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THE EFFECT OF PRECIPITATE-MATRIX INTERFACE SINKS ON THE GROWTH OF
VOIDS IN THE MATRIX*

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A qualitative discussion of the differing roles played by coherent and incoherent precipitates as point defect sinks is presented. Rate theory is used to obtain semi-quantitative estimates of the growth of cavities in the matrix when either type of precipitate is present. Methods for deriving the sink strengths of precipitates of arbitrary shape are developed. In three materials where available microstructural information allows an analysis, precipitates are found to cause only a small relative suppression of cavity growth via the mechanisms here considered.

1. INTRODUCTION

The irradiation of alloys with energetic particles is often found to produce very complex microstructures. In addition to the voidage and dislocation network structure commonly found in pure metals, or the precipitates intentionally introduced by prior heat treatment, new second phase precipitates are often observed which do not occur in unirradiated materials with the same thermal history.

The potential complications in complex alloys such as the austenitic steels were apparent in fact in some of the earliest observations of void swelling. For example, copious precipitation of $M_{23}C_6$ was observed [1] in neutron irradiated cold-worked M316, sigma phase FeCr precipitates were found in annealed 304 steel [2], while a specific thermomechanical treatment of AISI 348 was found to produce both NbC and sigma phase precipitation[3]. These are but three instances of what has subsequently proved to be a widespread phenomenon now bearing the name of irradiation phase instability. This topic has developed into a challenging field of study in its own right [4,5,6].

Within the field of irradiation phase instability two distinct approaches are possible. The first is concerned with the mechanisms by which particular features such as precipitation appear and evolve. The second, on the other hand, attempts to rationalize the present and predict the future development of a property such as swelling in terms of the features currently prevailing. Of course the two approaches are complementary to each other and ultimately no sharp division may be precisely realizable. Our intent here is to focus upon the second of the afore-mentioned approaches. The work is a continuation of a recent appraisal [7] of precipitate-related effects on swelling.

In that previous work three modes by which precipitation could affect swelling were identified. These were termed direct, by cavity-precipitate association; indirect, by precipitate-related changes in the overall sink strength of the material; and mediated, by precipitation-related changes in the characteristics of the matrix. In the present paper we concentrate on effects on the growth of matrix cavities through precipitate-related changes in the sink strength of the material.

2. BACKGROUND

Two extreme models of precipitate effects on void swelling are treated in this paper, using an approach based upon rate theory [8-11]. In the idealized case of a coherent precipitate, the interface is typified as an internal surface where constrained recombination of defect and anti-defect occurs. The interface of the coherent precipitate with the matrix is modeled as containing a distribution of saturable traps. Under uniform irradiation, saturable traps acquire a steady-state occupation probability as a result of a balance between defect capture, defect thermal release and extrinsic recombination with the anti-defect [12,13]. This fractional occupancy is an additional degree of freedom of the system. It is determined by an additional steady-state condition which augments the usual continuity conditions for the generation and loss of point defects throughout the entire medium.

For the interface of the incoherent precipitate with the matrix, on the other hand, such an additional constraint does not exist. The incoherent precipitate simply accepts any excess point defect flux that happens to impinge on it. Since in general there will be an excess flux of one defect type due to the system bias, this of course implies that an incoherent interface also

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may be a site of enhanced point defect aggregate growth. Incoherent interfaces may behave as regions of rapid defect transport akin to large angle grain boundaries. In this case the precipitate-matrix interface may serve as a surface of enhanced collection by which additional point defects are channeled to cavities.

The enhanced growth of cavities attached to such precipitates has recently been explored by Mensur [14]. It was found that significant increases in the growth of the attached cavities are possible by point defect collection. This is an important direct effect of precipitation on the growth of precipitate-attached cavities which is only briefly discussed in the present paper. Here we concentrate in detail on the indirect effect of the sink strength of precipitates on the growth of matrix cavities.

The distinction described above between coherent and incoherent precipitates is important. In fact, in one limit to be described subsequently, we find that the sink strength of a precipitate of a given morphology is essentially independent of whether the precipitate-matrix interface is coherent or incoherent. Nevertheless, the effect of the precipitates on the growth of matrix voids does depend upon the precipitate interfacial character. The difference stems from the fact that there is the auxiliary steady-state constraint described above in the case of the coherent precipitate. Somewhere in the hinterland between coherent and incoherent lies the role of the semicoherent precipitate. It appears reasonable to presume that surface dislocations on the semi-coherent interface also provide fast diffusion paths between interconnected trap sites. Thus, if the area density of such paths is high enough, defect aggregates may well exhibit enhanced growth upon them, as for the case of incoherent precipitates. This problem is worthy of further study, since coherency loss by irradiation has been observed experimentally [15].

3. RATE THEORY

This section summarizes some formal developments of rate theory on the effect of precipitates on the growth of a matrix void. Let G_β and S_β be the generation rate and total sink strength respectively of the defect of type β ($\beta \equiv v$ for the monovacancy and $\beta \equiv i$ for the self-interstitial). If D_β is the diffusivity of species β and c_β the atomic fraction, the two appropriate rate equations are

$$G_v - D_v S_v c_v - \alpha c_i c_v = 0 \quad (1)$$

and

$$G_i - D_i S_i c_i - \alpha c_i c_v = 0 \quad (2)$$

Here α denotes the intrinsic recombination coefficient.

Equations (1) and (2) are readily solved as they stand [10]. However, when saturable traps are present, whether associated with isolated solute atoms or special sites on a coherent precipitate-matrix interface, it is simpler to first invoke the necessary additional steady-state constraint. To be specific, let us consider vacancy trapping. Then if S_{vg} denotes the sink strength of such traps for the different self-defects and G_{vv} is the thermal release rate from these traps, we have

$$D_v S_{vg} c_v - D_i S_{vi} c_i - G_{vv} = 0 \quad (3)$$

To simplify matters as much as possible, we suppose that in the temperature range of interest vacancy emission from other than the vacancy traps may be neglected. In this case, $G_v = (G + G_{vv})$, where G is the displacement rate. Self-interstitial thermal emission from every sink type is also negligible in this situation, thus $G_i = G$. One may eliminate G_{vv} immediately via Eq. (3) and so obtain c_i and c_v from Eqs. (1) and (2). The results are

$$c_v = \frac{D_i \bar{S}_i}{D_v \bar{S}_v} c_i = \frac{D_i S_i}{2\alpha} \left\{ (1 + v)^{1/2} - 1 \right\} \quad (4)$$

where

$$v = \frac{4\alpha G \bar{S}_i}{D_i D_v \bar{S}_v S_i^2} \quad (5)$$

and the $\bar{S}_\beta$ denote total strengths of all sink types excluding saturable traps:

$$\bar{S}_\beta = S_\beta - S_{v\beta} \quad (6)$$

For the sake of simplicity we suppose also that matrix cavities (voids) are neutral sinks of radius r_c . Their growth rate $\dot{r}_c$ is then given by

$$r_c \dot{r}_c = D_v c_v - D_i c_i \quad (7)$$

upon neglect of the higher order sink corrections and thermal emission from the voids. Hence we find from the above that

$$r_c \dot{r}_c = \frac{D_i D_v S_i}{2\alpha S_i} (\bar{S}_i - \bar{S}_v) \left\{ (1 + v)^{1/2} - 1 \right\} \quad (8)$$

The two limiting cases of interest are those of large and small intrinsic recombination. These yield respectively

$$r_c \dot{r}_c = (\bar{S}_i - \bar{S}_v) \left\{ \frac{D_i D_v c_i}{\alpha S_i S_v} \right\}^{1/2}, \quad v \gg 1, \quad (9)$$

and

$$r_c \dot{r}_c = G (\bar{S}_i - \bar{S}_v) / \bar{S}_v S_i, \quad v \ll 1 \quad (10)$$

Since the growth rate of the void in the absence of traps follows from Eqs. (5) and (8) by simply setting $S_1 = \bar{S}_1$, (i.e., $S_{V1} \rightarrow 0$), these results show that, when intrinsic recombination dominates, trapping does not influence the form of the growth rate. The latter is modified only when intrinsic recombination effects are not completely dominant. In the limit of low recombination there is then a fractional reduction by a factor ($\bar{S}_1/S_1$), all other things being equal [16].

To contrast the effects of coherent and incoherent precipitates, consider the situation where dislocations, voids, coherent precipitates with interface vacancy traps, and solute atom vacancy traps comprise the possible major elements of the microstructure. The quantities appearing in Eq. (10) are then

$$\begin{aligned}\bar{S}_1 &= Z_1 \rho_D + S_c + S_{IP}; \quad S_1 = \bar{S}_1 + S_{V1} \\ \text{and } \bar{S}_v &= Z_v \rho_D + S_c + S_{IP}.\end{aligned}\quad (11)$$

Here ρ_D is the dislocation density and Z_1 and Z_v are its associated capture efficiencies for self-interstitials and vacancies. Further, S_c and S_{IP} are sink strengths for matrix cavities and incoherent precipitates respectively, both being here taken as neutral sinks. Thus, when the right-hand member of Eq. (10) is sensibly constant in time [16], the matrix cavity radius after a dose Δ is

$$r_c = \left[\frac{2(Z_1 - Z_v)\rho_D \Delta}{(Z_v \rho_D + S_c + S_{IP})(Z_1 \rho_D + S_c + S_{IP} + S_{V1})} \right]^{1/2} \quad (12)$$

This result enables us to illustrate the major distinctions between coherent and incoherent precipitates in the limit of low intrinsic recombination. Let us compare the matrix cavity radius in three microstructures 0, 1, and 2, the first containing cavities and dislocations only, the second containing, in addition, incoherent precipitates only, and the third coherent precipitates as the only extra sink type. Then, after the same dose, it follows that

$$\frac{r_c^{(1)}}{r_c^{(0)}} = \left(\frac{\rho_D^{(1)}}{\rho_D^{(0)}} \right)^{1/2} \frac{S_{Dc}^{(0)}}{(S_{Dc}^{(1)} + S_{IP})}, \quad (13)$$

whereas

$$\frac{r_c^{(2)}}{r_c^{(0)}} = \left(\frac{\rho_D^{(2)}}{\rho_D^{(0)}} \right)^{1/2} \frac{S_{Dc}^{(0)}}{[S_{Dc}^{(2)} \{ S_{Dc}^{(2)} + S_{V1} \}]^{1/2}}, \quad (14)$$

where $S_{Dc}^{(x)} = (\rho_D^{(x)} + S_c^{(x)})$ in each of the three cases. (We may set $Z_1 = Z_v = 1$ after computing

ratios). It is evident, therefore, that if S_{IP} and S_{V1} are comparable, and all other factors are taken as equal in 0, 1, and 2 (for illustrative purposes only), then incoherent precipitates give the greater reduction of matrix cavity growth. Of course, this does not imply that the total void swelling is smaller, because the same physical assumptions leading to this result imply also that voids grow on the incoherent particles [7]. The distinction embodied in Eqs. (13) and (14) is that precipitates which are not inhibited in their ability to accept self-defects (incoherent) are better extrinsic recombination sites than those whose ability is constrained by a condition such as Eq. (3) (coherent).

The strength S_{V1} embodies trapping at the coherent precipitate and trapping at solute atom traps. In this more general case Eq. (3) is really the sum of two distinct steady state conditions, one for each trap type. Similarly, the sink strengths S_{IP} are sums for each trap type. They can be found individually by solving for the two types of occupation probability by a generalization of the methods of ref. [10]. Our reason for raising the matter here is to note the additive fashion in which they both implicitly appear in Eq. (12) through the one parameter S_{V1} .

In this vein it is instructive to assess in one limit the relative potency of traps distributed over the interface of a precipitate as compared to the same number of traps dispersed in the matrix. To this end we compare Eq. (3) above, the steady-state condition valid for interface vacancy traps, with Eq. (8) of ref. [13], the steady state condition valid for vacancy traps dispersed in the matrix. The terms describing recombination of free interstitials with trapped vacancies are there found to be respectively $c_1 D_1 S_{V1}$ and $C_1 D_1 4\pi r_p C_v$, where r_v is the radius of recombination of a vacancy-trap complex with an interstitial and C_v is the concentration of trapped vacancies, i.e., the concentration of traps occupied by vacancies. The quantities c_1 and C_1 are identical in the two notations except for a factor of Ω . In the limit of strong binding it is shown in the Appendix that $S_{V1} \rightarrow 4\pi r_p C_p$ where r_p and C_p are the radius and concentration of precipitate particles. It has also been shown [17] that in the limit of strong binding $C_v \rightarrow C^t/2$, where C^t is the dispersed trap concentration per unit volume. Thus from the above relationship we make the identification that $r_p C^t/2$ for trapping at dispersed traps is formally replaced by $r_p C_p$ for trapping at precipitate-matrix traps regardless of the trap density on the precipitate-matrix interface. Suppose, for example, that there are C^t traps per unit volume but now distributed on the precipitate-matrix interface. Their effectiveness is to be compared to C^t traps dispersed in the matrix. We have, for spherical precipitates occupied by interfacial traps at the highest possible effective density,

$C^t = C_p 4r_p^2/r_v^2$. Comparing this expression for precipitate-matrix interface traps to that for dispersed traps, $r_v C^t/2$, we find that the traps on the interface are less effective than the traps in the matrix by the factor $r_v/2r_p$.

It should also be noted that the result in Eq. (13) is somewhat different than an earlier result by one of us [7]. That result, Eq. (11) of ref. 7, is given in the present notation as

$$\frac{dr_c^{(1)}}{dr_c^{(0)}} = \frac{p_d^{(1)}}{p_d^{(0)}} \left(\frac{S_{Dc}^{(0)}}{S_{Dc}^{(1)} + S_{IP}} \right)^2 \quad (15)$$

specialized to the present case of negligible intrinsic recombination. This equation was derived to describe a somewhat different situation than Eq. (13) above. The difference arises because in the latter analysis the growth rates of a matrix test cavity of given size in two different environments were considered, whereas Eq. (13) gives the cavity sizes after a given dose in the two materials.

4. THE SINK STRENGTHS OF PRECIPITATE PARTICLES OF ARBITRARY SHAPE

We presume the coherent interface model with saturable trapping of one defect type applies. Our intent is to determine the maximum possible effect of such particles. Clearly, this is where intrinsic recombination effects are negligible [see Eqs. (8) and (9)], where there are no incoherent precipitates competing for defects [see Eq. (13)], and where solute atom trapping in the matrix is relatively small. The quantities S_{Dc} , the dislocation plus cavity sink strength, are presumed known from direct measurement; thus S_{V1} , the sink strength of the precipitate for the anti-defect alone remains to be specified.

The determination of this quantity is quite complicated in general [12], but a natural upper bound exists. Namely, it is that which prevails when the interface density of traps and the binding energy of the point defect to the interfacial traps are high. Then every approaching interstitial finds a trapped vacancy with which to recombine. The precipitate then acts like a perfect sink for interstitials. Thus, in this limit the sink strength of the coherent precipitate is essentially the same as that of the incoherent precipitate. (Note again, however, our discussion at the end of the background section. This also applies to what we say concerning non-spherical precipitates below.) The detailed results of ref. 10 for spherical particles of radius r_p bear this out; there it is shown that $S_{V1} \lesssim 4\pi C_p r_p$ where C_p is the precipitate volume concentration.

In most cases encountered, however, precipitates are not even approximately spherical. Fortunately, Flynn [18] has given the

appropriate generalization of the ideal sink strength for this case; the radius r_p for the sphere is to be replaced by κ for other geometries, where κ is the electrical capacitance of an isolated metal electrode of the same size as the precipitate. A brief discussion of the applicability of this result to the present problem is given in the Appendix. Here we shall simply cite the maximum S_{V1} which results from its use, i.e.,

$$S_{V1} = \frac{4\pi\epsilon\kappa}{v_p} \quad (16)$$

where v_p is the volume of one precipitate and ϕ the volume fraction. When each particle is spherical, at fixed volume fraction, $S_{V1} \propto r_p^{-2}$. Equations (14) and (16) are then simply a reiteration of a result described previously [10] that a fine dispersion is more efficient at reducing cavity growth than a coarse one [7,16]. For a set of identical particles of a given shape, the value of S_{V1} is increased over that for spheres of the same volume by the ratio κ/R_p , where R_p is the sphere capacitance (radius).

The general ellipsoid covers many cases of interest. If the semi-axes are L, M , and N (with $L \geq M \geq N$) its capacitance is [19]

$$\kappa = (L^2 - N^2)^{1/2} / F(\theta, k) \quad (17)$$

where

$$\theta = \sin^{-1} \{1 - (N/L)^2\}^{1/2} \quad (18)$$

$$k = \left\{ \frac{L^2 - M^2}{L^2 - N^2} \right\}^{1/2} \quad (19)$$

and F is the normal Elliptic Integral of the first kind:

$$F(\theta, k) = \int_0^\theta \frac{d\psi}{\{1 - k^2 \sin^2 \psi\}^{1/2}} \quad (20)$$

The thin lenticular disc ($L = M \gg N$) thus has a capacitance $\kappa_D \approx (2L/\pi)$ and the prolate spheroid ($L = N$) a capacitance

$$\kappa_{PS} = \frac{(L^2 - N^2)^{1/2}}{2n \left[\frac{L}{N} + \left\{ \left(\frac{L}{N} \right)^2 - 1 \right\}^{1/2} \right]} \quad (21)$$

which in the limit of $N \rightarrow L$ reduces to the value $\kappa = L$ appropriate to a sphere of this radius. To a first approximation one finds that in all these cases $\kappa \sim 0.3 A^{1/2}$, where A is the surface area.

Introducing $R_p = (LMN)^{1/3}$ to denote the radius of the sphere of the same volume and using Eq. (16), the shape dependence of $Sv_1 = (3\phi/R_p^2)(\kappa/R_p)$ is contained in the last factor. For the prolate spheroid we find that κ/R_p varies monotonically from 1 to 2 when the eccentricity L/N varies from 1 to 20, i.e., from spherical to cigar shaped precipitate. For fixed L/N and variable M/L between prolate spheroid and lenticular disc, κ/R_p is found to vary in the manner shown in Fig. 1. Thus acicular coherent precipitates have the greatest potency for reducing void growth.

Fig. 1: Variation in sink strength at constant volume with the shape of the precipitate.

5. ANALYSES OF EXPERIMENTAL OBSERVATIONS

We consider three systems where coherent precipitates of different morphologies have been observed. The γ' precipitates in PE16 provide an example of spherical particles [20]. Their radius was reported as 5 nm and volume concentration $C_p = 2 \times 10^{-22} \text{ m}^{-3}$. The swelling of this alloy was small, being about 30 times less than that of pure Ni after 40 displacements per atom (dpa), while ρ_D was in excess of 10^{15} m^{-2} for all doses above 2 dpa. If one attempts to ascribe all potential trapping effects to the γ' particles, it follows that $Sv_1 < 1.3 \text{ pp}$. Such a small fractional contribution to the total sink strength clearly cannot make the process considered the dominant cause of the swelling suppression. In fact, this was established experimentally [21] some years ago by a comparison of the swelling in Ni-Al alloys with and without such precipitates.

As an example of (approximately) disc-shaped precipitates we will re-examine the possible effect of coherent θ' particles in Al-Cu alloys [15]. A specimen containing $\sim 10^{19} \text{ m}^{-3}$ of

such precipitates, of radius 225 nm, exhibited about an order of magnitude smaller swelling than a control specimen of pure Al irradiated to the same neutron fluence of $\sim 3 \times 10^{26} \text{ n/m}^2$. As a result of a rate theory analysis accompanying the report of these observations, it was claimed that the effect could be rationalized by extrinsic recombination processes at the precipitate-matrix interfaces. However, the treatment differed from that upon which the present analysis is based in that individual trap states were treated independently. This, we believe, is only appropriate when the surface trap density is very small. The analysis preceding Eq. (15) of the present paper gives the factor by which the independent trap assumption overestimates the effectiveness of traps on a precipitate matrix interface in the limit of high binding energy and high surface density of traps.

In the alloy specimen investigated, the measured values of the parameters were $r_c = 72 \text{ nm}$, $C_c = 6 \times 10^{19} \text{ m}^{-3}$ and $\rho_D = 5 \times 10^{13} \text{ m}^{-2}$. These yield $S_{DC} = 10^{14} \text{ m}^{-2}$ whereas the precipitate data given above leads to $Sv_1 \sim 2 \times 10^{13} \text{ m}^{-2}$. Thus the latter contribute only a minor part of the total sink strength. The microstructural details for the pure Al control specimen were not measured unfortunately. Thus, there is no option but to assume them roughly the same as in the alloy. If this course is adopted then the ratio of the alloy to pure Al swelling, as given by Eq. (14), is simply $\sim [1 + Sv_1/S_{DC}]^{-3/2}$, which is about 3/4. We think it very unlikely, therefore, that the swelling reduction can be ascribed to a reduction in void growth caused by the coherent particles in this system either.

A final example serves as a testing ground for another precipitate morphology. Table 1 repeats some previously reported [7] microstructural details for two 316 stainless steels containing different levels of P and Si. The precipitates can be approximated as elongated ellipsoids. Now in both cases elongated ellipsoids with axes lengths equal to one half the dimensions given yield $k = 1$, upon applying Eq. (19). In other words their capacitance approaches that for a highly eccentric prolate spheroid, whence Eqs. (16) and (21) lead to $Sv_1 = 4\pi C_p L / \ln(2L/N)$. For the two data sets (a) and (b) one finds respectively $Sv_1 = 2.8 \times 10^{14} \text{ m}^{-2}$ and $Sv_1 = 5.7 \times 10^{13} \text{ m}^{-2}$. The void sink strength in (b), if computed from $4\pi r_c C_c$, turns out to be about an order of magnitude less than the dislocation density. Thus the major sinks in (a) are the precipitates, in (b) the dislocations. The qualitative point then follows from Eq. (14) if microstructure (2) of that equation is identified first with (a) and then with (b) and the reference state (0) eliminated. One obtains $r_c^{(a)}/r_c^{(b)} \sim [\rho_D^{(b)}/Sv_1^{(a)}]^{1/2}$. This is about unity, a result which prevails even if all sink strengths are appropriately included. Thus it is found that the precipitates, when modeled as coherent, do not explain the observed reduction in swelling by suppression of cavity growth.

Table 1

Alloy	Conc. P (%)	Conc. Si (%)	Dislocation Density (m^{-2})	Cavity Diameter (nm)	Cavity Density (m^{-3})	Precipitate Density (m^{-3})	Precipitate Side Lengths (nm)
a	0.08	1.4	8×10^{13}	—	—	6×10^{20}	$300 \times 20 \times 10$
b	0.04	0.7	3.1×10^{14}	35	1.6×10^{20}	2×10^{20}	$200 \times 10 \times 5$

If on the other hand, the precipitates of the last example were considered semi-coherent or incoherent and the cavities were in the matrix then Eq. (13) would apply. As before, microstructure (1) of Eq. (13) is identified first with (a) and then with (b) and the reference state (0) eliminated. Using the above numbers gives $r_c^{(a)}/r_c^{(b)} \sim 0.5$ in this case. We noted, however, that the cavities in (b) appear to be attached to the precipitates [7]. If the precipitate-matrix interfaces channel defects to the cavities then Eq. (13) would no longer apply. Using an analysis similar to that of ref. [14] for such cavities one can show that instead of Eq. (12) one obtains

$$r_c \approx \left[\frac{3\kappa_{pc} \rho_D (Z_1 - Z_v) \Delta}{S_v S_1} \right]^{1/3} \quad (22)$$

Here κ_{pc} is the capacitance of the precipitate-cavity pair. This leads to $r_c^{(a)}/r_c^{(b)} \sim 0.75$. Thus, in either case one finds that the presence of incoherent precipitates cannot fully explain the observed reduction of at least an order of magnitude in cavity size.

In ref. [7] it was claimed that the presence of the precipitates could account for the observed reduction. This is not substantiated by the present work. The origin of the discrepancy lies in the difference between Eqs. (13) and (15) above. As described following these equations, Eq. (13) gives the radii of cavities in two different microstructures at a fixed dose while Eq. (15) gives the relative growth rates of a constant size test cavity in two different microstructures. The order of magnitude reduction deduced in ref. [7] applies to the growth rate of a test cavity of the same size in both microstructures. As shown above, however, the actual cavity size at fixed dose is predicted to be reduced only about a factor of 2 or less.

These three examples suffice to indicate that though precipitates act as point defect sinks, the verification of their importance in reducing the growth of cavities in the matrix may well prove to be the exception rather than the rule.

6. SUMMARY

A rate theory approach to void growth has been developed which encompasses the presently-conceived potential roles of precipitate-matrix interfaces as point defect sinks. The effect of these additional point defect sinks on the growth of cavities in the matrix

is investigated. Methods for treating particles of arbitrary shape are described. Three material examples have been chosen. In no case have the effects considered proved to be a dominant factor in reducing cavity growth. In retrospect, it is somewhat surprising that so apparent a feature as precipitation has proved to have so little relative effect on the suppression of growth of matrix cavities in the cases we have examined. It would, however, be hazardous to attempt to formulate general rules on the basis of so few examples.

APPENDIX

The object of this section is to indicate the connection between the anti-defect sink strength of a random array of defect-trapping precipitates and the electrical capacitance of one of them.

Following the procedure described in detail elsewhere [22], one such precipitate is embedded in the effective medium of total sink strength S . The field equation for each defect type,

$$D\nabla^2 c - DSc + G = 0, \quad (A1)$$

is then to be solved subject to specified boundary conditions on the surface of the precipitate. From this the flux $J_p = (D/\Omega) \int (\partial c / \partial n) dA$, where n is the coordinate along the surface normal at the area element dA , is to be computed. Since the loss rate per atom for C_p randomly distributed objects per unit volume is $C_p J_p \Omega$, their sink strength, S_p , and any thermal emission, G_p , from them is to be obtained from

$$D S_p c - G_p = C_p J_p \Omega, \quad (A2)$$

where c is the far-field concentration, $c = (G/DS)$, following from Eq. (A1).

Suppose the surface contains vacancy traps at an area density w and let f be their fractional occupancy. The boundary condition at the surface is then, for interstitials,

$$\frac{\partial c_i}{\partial n} = w a f c_i \quad (A3)$$

where a is a lattice spacing.

If we set $c_1 = c_1^\infty - u$, the equation for u becomes

$$\nabla^2 u - Su = 0. \quad (A4)$$

The term in S reflects the influence of all sinks other than the central precipitate on the flux J_p . It is the source of the higher order sink correction [22], which we here neglect. In this approximation, u is thus a solution of Poisson's equation for the prescribed geometry, with the boundary condition

$$\frac{\partial u}{\partial n} = -wa(c_1^\infty - u_0)f \quad (A5)$$

on the inner surface, at which u has the value here denoted by u_0 . At infinite distance from the precipitate u is zero.

In the corresponding electrostatics problem with the same geometry, the potential ϕ also satisfies Poisson's equation. Moreover, if ϕ_0 represents the potential of the electrode (i.e., precipitate) relative to the value at infinity, the total surface charge on the object is

$$-\frac{1}{4\pi} \int \left(\frac{\partial \phi}{\partial n} \right) dA = \kappa \phi_0 \quad (A6)$$

where κ is its capacitance. This specifies the relation between the area integral of the normal derivative and the boundary value possessed by a solution of Poisson's equation. In our diffusion problem, ϕ_0 corresponds to u_0 . The latter we assume constant over the surface at the value $-(4\pi\kappa)^{-1} \int (\partial u / \partial n) dA$ derived from Eq. (A6). Then integrating Eq. (A5) over the surface, approximating f and w also by constants, yields

$$\int \frac{\partial u}{\partial n} dA = \frac{-4\pi\kappa f c_1^\infty}{f + s} \quad (A7)$$

where $s = 4\pi\kappa/waA$. The flux J_p of Eq. (A2) is obtained from the above; there are no emission terms for interstitials ($G_p \rightarrow 0$). Hence, for vacancy-trapping precipitates, with the p label on S changed to (V) to denote the sink strength of a vacancy-trapping precipitate for interstitials,

$$S_{V1} = 4\pi\kappa C_p f / (f + s). \quad (A8)$$

This has a maximum value of $4\pi\kappa C_p$ when $s \ll f$. Since $\kappa \sim A^{1/2}$, the limit is most readily attained for large precipitates. A more detailed treatment [12] for spherical precipitates elucidates the further requirement that high

vacancy binding is also necessary for such an ideal sink result to apply.

A more detailed analysis allowing f and w to vary over the surface does not appear to alter the general conclusion given above.

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