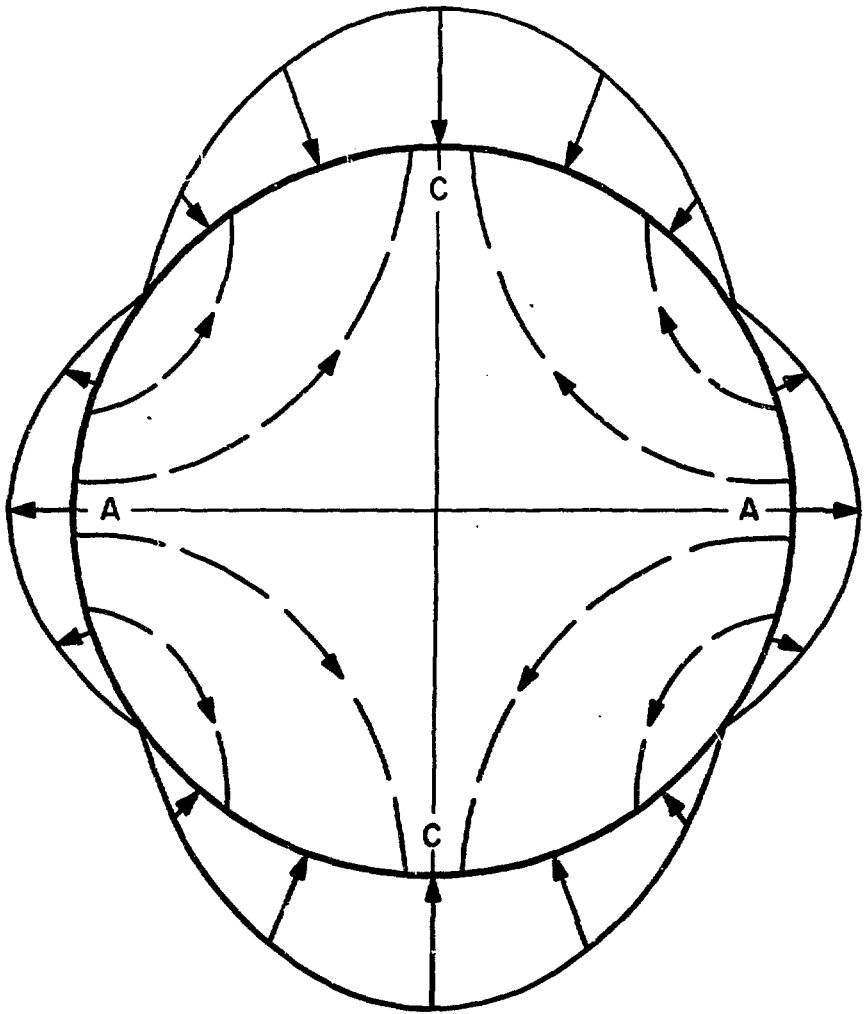
Figure Captions

Fig. 1. Vacancy flow lines (dashed) in a spherical grain when it is subjected to the normal stress. Interstitials flow in the opposite directions.

Fig. 2. Two zones (shaded) of attractive interaction for interstitials around a void under triaxial stress.

Fig. 3. Maximum elastic interaction energy for an interstitial around a void in units of thermal energy change.

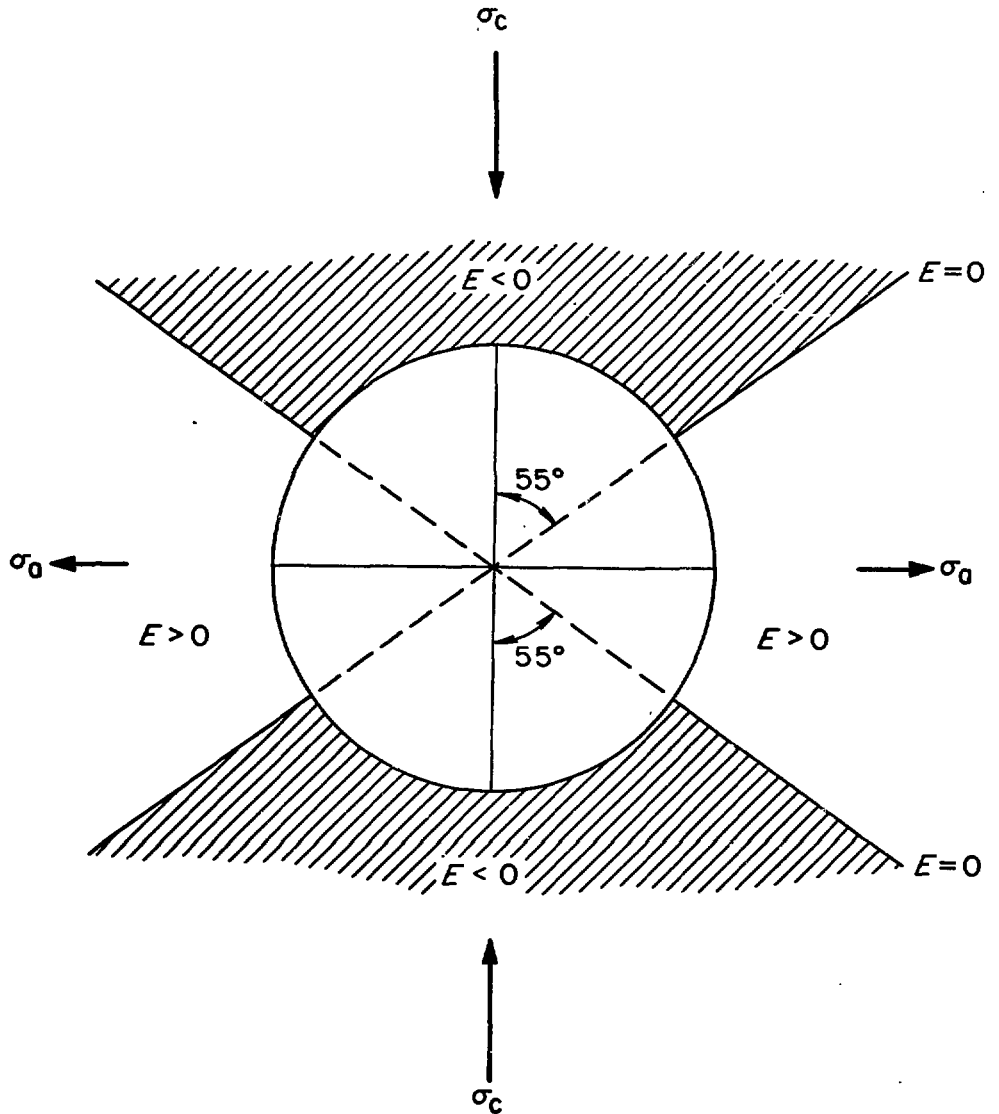
Fig. 4. Relative potential energies for point defects ($e_v = -0.1$, $e_i = 0.3$) near a void in the stressed grain.



Vacancy Flow Lines in a Spherical Grain When it is Subjected to the Normal Stress. Interstitials Flow in the Opposite Directions.

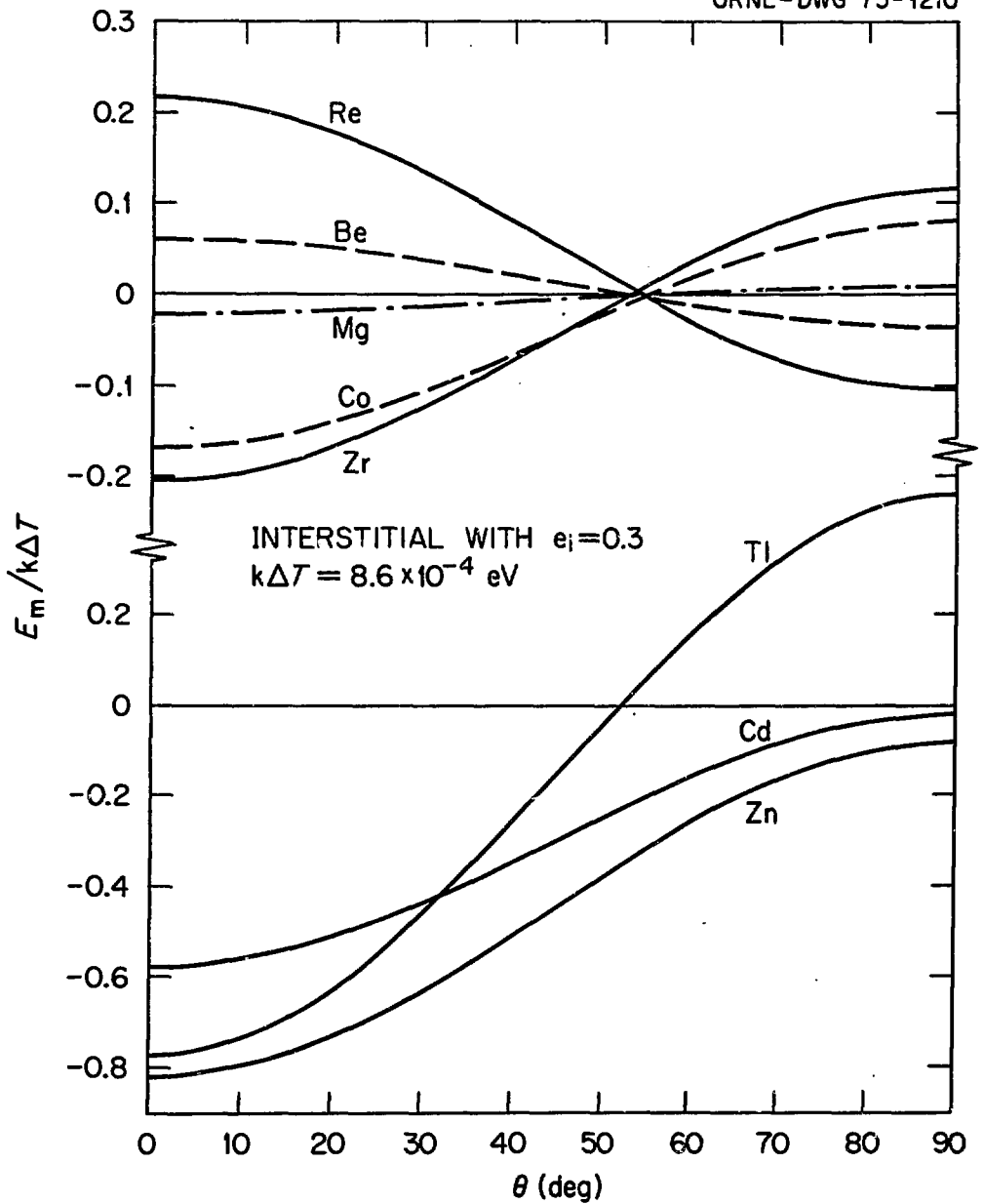
Fig. 1

γ_{00}



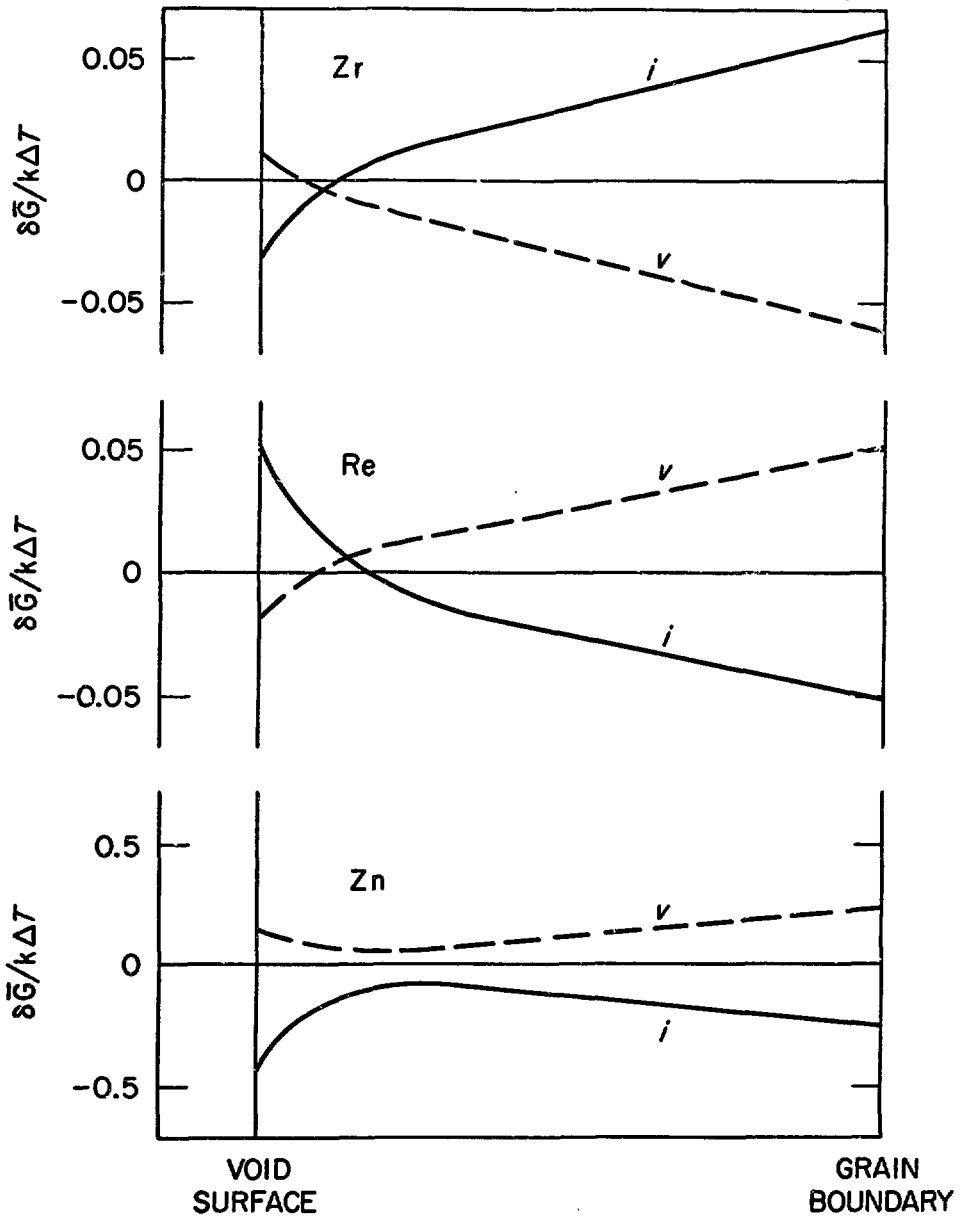
Two Zones (Shaded) of Attractive Interaction for Interstitials Around a Void Under Triaxial Stress

Fig. 2 Yoo



Maximum Elastic Interaction Energy for an Interstitial Around a Void in Units of Thermal Energy Change.

Fig. 3 Yoo



Relative Potential Energies for Point Defects ($e_v = -0.1$, $e_i = 0.3$) Near a Void in the Stressed Grain.

Fig. 4 Yoo