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EFFECTS OF POINT DEFECT TRAPPING AND SOLUTE SEGREGATION ON IRRADIATION-INDUCED SWELLING AND CREEP*

L. K. Mansur

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

NOTICE

ABSTRACT

The theory of irradiation swelling and creep, generalized to include impurity trapping of point defects and impurity-induced changes in sink efficiencies for point defects, is reviewed. The mathematical framework is developed and significant results are described. These include the relation between vacancy and interstitial trapping and the effectiveness of trapping as compared to segregation-induced changes in sink efficiencies in modifying void nucleation, void growth, and creep. Current understanding is critically assessed. Several areas requiring further development are identified. In particular those given special attention are the treatment of nondilute solutions and the consequences of current uncertainties in fundamental materials properties whose importance has been identified using the theory.

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1. INTRODUCTION

When a vacancy or interstitial disappears from the matrix by a process other than by recombination with the opposite type point defect, it is in principle possible for it to contribute to the deformation processes of swelling and creep. Solutes may affect the rates of deformation by modifying the rate of recombination either by trapping point defects and thereby directly catalyzing the recombination process, or by changing the capture efficiencies for point defects of sinks such as cavities and dislocations thereby altering the partitioning of point defects to sinks, and also indirectly influencing the recombination rate. The theory underlying these effects has been described in detail recently [1]. Since this work has reached a certain stage of maturity, it may prove useful to review and assess the theory from the aspects of a possible broader synthesis of related ideas, problems most critical to future progress, key experiments to perform, and most sensitive parameters to manipulate to control deformation rates. This is the purpose of the present paper. A brief background is sketched in section 2, the theory and significant results are reviewed in section 3, and the assessment undertaken in section 4.

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2. BACKGROUND

The understanding of radiation-induced swelling and creep largely rests on a theory of reaction rates scaled primarily by the generation rates of point defects, the coefficients of diffusion and recombination, and the capture efficiencies of sinks such as voids and dislocations for point defects.

2.1 Sink efficiencies

The sink efficiencies determine the rates of absorption of point defects at sinks in a given environment. Therefore, they also determine the relative rates of loss of point defects to various type sinks present in a material. This partitioning in turn dictates the rates of deformation which are due to asymmetries in absorption both among different types of sinks [1] and between members of a given sink type oriented differently with respect to an applied stress [2].

This sink efficiency or capture efficiency concept was invoked by Ham [3] in his analysis of the efficiency of dislocations for absorption of solute atoms. A number of derivations have been published more recently for the efficiencies for point defects of dislocations [4,5,6], dislocation loops [7,8,9], precipitates [10,11], grain boundaries [12], and cavities [11] for application in the theory of void growth. A recent review of the state of experimental knowledge of the sink efficiencies of voids, dislocation loops and grain boundaries is available [13].

There are a number of modes by which solute atoms, by segregating to sinks, may be visualized to affect sink efficiencies. These include the possibilities of changes in the diffusivity and changes in the elastic interaction energies of point defects produced by regions of different composition near the sinks. Examinations of these effects have been published for the diffusivity effect at voids [14] and dislocations [15] and the elastic interaction effect at voids [11] and dislocations [16].

Other possibilities for modes by which solute segregation may effect sink efficiencies concern the detailed structure of the sink-matrix interface [13]. These include possible modifications in the diffusivity of point defects along the interface by solute-induced changes in surface morphology; and blockage of the migration paths or changes in the formation energy of ledges and kinks on void surfaces, or jogs on dislocations. Analyses of these possibilities at a depth similar to the studies mentioned in the previous paragraph remain as a recommendation of the present assessment.

2.2 Diffusion and Recombination

It is interesting to recall the nearly parallel developments in the essential idea of trapping for the understanding of hydrogen or chemical interstitial diffusion in one subfield of materials science and self-interstitial or vacancy diffusion in another. It appears that Darken and Smith [17] first hypothesized the existence of trapping centers for hydrogen in steel and gave a rough analysis of the problem. This was based on their observation that the absorption rates of hydrogen is more rapid than the corresponding evolution rate. Since that time there has been extensive development of the theory of diffusion with trapping for chemical interstitials. The theory has been developed for application to permeation experiments. At about the same time, the theory of vacancy and self-interstitial trapping was developed for analysis of annealing experiments. While the specific analyses pertain to permeation on the one hand and annealing on the other, these theories are similar when only one mobile and trapped species is involved viz., chemical interstitials, self-interstitials, or vacancies. When both mobile and trapped vacancies, and self-interstitials are involved the theory becomes more complex because of the several terms coupling all processes through vacancy-interstitial recombination. Indeed the entire effect on deformation rates in the quasi-steady state is through this coupling.

In the late 1950s, low dose, low temperature irradiation experiments were performed to produce and study the annealing behavior of point defects. Various processes were discovered with different thermal activation characteristics as indicated by isochronal annealing of the radiation-produced resistivity component due to lattice damage. The existing data and uncertain interpretations prevailing at that time have been described in some detail [18]. Yet by early 1960s a more detailed picture of point defect annealing had been worked out. A prominent feature of this work was the inclusion of trapping reactions of point defects at impurity traps. This type of theory continues to be extensively used to interpret the complex recovery characteristics in low temperature annealing experiments [19].

More recently the theory of trapping has been further developed and coupled with the theory of radiation-induced void nucleation [20], void growth [20-28], and creep [20,29]. Significant reductions in deformation rates are predicted to result from point defect trapping. In the present paper our discussion of point defect trapping is based upon the theoretical development contained in References [20 and 29].

3. THEORY

3.1 Framework

The general set of time dependent equations governing point defect conservation with multiple traps in the presence of concentration gradients is utilized [20]. However, the essential trapping effects may be demonstrated with a set of quasi-steady state spatially independent equations obtained from these. This amounts to restricting the discussion to infinite media without transients in the point defect concentrations — the resulting loss of generality occurs only in areas which are of no concern in the present paper.

Spatial and temporal effects are interesting in themselves and are the subjects of studies to be published [30]. Below are given the relationships which govern the various free and trapped point defect concentrations. These equations balance the rates of gain of the corresponding type defect against the rates of loss by various processes. The definitions of the mathematical symbols are given following the equations.

Free Vacancies

$$G_v + \sum_{\ell} \tau_{v\ell}^{-1} C'_{v\ell} - RC_i C_v - C_v \sum_{\ell} R_{i\ell} C'_{i\ell} - C_v \sum_{\ell} \kappa_{v\ell} (C_{\ell}^{t} - C'_{v\ell} - C'_{i\ell}) - K_v C_v = 0 \qquad (1)$$

Free Interstitials

$$G_i + \sum_{\ell} \tau_{i\ell}^{-1} C'_{i\ell} - RC_i C_v - C_i \sum_{\ell} R_{v\ell} C'_{v\ell} - C_i \sum_{\ell} \kappa_{i\ell} (C_{\ell}^{t} - C'_{v\ell} - C'_{i\ell}) - K_i C_i = 0 \qquad (2)$$

The above summations range over the $\ell = 1,2, \ldots p$ types of traps. The equations given below describe point defect conservation at each of the $\ell = 1,2,\ldots p$ types of traps.

Vacancies Trapped at Solutes

$$C_v \kappa_{v\ell} (C^{t} - C'_{v\ell} - C'_{i\ell}) - \tau_{v\ell}^{-1} C'_{v\ell} - C_i R_{v\ell} C'_{v\ell} = 0 \qquad (3)$$

Interstitials Trapped at Solutes

$$C_i \kappa_{i\ell} (C_{\ell}^{t} - C'_{v\ell} - C'_{i\ell}) - \tau_{i\ell}^{-1} C'_{i\ell} - C_v R_{i\ell} C'_{i\ell} = 0 \qquad (4)$$

Vacancy clusters or loops generated in collision cascades may be included in this formalism.

Vacancies "Trapped" at Vacancy Loops

$$G\varepsilon_v + K_v^{VL} C_v - G_T^{VL} - K_i^{VL} C_i = 0 \qquad (5)$$

The G's describe the generation rates of vacancies and interstitials (subscripts v and i) per unit time per unit volume. $G_v = G(1 - \varepsilon_v) + G_T$ where G is the radiation-generation rate and ε_v is the fraction retained in vacancy clusters here modeled as vacancy loops. G_T is the thermal generation rate, where $G_T = \sum_j G_T^j = D_v C_v^e \sum_j \xi^j S_v^j$. Here $D_v = D_v^0 \exp\left(-E_v^m/RT\right)$ is the vacancy diffusion coefficient where D_v^0 is a constant, E_v^m is the vacancy migration energy, k is Boltzmann's constant and T is absolute temperature. For fcc materials

$$C_v^e = \left[\Omega^{-1} - \sum_\ell C_{v\ell}^{e\prime} - 12 \sum_\ell C_\ell^t \left(1 - C_{v\ell}^{e\prime}/C_\ell^t\right)\right] \exp\left(S_v^f/k\right) \exp\left(-E_v^f/kT\right) \tag{6}$$

is the bulk thermal concentration of free vacancies, where Ω is atomic volume, $C_{v\ell}^{e\prime}$ is the concentration of thermal vacancies bound at trap type ℓ, C_ℓ^t is the concentration of traps of type ℓ and S_v^f and E_v^f are respectively the entropy and energy of free thermal vacancy formation. ξ^j is the ratio of free thermal vacancies at sink type j to that in the bulk. For voids $\xi^V = \exp\left[\left(\frac{2\gamma}{r_V} - P_g\right)\Omega/kT\right]$, where γ is the surface tension, r_V is the void radius and Pg is the pressure of any contained gas; for dislocation loops $\xi^\ell = \exp\left[\pm \left(\gamma_f + E_\ell\right) b^2/kT\right]$, where γ_f is the stacking fault energy, E_ℓ is the loop elastic energy and b is a lattice dimension; for dislocations $\xi_v^d = 1$. S_v^j is the strength for vacancies of the sink of type j; for voids $S_v^V = 4\pi\int r_V Z_v^V(r_V) n(r_V) dr_V$, $= 4\pi \bar{r}_V \bar{Z}_v^V N_V$ if average values are used, where $Z_v^V(r_V)$ is the capture efficiency for vacancies of a void of size r_V, $n(r_V)dr_V$ is the number of voids per unit volume between radii r_V and $r_V + dr_V$. $\bar{r}_V$ is the average void radius and N_V is the total number of voids per unit volume and $\bar{Z}_v^V$ the average capture efficiency. For dislocations $S_v^d = Z_v^d L$ where Z_v^d is the capture efficiency of a dislocation for vacancies and L is the dislocation density. Dislocation loops may be modeled as effective spherical sinks where the form of their sink efficiency follows that for voids or as equivalent lengths of dislocation line where the form follows that for dislocation lines. For interstitial generation

$G_i = G(1 + \varepsilon_i)$ where ε_i is the fraction of interstitials injected when the experiment being modeled is a self-ion injection experiment. The diffusion coefficient and sink strengths for interstitials are obtained from the expressions above for vacancies by replacing v with i.

The terms RC_iC_v, K_vC_v and K_iC_i describe respectively the loss of free vacancies and interstitials by mutual recombination, and loss of free vacancies and free interstitials to sinks. C_v and C_i are respectively the concentrations of free vacancies and interstitials per unit volume. $R = 4\pi r_0(D_i + D_v)$ is the coefficient of recombination where r_0 denotes the radius of the recombination volume. K_v and K_i are the loss rates to all sinks per point defect for vacancies and interstitials respectively. Thus $K_v = \sum_j K_v^j$ and $K_i = \sum_j K_i^j$ where j represents each sink type such as void, dislocation, precipitate, and grain boundary. These coefficients are simply related to the sink strengths given above as $K_v^j = D_vS_v^j$ and $K_i^j = D_iS_i^j$.

The remaining terms in equations (1–5) above account for the fates of point defects associated with trapping. $C'_{i\ell}$ and $C'_{v\ell}$ denote the concentrations of interstitials and vacancies bound at trap type ℓ. $R_{i\ell} = 4\pi r_{i\ell}D_v$ and $R_{v\ell} = 4\pi r_{v\ell}D_i$ denote the coefficients of recombination of free vacancies with trapped interstitials and free interstitials with trapped vacancies respectively at trap type ℓ, where $r_{i\ell}$ and $r_{v\ell}$ are the radii of recombination for these complexes. $\tau_{v\ell} = \left(b^2/D_v^0\right) \exp\left[\left(E_{v\ell}^b + E_v^m\right)/kT\right]$ and $\tau_{i\ell} = \left(b^2/D_i^0\right) \exp\left[\left(E_{i\ell}^b + E_i^m\right)/kT\right]$ express the mean time a vacancy or interstitial is trapped at trap type ℓ where b is the order of an atomic distance and $E_{v\ell}^b$ and E_i^b are the binding energies of vacancies and interstitials to trap type ℓ. The capture coefficients of trap type ℓ for vacancies and interstitials are denoted respectively by $\kappa_{v\ell} = 4\pi r'_{v\ell}D_v$ and $\kappa_{i\ell} = 4\pi r'_{i\ell}D_i$. The products of these κ's with $\left(C_\ell^t - C'_{v\ell} - C'_{i\ell}\right)$

yield the capture rate at trap type ℓ per free vacancy or interstitial. The subtraction of the trapped vacancy and interstitial concentrations, $C'_{v\ell}$ and $C'_{i\ell}$ from the trap concentration C^t_ℓ accounts for the probability of current occupation of a trap by a previously trapped defect. In that case the trap is no longer a trap but a recombination center. Allowing both a $C'_{v\ell}$ and a $C'_{i\ell}$ accounts for the possibility of a positive binding energy for both the vacancy and the interstitial at one type trap.*

It may also be remarked that in some cases a given type of trap may have a variety of binding energies for an interstitial, say, based on the possibility of a number of nonequivalent configurations for the trap-trapped defect complex. The above equations cover this possibility when ℓ is interpreted as ranging over the labels of the spectrum of configurations at a given trap as well as over the labels of different traps.

3.2 Relation between Vacancy and Interstitial Trapping

The relation between vacancy trapping and interstitial trapping may be conveniently reviewed at this point. To demonstrate this we evoke the effective diffusion coefficient picture. Consider a case where interstitial trapping and vacancy trapping are occurring simultaneously, each at only one type of trap. We define the effective diffusion coefficients as follows [20]

$$D_i C_i = D_i^{ef}\left(C_i + C_i'\right) \tag{7a}$$

$$D_v C_v = D_v^{ef}\left(C_v + C_v'\right) \tag{7b}$$

meaning that the entire population of defects of one type is characterized by a single diffusivity D^{ef}. Figure 1 shows the ratio of the effective diffusion coefficient of vacancies to the free diffusion coefficient as a function of the binding energy of the vacancy to the solute.

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*In this conference the computer simulation results of Baskes and Wilson [31] show large binding energies for both vacancies and interstitials at some types of traps, implying that this generality we have allowed in our model may be necessary.

If the same solute atom of concentration C^t is a trap for vacancies and interstitials then the coefficients obtained from eqs. (1–4) and (7) may be written

$$D_i^{ef} = D_i \Big/ \left[1 + \kappa_i\tau_i\left(C^t - C_v' - C_i'\right)/\left(1 + \tau_i C_v R_i\right)\right] \tag{8a}$$

and

$$D_v^{ef} = D_v \Big/ \left[1 + \kappa_v\tau_v\left(C^t - C_v' - C_i'\right)/\left(1 + \tau_v C_i R_v\right)\right] \quad , \tag{8b}$$

while if vacancy and interstitial trapping take place at two different solutes whose concentrations are C_v^t and C_i^t we have

$$D_i^{ef} = D_i \Big/ \left[1 + \kappa_i\tau_i\left(C_i^t - C_i'\right)/\left(1 + \tau_i C_v R_i\right)\right] \tag{9a}$$

and

$$D_v^{ef} = D_v \Big/ \left[1 + \kappa_v\tau_v\left(C_v^t - C_v'\right)/\left(1 + \tau_v C_i R_v\right)\right] \quad . \tag{9b}$$

Using the definitions [7] and following a procedure similar to that detailed in section 2.5 of ref. [20] for interstitial trapping, the following governing equations may be obtained.

$$G_i - R'\left(C_i + C_i'\right)\left(C_v + C_v'\right) - K_i^{ef}\left(C_i + C_i'\right) = 0 \quad , \tag{10}$$

$$G_v - R'\left(C_i + C_i'\right)\left(C_v + C_v'\right) - K_v^{ef}\left(C_v + C_v'\right) = 0 \quad , \tag{11}$$

where

$$R' = 4\pi r_0\left(D_i^{ef} + D_v^{ef}\right) \tag{12}$$

and

$$K_{i,v}^{ef} = D_{i,v}^{ef} S_{i,v}$$

where S is the sink strength. Note also that $K_i^{ef}\left(C_i + C_i'\right) = K_i C_i$ and $K_v^{ef}\left(C_v + C_v'\right) = K_v C_v$ by definition of the effective diffusion coefficients, eqs. (7).

We can now answer the question "When do vacancy and interstitial trapping produce equal contributions to the fraction of point defects recombining?" When $D_i^{ef} >> D_v^{ef}$ most of the recombination is produced by the migration of the interstitial to the more slowly migrating vacancies. When $D_v^{ef} >> D_i^{ef}$ the converse is true. When $D_i^{ef} = D_v^{ef}$, the migration of both species contributes equally. Using eqs. (8) we obtain the equivalence

$$\frac{D_i}{\left[1 + \kappa_i \tau_i \left(C^t - C_i' - C_v'\right) / \left(1 + \tau_i C_v R_i\right)\right]} = \frac{D_v}{\left[1 + \kappa_v \tau_v \left(C^t - C_v' - C_i'\right) / \left(1 + \tau_v C_i R_v\right)\right]} \,. \quad (13)$$

From this relation

$$\frac{D_i^0}{r_i'} \exp\left[-\left(E_i^m + E_i^b\right)/kT\right] \approx \frac{D_v^0}{r_v'} \exp\left[-\left(E_v^m + E_v^b\right)/kT\right] \,, \quad (14)$$

for much of the parameter space explored in this paper. Equation (14) may be re-expressed as

$$E_i^b = E_v^m - E_i^m + E_v^b + kT \, \ln \frac{D_i^0 r_v'}{D_v^0 r_i'} \,. \quad (15)$$

Thus interstitial trapping requires greater binding energy than does vacancy trapping to produce the same effect. The most important terms in the right-hand side of this equation are $E_v^m - E_i^m + E_v^b$, for typical metals $E_v^m - E_i^m$ being approximately 0.5 to 1 eV. The logarithm term is small in comparison. The relation (15) without the logarithm term is given in ref. [20], and with a form of this term in ref. [27]. Equation (15) above covers the possibility that $r_v' \neq r_i'$ and equation (13) above is the exact condition for equivalence.

When the equations (1–5) are solved for the free vacancy and interstitial concentrations it is found that these are reduced from their corresponding values with no trapping. These reductions are at the root of the reductions in deformation rates caused by trapping, which are detailed subsequently. First, however, the essential relations derived from models of swelling and creep and expressing these deformation rates in terms of the free defect concentrations are recalled. These relations are written in forms which explicitly contain the capture efficiencies of the sinks absorbing free defects. The possible effects of altering these efficiencies by solute segregation, the second main topic of this paper, may then be recognized.

3.3 Relations Describing Swelling

The void nucleation, void growth, and creep rate equations given in earlier papers [1,11] are summarized below. The void nucleation rate is given by

$$M = 2\left(6\pi^2\Omega\right)^{1/3} D_v C_v^2 \Big/ \sum_{n=1}^{\infty} \frac{\exp[\Delta G(n)/kT]}{n^{1/3}\, Z_v^V(n)} \tag{16}$$

where the free energy of formation of a vacancy cluster of size n is given by

$$\Delta G(n) = -kT \sum_{\ell=1}^{n-1} \ln \left\{ \frac{\ell^{1/3} Z_v^V(\ell) D_v C_v}{(\ell+1)^{1/3}\left[Z_i^V(\ell+1) D_i C_i + Z_v^V(\ell+1) D_v C_v^e(\ell)\right]} \right\} \quad . \tag{17}$$

The void growth rate is given by

$$\frac{dr_v}{dt} = \frac{\Omega}{r_v} \left\{ Z_v^V(r_V) D_v \left[C_v - C_v^e(r_v)\right] - Z_i^V(r_v) D_i C_i \right\} \quad . \tag{18}$$

Equation (18) can be reworked to emphasize the great sensitivity of the void growth rate to the capture efficiencies of the sinks for vacancies and interstitials. The C's in this equation are the free defect concentrations. To focus on the effect of segregation we ignore trapping of point defects and thermal emission of vacancies from sinks. Solving the resulting simplified set of conservation equations obtained from eqs. (1) and (2) yields [1]

$$\frac{dr_V}{dt} = \frac{D_i D_v \Omega}{2R\bar{r}_V} \left[\left(1 + \frac{4RG}{K_i K_v} \right)^{1/2} - 1 \right]$$

$$\times \left[2\pi\bar{r}_\ell N_\ell \left(\bar{Z}_i^\ell \bar{Z}_v^V - \bar{Z}_v^\ell \bar{Z}_i^V \right) + L \left(Z_i^d \bar{Z}_v^V - \bar{Z}_i^V Z_v^d \right) \right. \tag{19}$$

$$\left. + 4\pi\bar{r}_p N_p \left(\bar{Z}_i^p \bar{Z}_v^V - \bar{Z}_v^p \bar{Z}_i^V \right) \right] .$$

The symbols V, ℓ, d, and p denote the sinks; voids, interstitial dislocation loops, network dislocations, and precipitates behaving as unsaturable sinks rather than traps. N_ℓ, L, and Np are the densities of loops (#/unit volume), network dislocations (line length/unit volume), and precipitates (#/unit volume). The terms expressing differences of products of Z's in parentheses express the bias of loops, dislocations, and precipitates with respect to voids. In these terms the possible leverage of solute segregation on swelling is evident. Since the differences in parentheses are generally smaller than the terms being differenced, small changes in the minuends or subtrahends arising from *small* changes in any of the sink efficiencies cause large changes in swelling. Yet it has been shown that *large* changes in capture efficiencies of sinks may result from solute segregation [11,14–16].

3.4 Relations Describing Creep

Sink efficiencies are also of fundamental importance in models for irradiation creep. I-creep is that component of creep by dislocation glide enabled by interstitial climb of dislocations due to the net vacancy flux to voids during swelling. It has been shown [32] that this creep component is directly proportional to swelling. Thus any conclusions we draw later for the effects of trapping on swelling also apply to I-creep. There are two related creep processes proposed recently which are not driven by swelling. Rather, they are driven by the preferred absorption of interstitials at dislocations whose Burgers vectors are near parallel to the stress axis, with the corresponding excess vacancies absorbed at the dislocations whose Burgers vectors are near perpendicular to the stress axis (for uniaxial stress). The climb component of creep produced by the stress induced preferred absorption (SIPA) we term PA-creep. It may be expressed [33] as

$$\dot{\varepsilon}_{PA} = \frac{2\Omega L}{9}\left(\Delta Z_i^d D_i C_i - \Delta Z_v^d D_v C_v\right) \quad . \tag{20}$$

Typically, the second term in parentheses, corresponding to preferred absorption of vacancies at dislocations whose Burgers vectors are near perpendicular to the stress axis, may be ignored.* The climb-enabled-glide component of creep produced by preferred absorption termed preferred absorption glide or PAG-creep may be expressed as [2]

$$\dot{\varepsilon}_{PAG} = \frac{4}{9}\frac{\varepsilon}{b}(\pi L)^{1/2}\,\Omega\Delta Z_i^d D_i C_i \quad . \tag{21}$$

Thermal vacancy emission is important at high temperatures and there are creep components due to the climb caused by preferred emission, PE-creep (a form of Herring-Nabarro creep), as well as creep due to glide enabled by preferred emission, PEG-creep. These have been discussed recently [2] but are unimportant to the present paper since they are not affected by trapping in dilute alloys [28].

In equations (20) and (21) $\varepsilon = \sigma/E$, the applied stress reduced by Young's modulus and ΔZ_i^d is the difference in capture efficiencies for interstitials at aligned and nonaligned dislocations. ΔZ_i^d is linear in ε. Again, as in the case for swelling, we see the basic difference in the possibilities for point defect trapping and segregation to affect creep. In our picture, segregation would primarily affect ΔZ_i^d, while trapping would primarily reduce the free interstitial concentration, C_i.

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*As stated above, excess vacancies are absorbed at these dislocations but this is a consequence of preferential excess absorption of interstitials at the orthogonal dislocations and conservation of mass. It occurs in the absence of preferential absorption of vacancies.

3.5 Representative illustrations

3.5.1 Trapping vs changes in sink efficiency

Figure 2 summarizes the relative potentials of segregation and trapping to change the swelling rate. On the 45° axis is the bias, on the horizontal axis is the solute concentration in the matrix, and on the vertical axis is the swelling rate normalized to the swelling rate with no trapping and 10% bias. This figure vividly illustrates the leverage of small changes in the bias. The figure is computed for vacancy trapping at the rather large binding energy of 0.5 eV (or for interstitial trapping at 0.5 eV + $E_v^m - E_i^m \sim 1.7$ eV). Even with this large binding energy it takes an increase in fractional atomic solute concentration from zero to greater than 10^{-3} to effect a factor of 2 reduction in swelling at 10% bias, for example. On the other hand a reduction in bias by a factor of two produces a reduction in the swelling rate by about a factor of two. Yet in principle a small segregated region near dislocations or voids consisting of only enough solute to "poison" a sink, in principle $<10^{-5}$ solute concentration may change capture efficiencies by large factors and hence produce large changes in the bias.

Several other aspects of Figure 2 will be mentioned. First is the fact that the relative swelling rate is plotted rather than the relative swelling. This represents a more generally applicable result since it eliminates the problem of choosing a model for the evolution of dislocation density with dose, which very strongly determines the integrated swelling at a given dose [1]. Dislocation density develops differently in different materials and under different conditions. To model a specific material in a given experiment the dislocation evolution behavior must be modeled as has been done for a large number of cases in ref. [1].* However, regardless of the history of evolution up to a given dose the relative swelling rate will follow the behavior described in Figure 2 for the sink strengths and other conditions modeled. The second point is that the swelling rate goes to zero at small but nonzero values of the bias. This reflects the fact that thermal emission of vacancies from voids is important at elevated temperatures and small bias. Below a given bias, which is approximately 1% for the temperature and other conditions of this figure, and with no trapping the radiation-induced void growth rate is not sufficient to counterbalance the shrinkage by thermal emission and a negative growth rate results. As the concentration of traps increases, a larger bias is required to sustain a positive swelling rate since the free point defect concentrations and hence the radiation-induced swelling rate are decreased by trapping. This last point also motivates a third comment. This figure is a convenient way to illustrate that the swelling rate is not simply proportional to the fraction of point defects being removed at sinks, since this last quantity never goes negative. The reader may find in the literature a number of cases where the effect of trapping on the fraction of point defects removed at sinks (the fraction removed at sinks = unity minus the fraction recombining) is identified with the effect of trapping on swelling. This result can only apply for a very special condition. The fraction of defects annihilated at sinks is proportional to the swelling rate only when the enhanced thermal concentration of vacancies at voids as compared to dislocations is neglected (i.e., only when ξ^V is set equal to ξ^d) (compare ξ^V and ξ^d defined after equation (6)) [34].

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*This is not to say we advocate the use of swelling rate rather than swelling for comparing theory with experiment. A judgment must be made on a case by case basis whether it is desirable or not to eliminate the uncertainty introduced into the theoretical prediction by using an imperfect dislocation evolution model at the expense of introducing uncertainty by using a swelling rate which is approximated from integral swelling measurements at discrete doses. These problems are eliminated when the evolution of dislocation density is measured as a function of dose.

Figure 3 compares the relative effects of binding energy and solute concentration in the swelling rate. To obtain a reduction in swelling rate which is noticable on the scale of Figure 3 even at the highest solute concentrations investigated, vacancy binding energies of about 0.2 eV are necessary. By the previous results, interstitial trapping would then not be effective at binding energies less than about 0.2 eV + $E_v^m - E_i^m$. Since vacancy binding energies are often reported to be $\lesssim$0.1 eV we expect that vacancy trapping in those systems could not be important in suppressing swelling. However, interstitial binding energies are reported to be $\gtrsim$1 eV in some cases. In those cases then, and provided $E_v^m - E_i^m$ is less than the interstitial binding energy by >0.2 eV, interstitial trapping could produce a significant reduction of swelling.

3.2.2 Void nucleation with trapping

In the previous section we have in essence performed the gedanken experiment of placing a test void arbitrarily chosen to be of radius 10 nm into a pure metal and then into the same metal containing traps. We then have reported the relative growth rates under the two conditions. However, the initial density of voids is also influenced by trapping as described by eqs. (16) and (17). It is found that the nucleation rate is reduced by point defect trapping to a much greater extent than is the void growth rate. Figure 4 gives the computed nucleation rate as a function of vacancy binding energy for a typical heavy ion bombardment experiment.

3.2.3 Irradiation creep with trapping

Point defect trapping reduces irradiation creep rates. Since both PA-creep and PAG-creep are affected only through their proportionality to free interstitial concentration, the ratio of strain rate by PA- and PAG-creep with trapping to that without trapping equals the ratio of free interstitial concentrations with and without trapping. Thus our results below apply to PA-creep, PAG-creep and the physical case where both are operating simultaneously [2].

Figure 5 shows the reduction in creep rate with solute concentration for vacancy trapping with a binding energy of 0.5 eV (or for interstitial trapping with a binding energy of $\sim E_v^m - E_i^m + 0.5$ eV) at typical reactor and charged particle dose rates and temperatures. The PA/PAG-creep rate is less sensitive to trapping than is the void nucleation rate or the void growth rate. For charged particle conditions the reduction is greater than for reactor conditions for the cases we have modeled. These results are not surprising since void nucleation and growth are proportional to small differences in functions of the interstitial and vacancy concentrations while the PA/PAG-creep rate is directly proportional to an absolute and therefore less sensitive quantity, the free interstitial concentration.

Figure 6 shows the relative creep rates as functions of the dose rate and the sink strength. These curves reveal a quite interesting result. At just the typical reactor conditions, 10^{-8} to 10^{-6} dpa/s and 500°C, the effect of trapping rises from negligible at 10^{-8} dpa/s to substantial at 10^{-6} dpa/s. At dose rates of order 10^{-8} dpa/s nearly all the point defects are removed at sinks regardless of whether traps are present or not, even at the lowest sink strength. Similarly, as the sink strength is increased the effect of trapping at all dose rates is reduced since recombination, both in the matrix and at traps, is made less important in comparison to loss to sinks.

3.2.4 Irradiation creep with vacancy loops and trapping

Before leaving the subject of the reduction of creep by trapping we highlight the effects of including vacancy loops. We illustrate the effect of vacancy loops with no simultaneous trapping at solutes and then the combined effect of vacancy loops and trapping at solutes. Consider the special forms of eqs. (1–5) when there is only one solute vacancy trap present and the presence of vacancy loops is also included. We evaluate the important quantities as follows. We have $G_v = G - G\varepsilon_v + G_T^0 + G_T^{v\ell}$ where, as described earlier, ε_v is that fraction of vacancies generated which is retained in vacancy loops and $G_T^{v\ell} = Z_v^{v\ell} D_v C_v^{v\ell} L^{v\ell}$ is the thermal generation rate of vacancies emitted from vacancy loops whose capture efficiency for vacancies is $Z_v^{v\ell}$ ($Z_i^{v\ell}$ for interstitials). The thermal equilibrium vacancy concentration at vacancy loops is $C_v^{v\ell}$ and the effective dislocation line length per unit volume is $L^{v\ell}$. We also include the loss rate of point defects to vacancy loops so that the loss rate terms may be expressed as $K_v = K_v^0 + K_v^{v\ell}$ and $K_i = K_i^0 + K_i^{v\ell}$ where $K_v^{v\ell} = Z_v^{v\ell} D_v L^{v\ell}$ and $K_i^{v\ell} = Z_i^{v\ell} D_i L^{v\ell}$. The system of equations then becomes

Free Vacancies

$$G - G\varepsilon_v + G_T^0 + G_T^{v\ell} - \tau_v^{-1} C_v' - RC_v C_i - C_v \kappa_v (C^t - C_v') - (K_v^0 + K^{v\ell}) C_v = 0 \tag{22}$$

Free Interstitials

$$G - RC_v C_i - C_i R_v C_v' - (K_i^0 + K_i^{v\ell}) C_i = 0 \tag{23}$$

Trapped Vacancies (at Solutes)

$$C_v \kappa_v (C^t - C_v') - \tau_v^{-1} C_v' - C_i R_v C_v' = 0 \tag{24}$$

Trapped Vacancies (at Vacancy Loops)

$$G\varepsilon_v + K_v^{v\ell} C_v - G_T^{v\ell} - K_i^{v\ell} C_i = 0 \tag{25}$$

In eq. (25) the first two terms denote the creation and diffusional influx of vacancies to be "trapped" in vacancy loops. These two terms are analogous to the first term of eq. (24). The third term of eq. (25) describes loss of "trapped" vacancies by thermal release, the analog of the second term of eq. (24) and the last term of eq. (25) describes the flux of interstitials to vacancy loops and is the term analogous to the last term of eq. (24),* the recombination term.

After some algebra these eqs. (22) through (25) may b combined to yield a cubic equation for C_i.

$$C_i^3\left(R_v\tau_v K_i^0 R^*\right) + C_i^2\left[R^* R_v \tau_v G_T^0 + K_i^0 K_v^0 R_v\tau_v + K_i^0 \kappa_v^* R_v \tau_v\left(C^t - C'\right) + K_i^0 R^*\right]$$
$$+ C_i\left[G_T^0 R^* + R_v \kappa_v^*\left(C^t - C'\right)\tau_v G_T^0 + K_i^0 K_v^0 - R_v \tau_v G^* K_v^0\right] - G^* K_v = 0 \quad , \tag{26}$$

where

$$\frac{R^*}{R} = \frac{G^*}{G} = \frac{\kappa_v^*}{\kappa_v} = \frac{K_i^0}{K_i^0 + K_i^{v\ell}} \quad . \tag{27}$$

Comparing eq. (26) with eq. (40) of ref. (20) reveals that these equations are formally identical.† Here, however, R^*, G^*, and κ_v^* appear instead of R, G, and κ_v. Equation (40) of ref. (20) applies to vacancy trapping with no vacancy loops. Therefore, we have shown that the entire effect of vacancy loops is precisely described by a simultaneous reduction in the free vacancy capture

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*In equations (22–25) the time derivative of the respective free and trapped-at-solute and trapped-at-vacancy loop point defect concentrations are set equal to zero. This is justified in the absence of vacancy loops by the fact that C_i and C_v have much smaller relaxation times than those for changes in the sink strengths [1], so that C_i and C_v are in a steady state relative to the instantaneous sink strengths. It has been recently shown [35] that the vacancy loop distribution relaxation times are also short and hence that the vacancy loop distribution is in a steady state with respect to the instantaneous sink strength.

†There is a typographical error in eq. (40) of ref. (20). It is corrected by changing all R_i in that equation to R_v.

coefficient, in the generation rate of free defects, and in the free defect recombination coefficient by the ratio of the interstitial loss rate at all sinks excluding vacancy loops to the interstitial loss rate at all sinks, as given by eq. (27).

Heald and Speight [36] studied the effect of vacancy loops on swelling and creep in the absence of trapping and arrived at the conclusion that the presence of vacancy loops is equivalent to reducing the free defect generation rate and recombination coefficient as in the relations for R and G of eq. (27). Our work generalizes their result to the case where point defect trapping at solutes is taking place simultaneously.

Figure 7 displays the effects of vacancy trapping and vacancy loops on creep rate. The conditions represent a typical dose rate and temperature for reactor irradiation. The relative creep rate is plotted as a function of $K_i^{v\ell}/K_i^0 \left(= S_i^{v\ell}/S_i^0\right)$, the ratio of vacancy loop sink strength for interstitials to that for all sinks excluding vacancy loops. The plot covers the range from where the sink strength of vacancy loops is small compared to the sink strength of other sinks to where the vacancy loop sink strength is five times the sink strength of other sinks. Since vacancy loops are thought to be formed at a size of order a few nanometers and the average size at any instant in the steady state must be smaller than this due to thermal decay and net interstitial absorption, they are generally not resolved in postirradiation electron microscopic examinations. While their density may be estimated theoretically, the result is quite sensitive to detailed assumptions necessary, especially the uncertain value of ε_v [37]. We therefore investigate the effect of vacancy loops for a wide range of possible sink strengths. Without trapping, the reduction in creep rate is substantial at large vacancy loop sink strengths, about a factor of 5 for reactor conditions when $K_i^{v\ell}/K_i^0 = 5$. However, with trapping, the further reduction in creep rate due to vacancy loops is more modest. For vacancy trapping with a binding energy of 0.5 eV and solute concentration of

1%, the additional reduction in the creep rate due to vacancy loops is less than a factor of 2 up to a sink strength ratio $K_i^{v\ell}/K_i^0 = 5$. From these curves we also observe that as the vacancy loop sink strength increases the effect of trapping becomes less important as evidenced by the fact that the curves approach each other at high vacancy loop sink strength ratios. This is as required physically. As the sink strength is increased the loss rate of interstitials by recombination with both free and trapped vacancies is decreased, and in the limit of large $K_i^{v\ell}/K_i^0$ the curves with bulk recombination only (upper curve in fig. 7) and with bulk plus trap-assisted recombination (lower two curves in fig. 7) must approach each other since they also must approach the same value that would be obtained by neglecting bulk recombination and trapping altogether.

3.2.5 Segregation to sinks

The capture efficiency of a void for interstitials or vacancies may be approximated as [1]

$$Z_{i,v}(r_V) = \left[1 + \frac{1}{\left(1 + \frac{\delta}{r_V}\right)^2} \frac{D_{i,v}}{r_V w_{i,v}}\right]^{-1} \tag{28}$$

with the velocity of transfer of an interstitial, vacancy at the void surface $w_{i,v}$ given by

$$w_{i,v} = \frac{D_{i,v} \exp\left(-E^*_{i,v}/kT\right)}{a} \tag{29}$$

where E^* is the effective value of the possible energy barrier which the defect must overcome near the void surface; and

δ measures the width of the region near the void over which E^* acts. E^* arises physically as the difference in defect migration energy between the matrix and the regions surrounding the void or from the changes in the point defect-void elastic image interaction energy with and without the segregated region around the void. In either case, if $E^*_{i,v}$ is significant in comparison to $E^m_{i,v}$ then the defect absorption rate becomes reaction controlled at the void surface, while if $E^*_{i,v} << E^m_{i,v}$ the absorption rate is controlled by $E^m_{i,v}$, i.e., by diffusion through the matrix. A small amount of segregation of material through which point defects diffuse more slowly than through the matrix or which has elastic shear modulus greater than that of the matrix may lead to a value of $E^*_{i,v} \geq 0.1$ eV [11,14] and hence to a surface reaction controlled case. When this occurs, from eq. (28) we obtain

$$Z_{i,v}(r_v) \sim \frac{r_v w_{i,v}}{D_{i,v}} \sim \frac{r_v}{a} \exp\left(E^*_{i,v}/kT\right) \qquad (30)$$

for the surface reaction controlled case. If $E^*_{i,v} << E^m_{i,v}$, on the other hand, we obtain $Z_{i,v} \sim 1$ for the diffusion controlled case. Thus the capture efficiency is decreased and takes on a new functional form for reaction controlled cases. Recalling the definition of void sink strength given earlier it is seen that in the purely diffusion controlled case (and in the absence of multiple sink corrections) the sink strength is proportional to the void radius while for the purely reaction controlled case the sink strength is proportional to the void surface area. A treatment of kinetics including both these cases and covering the possible regimes of relative sink strength, sink strength/recombination importance, and dislocation density evolution is given in ref. [1]. We refer the reader to that work and characterize the results here by simply stating that changes in void sink efficiency may significantly alter the kinetics of void growth.

Segregation to dislocations in principle may alter their capture efficiencies for point defects. The effect may occur, analogously to the void case, either by changes in the elastic interaction with point defects or by constituting a material with a different diffusion coefficient near the dislocation. In the dislocation case, however, it is not possible even with a reaction controlled process, to basically change the geometrical factor to which the dislocation sink strength is proportional.

The dislocation sink strength is found to be proportional to the dislocation line length when the cylindrical diffusion equation is solved regardless of whether point defect absorption is diffusion controlled or reaction controlled at some effective capture radius about the dislocation. Therefore, although segregation to dislocations may produce changes in the magnitude of dislocation capture efficiencies for point defects and therefore in the magnitude of swelling, the type of kinetics will be similar as when point defect absorption is diffusion controlled.

In a system containing several types of sinks, segregation will occur at all sinks in general. Whether this results in a net increase or decrease in swelling is controlled by the bias terms of the form $(Z_i^d Z_v^V - Z_i^V Z_v^d)$ of eq. (19). In general, for dislocations and voids the only sinks present, segregation produces an increase in swelling when

$$\frac{Z_i^d}{Z_v^d}\,\frac{Z_v^V}{Z_i^V} > \frac{Z_i^{d0}}{Z_v^{d0}}\,\frac{Z_v^{V0}}{Z_i^{V0}} \tag{31}$$

and a decrease when the inequality is reversed, provided each of $\left(Z_{i,v}^{d,V} - Z_{i,v}^{d,V0}\right) << Z_{i,v}^{d,V0}$. Here the superscript ^{0} denotes the system without segregation and the strong inequality written above restricts the analysis to cases where the bias is changed by segregation but the capture efficiencies and hence sink strengths appearing in eq. (19) are not changed significantly. Relation [31] is the condition by which it may be determined whether the simultaneous changes in capture efficiency for interstitials and vacancies resulting from segregation to dislocations and voids result in a net increase or decrease in void swelling. If the segregation substantially alters the sink capture efficiencies so that the sink strengths are changed substantially, a condition similar in spirit to the condition on the bias written above, relation (31), may be again derived from eq. (19).

4. DISCUSSION

We now endeavor to perform a critical assessment in accordance with the theme of the workshop at which the paper was presented. We shall occasionally leave the domain of mathematically supported theory to be more speculative. Two areas deemed to be important and within which reasonable progress may be expected are evaluated.

4.1 Concentrated solutions

Above solute concentrations of about 0.1% corrections are needed [20] to the rate equations of current trapping models. Those corrections which are essentially geometrically-based are discussed in ref. [20]. For example, if the solute concentration is X (and for only nearest neighbor vacancy binding to substitutional traps) then an additional fraction of 12X sites is excluded from occupation by free vacancies. Accounting for this gives a larger ratio of trapped to free vacancies and consequently leads to changes in the fraction of defects recombining and in the deformation rates. However, as the solute concentrations are increased, entirely new physical processes may become prevalent and need to be included in the governing equations. Thus, each equation in the set of eqs. (1–4) must contain new terms. In addition the set of equations must be expanded, in principle containing an equation describing conservation of each of the species types whose concentrations are affected by radiation. The terms in these equations are expressed in a mathematically analogous manner to those in eqs. (1–4). We write the equations schematically. This avoids redefining the now larger number of mathematical symbols. In addition the full equation set is of only limited practical use at this time because of the dearth of fundamental information necessary for evaluating the basic parameters. This matter which we meet at every turn is discussed in section 4.2. Two qualifications are necessary. Firstly, as in the dilute trapping theory [20], higher order clusters are ignored. Thus, one trap may bind only one vacancy or interstitial. This can be generalized to more than one provided there is a fixed upper limit. Secondly, the equations only apply to solute concentrations below which a vacancy-trap or interstitial-trap complex can be deemed to be an isolated entity. Above this concentration the concept of a trap-trapped defect complex must be replaced by the concept of a many particle interconnected cluster of solute and solvent atoms and point defects. Only the vacancy conservation equations are written. The interstitial conservation equations follow in an obvious way. Schematic dilute solution governing equations for vacancy trapping may be written first for comparison as follows:

<u>Free Vacancies</u>

$$\begin{bmatrix}\text{Generation by Radiation}\\ \text{and Thermal Emission}\end{bmatrix} + \begin{bmatrix}\text{Thermal Release of}\\ \text{Trapped Vacancies}\end{bmatrix}$$

$$- \begin{bmatrix}\text{Recombination with}\\ \text{Free Interstitials}\end{bmatrix} - \begin{bmatrix}\text{Trapping at}\\ \text{Solutes}\end{bmatrix} - \begin{bmatrix}\text{Loss to}\\ \text{Sinks}\end{bmatrix} = 0 \tag{32}$$

<u>Trapped Vacancies</u>

$$\begin{bmatrix}\text{Trapping of}\\ \text{Free Vacancies}\end{bmatrix} - \begin{bmatrix}\text{Thermal Release of}\\ \text{Trapped Vacancies}\end{bmatrix}$$

$$- \begin{bmatrix}\text{Recombination with}\\ \text{Free Interstitials}\end{bmatrix} = 0 \ . \tag{33}$$

In concentrated solutions the following relations replace those above

Free Vacancies

$$
\begin{aligned}
&\begin{bmatrix}\text{Generation by Radiation}\\ \text{and Thermal Emission}\end{bmatrix} + \begin{Bmatrix}\text{Thermal Release from}\\ \text{I-Solute}\end{Bmatrix}\\
&+ \begin{bmatrix}\text{Thermal Release from}\\ \text{S-Solute}\end{bmatrix} + \begin{Bmatrix}\text{Radiation Breakup of}\\ \text{I-Solute/Vacancy Pair}\end{Bmatrix}\\
&+ \begin{Bmatrix}\text{Radiation Breakup of S-Solute/Vacancy}\\ \text{Pair Leading to Free I-Solute}\end{Bmatrix} - \begin{bmatrix}\text{Recombination with}\\ \text{Free Interstitial}\end{bmatrix}\\
&- \begin{bmatrix}\text{Trapping at}\\ \text{S-Solute}\end{bmatrix} - \begin{Bmatrix}\text{Trapping at}\\ \text{I-Solute}\end{Bmatrix} - \begin{bmatrix}\text{Loss to}\\ \text{Sinks}\end{bmatrix}\\
&- \begin{Bmatrix}\text{Displacement of I-Solute Leading}\\ \text{to I-Solute/Vacancy Pair}\end{Bmatrix} - \begin{Bmatrix}\text{Displacement of S-Solute Leading}\\ \text{to I-Solute/Vacancy Pair}\end{Bmatrix} = 0 \; .
\end{aligned}
\tag{34}
$$

Trapped Vacancies on Substitutional-Solute

$$
\begin{aligned}
&\begin{bmatrix}\text{Trapping of Free}\\ \text{Vacancies}\end{bmatrix} + \begin{Bmatrix}\text{Displacement of Solvent}\\ \text{Leading to S-Solute/}\\ \text{Vacancy Pair}\end{Bmatrix} - \begin{bmatrix}\text{Thermal Release}\\ \text{from S-Solute}\end{bmatrix}\\
&- \begin{bmatrix}\text{Recombination with}\\ \text{Free Interstitial}\end{bmatrix} - \begin{Bmatrix}\text{Radiation Breakup of}\\ \text{S-Solute Vacancy Pair}\\ \text{Leading to Free I-Solute}\end{Bmatrix}\\
&- \begin{Bmatrix}\text{Radiation Breakup of S-Solute/Vacancy Pair}\\ \text{Leading to I-Solute/Vacancy Pair}\end{Bmatrix} = 0 \; .
\end{aligned}
\tag{35}
$$

Trapped Vacancies on Interstitial-Solute

$$\left\{\begin{array}{l}\text{Trapping of}\\ \text{Free Vacancies}\end{array}\right\} + \left\{\begin{array}{l}\text{Generation by Radiation}\\ \text{on S-Solute}\end{array}\right\}$$

$$+ \left\{\begin{array}{l}\text{Generation by}\\ \text{Radiation on Solvent}\end{array}\right\} + \left\{\begin{array}{l}\text{Radiation Breakup of}\\ \text{S-Solute/Vacancy Pair}\\ \text{Leading to I-Solute Vacancy Pair}\end{array}\right\}$$

$$+ \left\{\begin{array}{l}\text{Displacement of I-Solute}\\ \text{Leading to I-Solute}\\ \text{Vacancy Pair}\end{array}\right\} - \left\{\begin{array}{l}\text{Thermal Release from}\\ \text{I-Solute}\end{array}\right\}$$

$$- \left\{\begin{array}{l}\text{Recombination with}\\ \text{Free Interstitial}\end{array}\right\} - \left\{\begin{array}{l}\text{Radiation Breakup of}\\ \text{I-Solute/Vacancy Pair}\\ \text{Leading to Free I-Solute)}\end{array}\right\}$$

$$- \left\{\begin{array}{l}\text{Reversion of}\\ \text{I-Solute/Vacancy}\\ \text{Pair}\end{array}\right\} = 0 \ . \tag{36}$$

Free S-Solute

$$\left\{\begin{array}{l}\text{Thermal Release of Vacancies}\\ \text{from S-Solute}\end{array}\right\} + \left\{\begin{array}{l}\text{Recombination of}\\ \text{S-Solute/Vacancy Pair}\\ \text{with Free Interstitial}\end{array}\right\}$$

$$+ \left\{\begin{array}{l}\text{Reversion of}\\ \text{I-Solute/Vacancy}\\ \text{Pair}\end{array}\right\} - \left\{\begin{array}{l}\text{Trapping of Vacancies}\\ \text{at S-Solute}\end{array}\right\}$$

$$- \left\{\begin{array}{l}\text{Displacement of S-Solute}\\ \text{Leading to I-Solute}\end{array}\right\} - \left\{\begin{array}{l}\text{Displacement of S-Solute}\\ \text{Leading to I-Solute}\\ \text{Vacancy Pair}\end{array}\right\}$$

$$- \left\{\begin{array}{l}\text{Displacement of Solvent}\\ \text{Leading to S-Solute/}\\ \text{Vacancy Pair}\end{array}\right\} = 0 \ . \tag{37}$$

Free I-Solute

$$\left\{\begin{matrix}\text{Displacement of S-Solute}\\ \text{Leading to I-Solute}\end{matrix}\right\} + \left\{\begin{matrix}\text{Radiation Breakup of S-Solute/}\\ \text{Vacancy Pair Leading to}\\ \text{I-Solute}\end{matrix}\right\}$$

$$+ \left\{\begin{matrix}\text{Thermal Release of}\\ \text{Vacancy from I-Solute/}\\ \text{Vacancy Pair}\end{matrix}\right\} + \left\{\begin{matrix}\text{Recombination of I-Solute/}\\ \text{Vacancy Pair with Free}\\ \text{Interstitial}\end{matrix}\right\}$$

$$+ \left\{\begin{matrix}\text{Radiation Breakup of I-Solute/Vacancy}\\ \text{Pair Leading to I-Solute}\end{matrix}\right\} - \left\{\begin{matrix}\text{Displacement of I-Solute Leading}\\ \text{to I-Solute/Vacancy Pair}\end{matrix}\right\}$$

$$- \left\{\begin{matrix}\text{Displacement of Solvent Leading}\\ \text{to I-Solute/Vacancy Pair}\end{matrix}\right\} - \left\{\begin{matrix}\text{Trapping of Vacancies}\\ \text{at I-Solute}\end{matrix}\right\} = 0 \; . \quad (38)$$

The main features here are to account for the displacement by radiation of the traps themselves and the fates of the displaced traps, as well as the fates of displaced solvent atoms and their corresponding vacancies in forming complexes by direct processes in addition to the usual formation of complexes by diffusion. Of course some of these terms will turn out to be negligible when evaluated quantitatively. We include them for conceptual completeness. They should not be discarded a priori without evaluation using the precise defect and trap complex parameters. For example if $E^m_{\text{I-Solute}}$, the migration energy of the I-solute, is small then we expect the concentration of I-solute to be small in comparison to that of S-solute except at low temperatures. The fundamental defect properties in these equations as well as in the dilute solution equation are extremely important to quantitative modeling of the effects of trapping.

4.2 Fundamental parameters

The mathematically rigorous development of the theory and the demonstrated agreement of some of the general predictions with experimental observation are now apparent. With this situation part of the onus of the existing "quantitative equivocation" in evaluating the effects of impurities on radiation-induced deformation can be seen clearly to rest on uncertainties in the fundamental defect properties. These quantities include vacancy and interstitial migration energies, point defect-trap binding energies and capture and recombination radii. For example, the answer to the question "Is interstitial trapping important in reducing deformation rates?" in a given system depends critically on the interstitial-trap binding energy and upon whether this is greater than the difference between the free vacancy and interstitial migration energies in the system in question. A wide range of vacancy migration energies has been used even for pure nickel. As has been stressed earlier [1,38,39,40] this leads to wide ranges in the predictions of temperature shift of swelling with changes in radiation dose rate and in the magnitude of reduction in swelling caused by the interstitials injected during self-ion bombardment of pure nickel. Now we see further that this range in the vacancy migration energy leads to a very wide range in the effect of interstitial trapping. To emphasize the point, suppose the binding energy of interstitials to a solute in nickel were as high as 1.2 eV. Then, if we take the vacancy migration energy as 1.38 eV [41] and the interstitial migration energy as 0.15 eV [42] and since $E_v^m - E_i^m$ is 1.23 eV we expect negligible effect on the deformation rates (equivalent to zero vacancy binding energy in Figs. 3 and 4). If, on the other hand, we adopt 1 eV as the vacancy migration energy [42] then the difference $E_v^m - E_i^m$ is now 0.85 eV and the binding energy exceeds this value by 0.35 eV. At 0.35 eV there is predicted a very substantial reduction in deformation rates as can be seen from Figs. 3 and 4.* This very large difference

*Since the vacancy self-diffusion energy $(E_v^f + E_v^m)$ is presumably better known than E_v^m we have followed the practice in the calculations mentioned of requiring $E_v^m + E_v^f = 2.8$ eV for nickel [41].

in effects is obtained using a self-consistent theory for two limits in a critical parameter. This example emphasizes that continued development of the theory without further information on fundamental parameters does not ensure quantitative understanding.

5. SUMMARY

5.1 Trapping

Point defect trapping at impurities decreases swelling and creep deformation rates by enhancing vacancy and interstitial recombination. For given conditions the effect on void nucleation is largest, the effect on void growth and swelling enabled climb-glide creep, I-creep, is intermediate, and the effect on preferred absorption driven climb creep, PA-creep, and on preferred absorption enabled climb-glide creep, PAG-creep is least. Interstitial trapping requires a larger binding energy to produce a reduction in deformation rates equivalent to vacancy trapping. The condition on vacancy and interstitial binding energies for equivalence is given by eq. (15). The treatment given here is directly applicable to the simultaneous inclusion of multiple vacancy and/or interstitial traps and/or a spectrum of binding energies at a given type trap. A system with trapping is mathematically equivalent to either of two fictitious systems with no trapping but with either effective diffusion coefficients described by eqs. (7–12) above or eqs. (15,16) and (17–23) of ref. [20], or with an effective recombination coefficient described by eqs. (12–14) of ref. [20]. In general, however, the effective coefficients depend on point defect concentrations.

A wide range of combinations of binding energy and solute concentration produce a given reduction in deformation rates. Below binding energies of about 0.2 eV for vacancy trapping or $\sim E_v^m - E_i^m + 0.2$ eV for interstitial trapping, point defect trapping is ineffective in reducing void growth or irradiation creep up to solute concentrations of $\sim 1\%$. At these energies, however, trapping is still effective in reducing void nucleation.

5.2 Segregation-induced Changes in Capture Efficiencies

Segregation of solute atoms is expected theoretically to produce significant changes in sink capture efficiencies. These modifications in capture efficiency may result from changes in diffusivity of point defects in the region near the sink or by changes in the elastic interaction of point defects with the sink. When the change in diffusivity or in interaction energy is known the capture efficiency may be evaluated (e.g., by eqs. (28) and (29) for voids). Depending upon the magnitude and sign of the modification in vacancy and interstitial capture efficiencies, either an increase or decrease in swelling may result. In general, segregation occurs simultaneously at all sinks. The increase or decrease in the bias terms of eq. (19) which are made up of combinations and differences of the capture efficiencies of the sinks in the system, determine the effect on swelling as expressed by eq. (31). Segregation may lead to interface reaction controlled absorption of point defects at sinks and hence change the growth kinetics of voids.

5.3 Trapping vs Segregation-Induced Changes in Capture Efficiency

From section 3, it is clear that a given solute atom can be more effective in changing deformation rates by segregating to a sink and affecting the capture efficiency rather than by acting as a trap in the matrix. It is reasonable to expect that in a material under irradiation segregation occurs by thermodynamical lowering of free energies as well as radiation-induced point defect fluxes. The sinks with segregation then determine the system bias. Additional segregation of the same type solute atom does not affect the bias as greatly as the initial segregation. For example, in eq. (29) an energy barrier at the void surface reduces the capture efficiency exponentially, but the thickness of a segregated layer only affects the capture efficiency linearly.

5.4 Vacancy Loops Formed in Point Defect Production Cascades

The simultaneous effect of solute trapping and vacancy loops has been demonstrated. In the quasi-steady state the system with vacancy loops is mathematically equivalent to a system with no vacancy loops but with reduced coefficients of point defect capture at traps, point defect generation, and bulk point defect recombination. The reduction is in the ratio of the total interstitial sink strength without vacancy loops to the total interstitial sink strength with vacancy loops, as given by eq. (27). In particular there can be no creep component due to the dislocations represented by the vacancy loop themselves in the quasi-steady state. Vacancy loops can only produce an initial offset in the direction of stress but no continuing creep component. This is because even though the population of vacancy loops on each plane may well be different, on a plane the arrival rate of interstitials and vacancies at vacancy dislocation loops must be equal in the steady state. This is because neither the vacancy loop average size nor number density can build up beyond a finite limit, by conservation of matter. That there is no net accumulation of vacancies or interstitials on the plane is described by eq. (5).*

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*Equation (5) may be replaced by three similar equations, one for each plane, if conservation of matter at each of three orthogonal planes is being modeled separately.

5.5 Concentrated solutions

The governing equations must be reformulated to model more concentrated solutions, even where trap mobility and higher order complexes are ingored. Essentially geometrical site exclusion and overlap corrections must be included. In addition, a number of additional physical processes must be modeled. These account for radiation-produced displacement of traps and the fates of these traps as well of the fates of displaced solvent atoms and their corresponding vacancies in forming complexes by direct processes in addition to their formation by diffusion.

5.6 Fundamental parameters

Samplings of results predicted theoretically are widely different using the several values of fundamental parameters lying within current uncertainty limits. The theory can be used to identify the important quantities in this respect as described in section 4.2. It is important to realize that further progress depends as much upon increased knowledge of fundamental parameters as on continuing development of the theory.

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FIGURE CAPTIONS

1. The relationship of the effective vacancy diffusion coefficient to the free vacancy diffusion coefficient, eq. (7b), as a function of solute-vacancy binding energy. Calculation for a system containing 10^{15} voids per cubic centimeter of average radius 100Å, a dislocation density of 5×10^{10} cm^{-2} 10% bias, a temperature of 500°C, and a dose rate of 10^{-6} dpa/s. The point defect parameters are $D_v^0 = 1.4 \times 10^{-2}$, $D_i^0 = 8.0 \times 10^{-3}$, $E_v^m = 1.38$ eV, $E_i^m = 0.15$ eV, $S_v^f = 1.5k$, $E_v^f = 1.42$ eV and the atomic fraction solute is 10^{-3}.

2. Three dimensional plot which demonstrates the relative sensitivity of swelling rate to changes in sink capture efficiency resulting in a change in bias and the sensitivity of swelling rate to vacancy trapping. The relative swelling rate at any point on the surface is calculated taking the ratio of the actual swelling rate with trapping and bias corresponding to the coordinates on the solute concentration and bias axes, to the swelling rate obtained with no trapping and 10% bias. Conditions are identical to those described in the caption of Figure 1, except that here the temperature is 550°C.

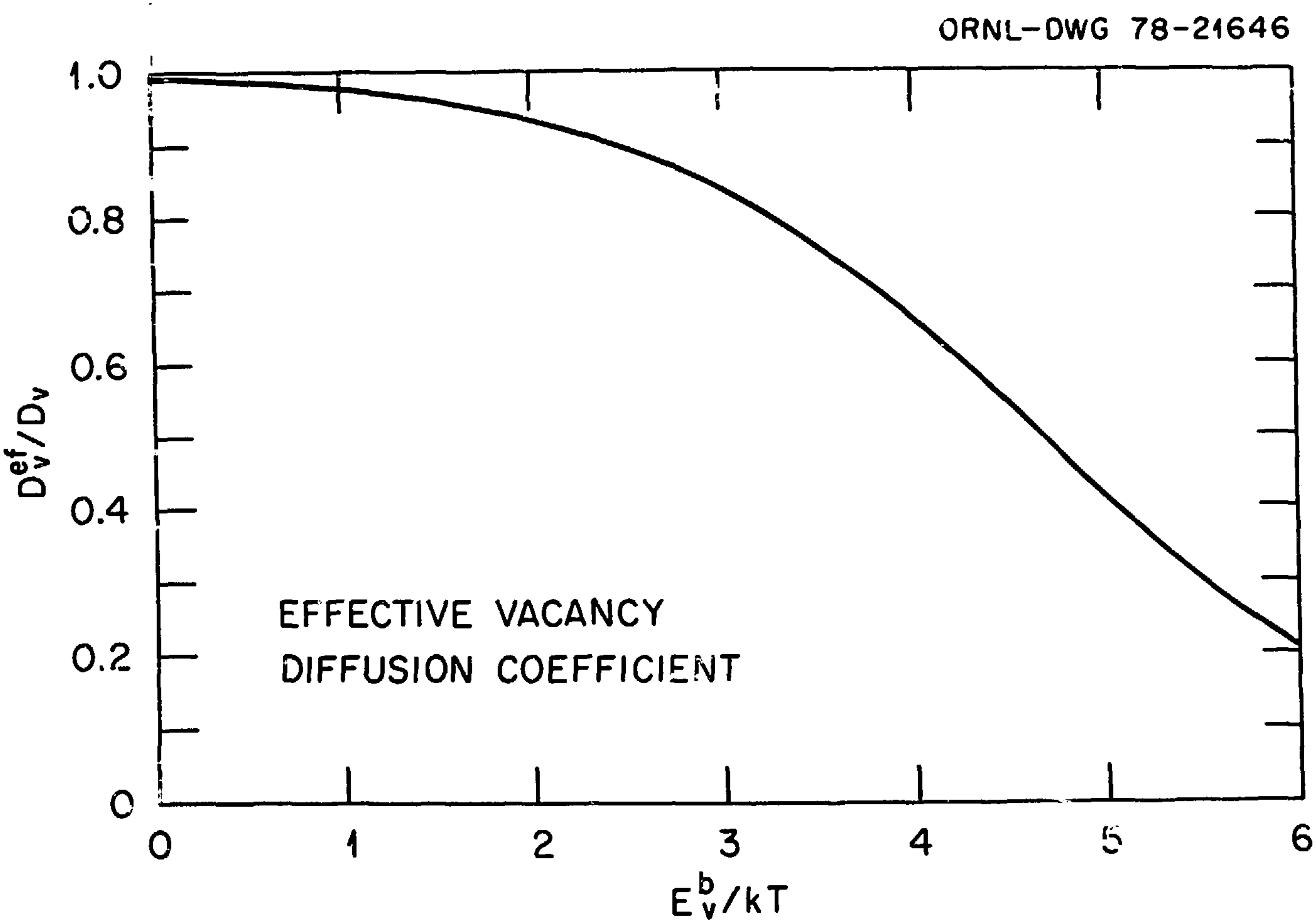
3. Three dimensional plot illustrating the effects on swelling rate of vacancy trapping as functions of binding energy and solute concentration. The relative swelling rate at any point on the surface is calculated by taking the ratio of the swelling rate with trapping corresponding to the trap parameters described by the coordinates on solute concentration and binding energy axes, to the swelling rate with no trapping. Conditions are identical to those described in the caption of Figure 2 with 10% bias.

4. Void nucleation rate with vacancy trapping at solutes as a function of vacancy-solute binding energy. The conditions here represent a typical heavy ion bombardment experiment. Model material contains a dislocation of density 10^{10} cm^{-2}, dose rate is 10^{-3} dpa/s and temperature is 600°C. Void surface free energy is 700 $ergs/cm^2$. Other parameters have the same values given in the caption of Figure 1.

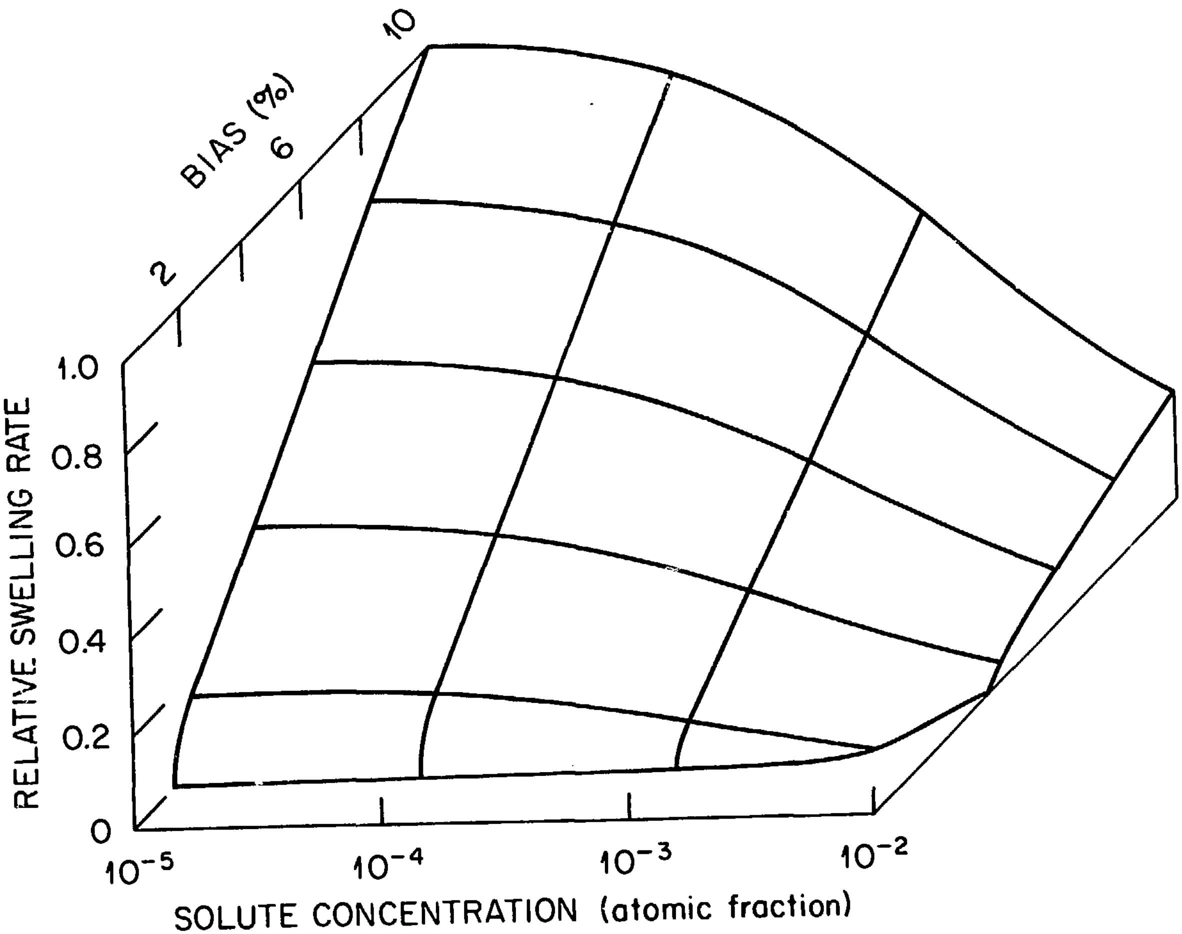
5. Effect of vacancy trapping on the creep rate with increasing solute content. Solid curve is typical for reactor irradiation and dotted curve is typical for charged particle bombardment. Parameters as given in the caption of Figure 1 (E_v^m = 1.2 eV), with additional stress-related quantities given in Table I of Ref. 28.

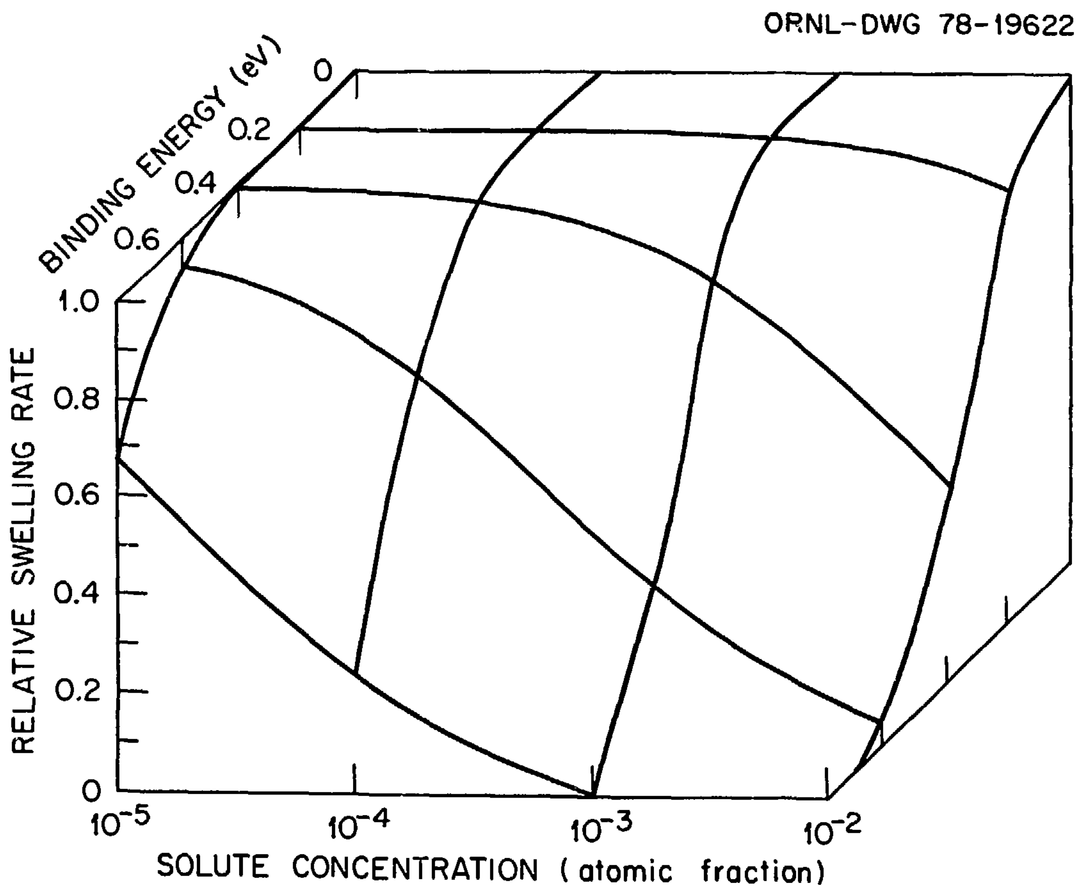
6. Effect of vacancy trapping on the creep rate over the range of reactor dose rates of interest, for T = 500°C and for a range of sink strengths.

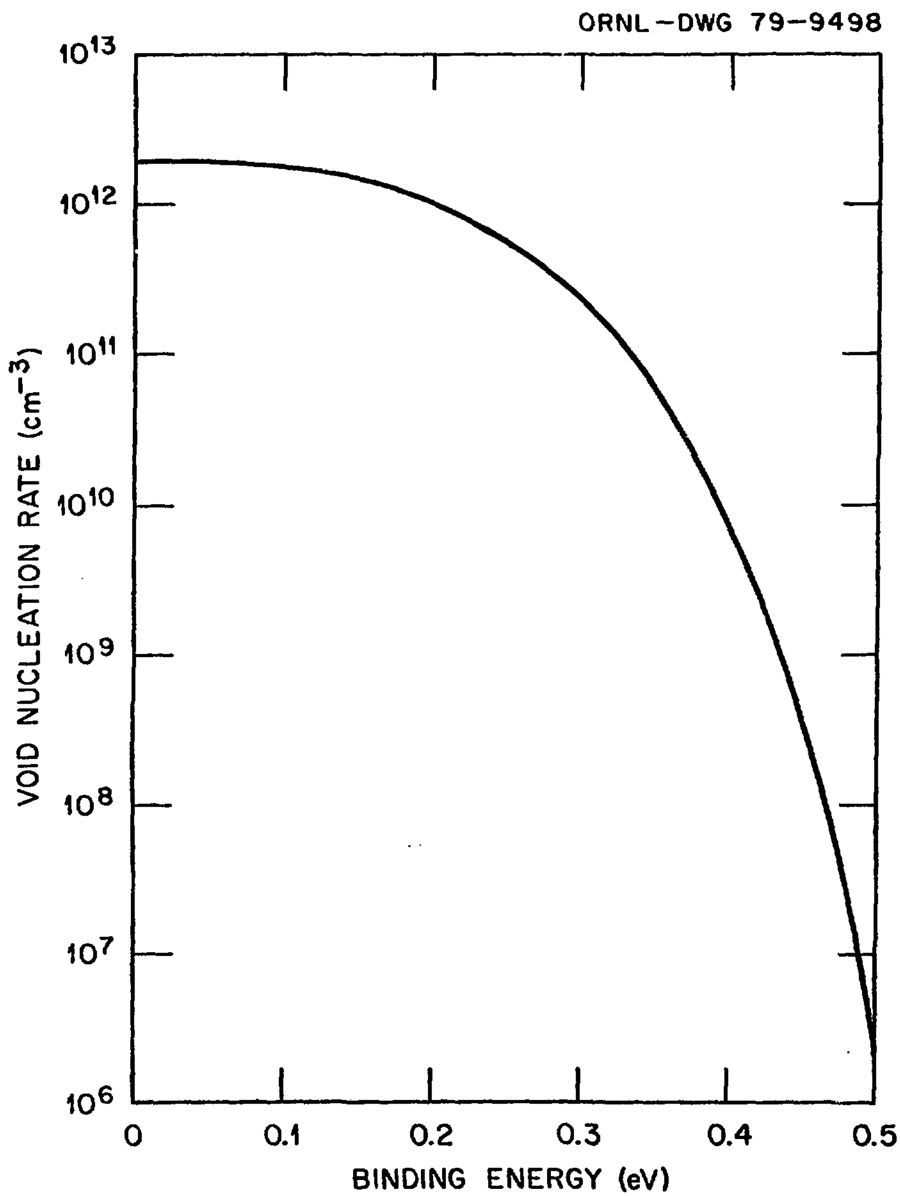
7. Combined effect of trapping and vacancy loops on the creep rate as a function of the vacancy loop sink strength for interstitials normalized to the sink strength for all other sinks, under typical reactor irradiation conditions.


ORNL-DWG 78-21646
1.0
0.8
0.6
0.4
0.2
0
D_v^{ef}/D_v
EFFECTIVE VACANCY
DIFFUSION COEFFICIENT
0
1
2
3
4
5
6
E_v^b/kT

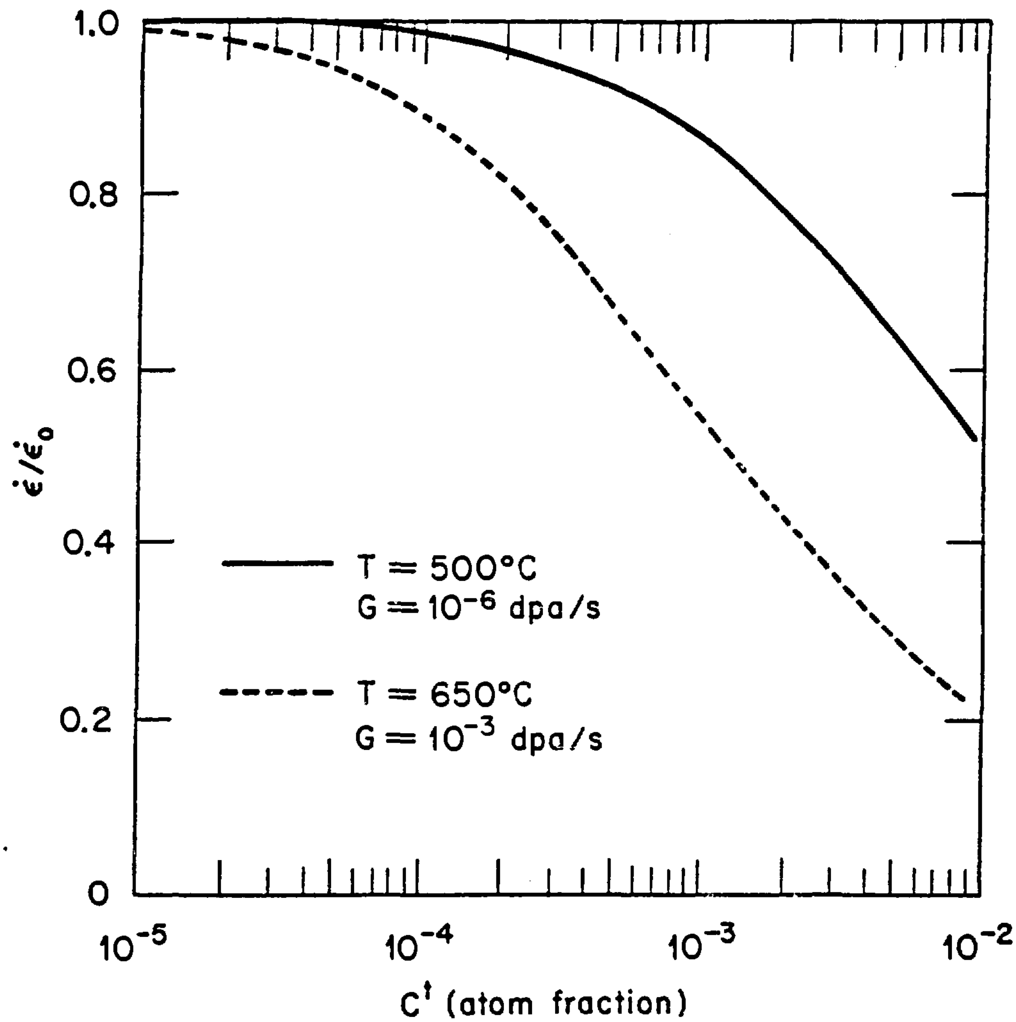
ORNL-DWG 78-21645R



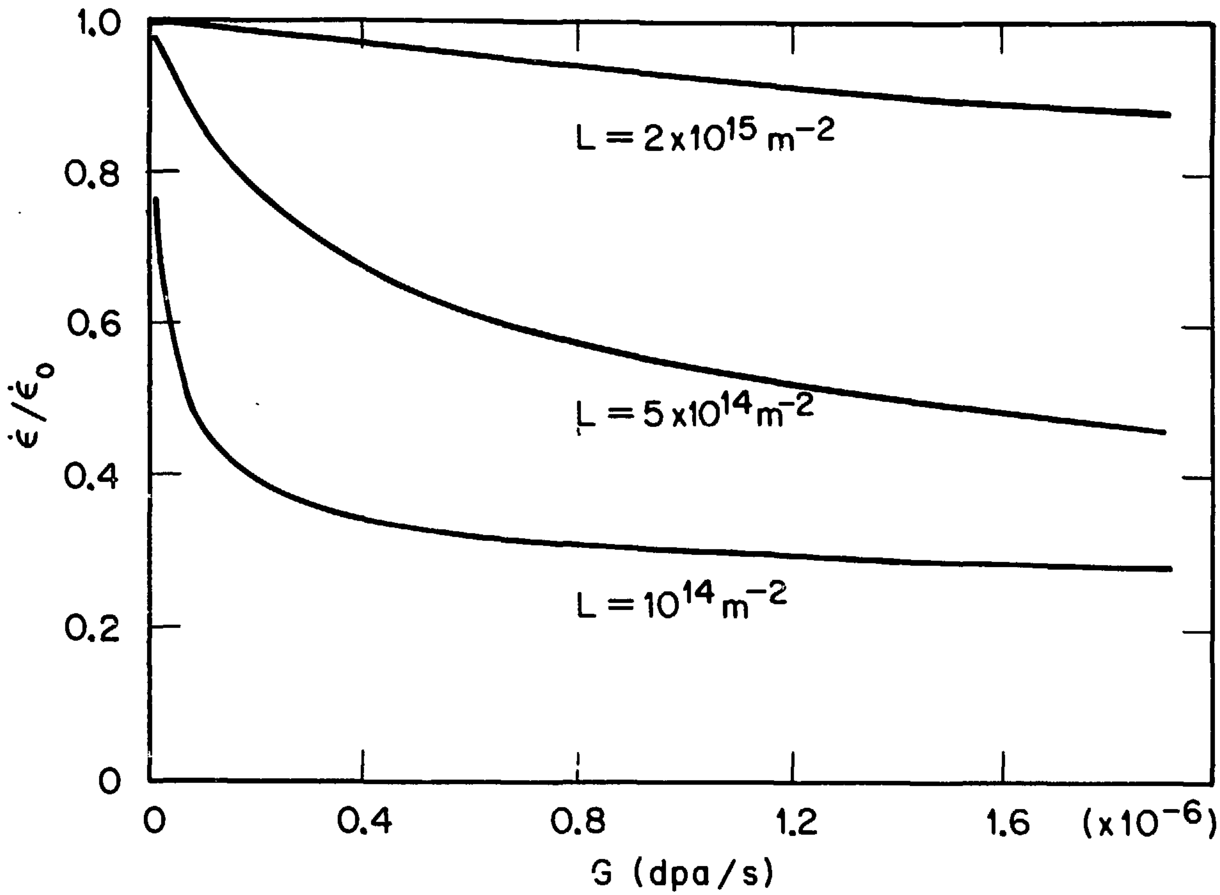

ORNL-DWG 78-19622
BINDING ENERGY (eV)
0
0.2
0.4
0.6
RELATIVE SWELLING RATE
1.0
0.8
0.6
0.4
0.2
0
10^{-5}
10^{-4}
10^{-3}
10^{-2}
SOLUTE CONCENTRATION (atomic fraction)


ORNL-DWG 79-9498
VOID NUCLEATION RATE (cm^{-3})
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
0
0.1
0.2
0.3
0.4
0.5
BINDING ENERGY (eV)

ORNL-DWG 78-9397



ORNL–DWG 78–9394



ORNL–DWG 78–9399