Inhibition of intergranular cavity growth in precipitate-hardened materials

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Vacancy production on boundaries decorated with precipitates is discussed. Initially the boundaries are considered to be perfect vacancy sources. Displacements due to vacancy diffusion to a cavity are equated with plastic deformation rates around a precipitate. Vacancy diffusion is shown to smooth out stress concentrations over the precipitates. Below a threshold stress this model cannot describe vacancy diffusion in the boundary. It is suggested that at low stresses the boundary is an imperfect source of vacancies. An alternative model is developed in which vacancy creation at low stresses is controlled by dislocation creep in the matrix. The theory is applied to cavity growth, and the operational regimes of various control mechanisms are discussed.

1. Introduction

The creep life of metals working under load at high temperatures is important in many aspects of power generation. Clearly, valid models of the failure processes help to understand the regions of safe operation even when the absolute value of the lifetime cannot be predicted accurately. One type of failure often seen results from the nucleation, growth and eventual coalescence of many cavities situated in grain boundaries. The cavities can show features which suggest that diffusive processes are an important factor in their growth. For instance the cavities can be rounded or penny shaped suggesting fast or slow surface diffusion relative to grain-boundary diffusion [1]. In the latter case, penny-shaped cavities in α iron can exhibit dendritic growth in the boundary [2]. This feature correlates well with grain-boundary vacancy diffusion controlled growth since such instabilities in the growing interface can be predicted from theory [3, 4].

Vacancy diffusion controlled growth theory predicts a growth rate proportional to stress to the power unity but correlation with experiment can be complicated by the continuing nucleation of cavities during testing. Several experiments have overcome this difficulty by nucleating all the cavities during the initial stages of creep [5], implanting cavities [6], prestraining [7] or measureing the growth rate of cavities nucleated during.

the initial stages of creep [1]. In general, the results do not correlate well with vacancy diffusion controlled growth theory.

Several modifications have been made to the diffusion theory which go some way to closing the gap between theory and experiment. The vacancy diffusion fluxes in the boundary can be coupled to the dislocation creep processes occurring further from the cavity [8]. This allows for the smooth transition between diffusion control at low stresses and dislocation creep control at high stresses. In the quite extensive changeover region, cavities can show the morphology of diffusion processes whilst having a growth rate correlating with dislocation creep rate. Allowances can also be made for slow surface diffusion producing crack-like cavities [9, 10].

The net result of the modifications is to describe cavity growth rates, either change in volume or grain-boundary area occupied, which correlate with a higher power of stress than unity and which are usually *faster than the grain-boundary vacancy diffusion mechanism alone*. Whilst this may provide a description of some single-phase metals it is certainly not true for many precipitatehardened alloys. This fortunate state of affairs manifests itself in growth rates which can be several orders of magnitude below rates predicted by grain-boundary diffusion [5, 7].

The growth rates can be reduced by geometri-

cally necessary accommodation creep strain between grains provided certain conditions are met [11]. If the cavities are not distributed evenly between boundaries then the displacement across the grain boundary resulting from cavity growth has to be accommodated by creep elsewhere. Provided the polycrystal is deforming by diffusion creep or at least is in the transition region with dislocation creep, the cavity growth may be accommodation controlled [12]. Accommodation is not necessary in bicrystals. Diffusion-controlled cavity growth has been found in bicrystals whilst being inhibited in polycrystals in the same precipitatehardened system [5, 13].

Geometrical constraint in neighbouring grains occurs when the accommodation of cavity volume by creep is slower than the mechanism actually creating the cavity. This condition can be met when both creep and cavity growth are diffusion controlled. However, diffusion creep is repressed in many precipitate-hardened alloys and it is possible that diffusion-controlled cavity growth is similarly inhibited. In this case the role of geometrical accommodation by creep is no longer clear cut.

The inhibiting effect of refractory particles may stem from the nature of the particle/matrix interface. Although vacancies can be created at the particle/matrix interface, it appears that vacancies are not created as freely as in the grain boundary [14]. The interfacial effects are known to limit the mobility of small particles particularly when the particle has a high melting point. The nature of the interfacial barrier for vacancy creation has been discussed by several authors often with reference to diffusion creep or particle dragging [15, 16].

The effect of particles on pore growth can be discussed by considering a cavity growing by a combined diffusive/dislocation process [8] with grain-boundary precipitates nearby. Provided the applied stress is sufficiently high, vacancies are created mainly adjacent to the cavity and diffuse to its surface. The displacement caused by vacancy creation is matched by dislocation creep further away from the cavity. In this respect the grainboundary precipitate and any fine dispersion of precipitates in the matrix provide resistance to dislocation creep. On lowering the stress, the vacancy creation zone expands until ultimately it closely approaches the precipitate. If now, we assume, as indicated earlier, that vacancies are not readily created at the matrix/particle interface, then the matrix around the particle must still creep to accommodate the grain-boundary displacements. Such a model has been considered previously in which the localized creep is produced by the punching of dislocation loops [17]. Similar models also consider the stress to be concentrated at the particle [18]. The particles often occupy a small fraction of the total grain-boundary area. The assumption implies that large stresses can be locally generated which easily punch loops thus producing a relatively small inhibition effect.

The present paper considers the assumption regarding stress concentrations over particles during cavity growth. The stress concentration is initially considered to extend onto the boundary adjacent to the particle. Vacancy diffusion fluxes and matrix creep around precipitates are coupled to establish if the arbitrarily chosen stress profile is stable. Large stress concentrations over particles are justified if the stress concentration profile sharpens up over the particles. Otherwise a tendency for the concentration profile to broaden will reduce the stress over the particle and hence reduce the rate of loop punching and localized dislocation creep. The analysis initially considers the boundary to be a perfect source for vacancies. This assumption is later shown to lead to inconsistencies. An alternative approach to the cavity growth problem is then suggested.

2. Stress profile on a boundary behaving as a perfect source for vacancies

Following a previous analysis [8], the normal boundary stress acting across a boundary containing a cavity is illustrated in Fig. 1. In region I, vacancy creation and diffusion in the grain boundary dominates grain displacement. The grains on adjacent sides of the boundary move apart at a rate dependent on the vacancy creation rate which is equivalent to the second derivative with distance of the normal boundary stress. In region II, dislocation creep dominates boundary displacements and few vacancies are created. Hence the second derivative of stress approaches zero and the stress is sensibly constant. The simultaneous existence of both regions requires that the displacement rate of material above regions I and II is equal, that the normal boundary stress should be continuous and sum to a force equal to the combined effect of applied load, internal gas pressure and surface tension restraint.



Figure 1 The cavity is growing by collecting vacancies created in region 1 of the grain boundary. The displacements in region 1 resulting from vacancy creation are accomodated in region 2 by dislocation creep.

The dislocation creep mechanism is more sensitive to stress than the diffusion mechanism. Decreasing the applied stress decreases the displacement rate above region II faster than above region I. The imbalance is corrected by increasing the size of region I. This increases the length of the diffusion path and decreases the vacancy flux, the cavity growth rate and hence also the displacement rate. In the absence of precipitates, decreasing the applied stress eventually causes adjacent diffusion-controlled regions to impinge. The cavity growth rate is then predicted to be entirely diffusion controlled.

Previously it was argued that the ability of the matrix/particle interface to create vacancies can be much reduced in comparison with a grain boundary. In this case when the grain boundary between cavities contains a precipitate the displacements in the region of the precipitate must be always matrix creep-controlled however low the applied stress. Creep requires that the stress in the matrix above the particle must be larger than the stress on the boundary. It is inevitable that shear in the matrix will cause the normal boundary stress to increase on the grain boundary adjacent to the precpitate (Fig. 2a).

The first derivative with distance of the boundary stress is proportional to the flux of vacancies. Since the production rate of vacancies will be assumed zero over the particle, the gradient of the boundary stress is zero at the particle. The stress can be discontinuous on moving from the matrix to the particle interior since the elastic constants differ. However, the analysis considers matrix creep and in the matrix the stress is continuous. For convenience the stress is assumed constant over the particle.

The second derivative of boundary stress with



Figure 2 An arbitary boundary stress profile is illustrated in which stress is concentrated over a precipitate decorating the boundary, this form of stress profile implies that a boundary acting as a "perfect" vacancy source is also a vacancy sink.

distance is negative in region I (Fig. 2a) changes to a positive value in region II before becoming negative again on approaching the precipitate. The creation rate of vacancies is proportional to the second derivative of normal boundary stress. Increasing the stress over the precipitate creates a localized source and sink for vacancies (Fig. 2b). The analysis now assesses the effect semiquantitatively.

3. Numerical analysis (one-dimensional)

Let the cavity have a radius a_1 , the particle a radius a_2 and let the plating zone extend a distance b_1 from the cavity surface (Fig. 2a). If the distance between the centres of cavity and precipitate is c then $c = a_1 + a_2 + b_1 + b_2$ where b_2 is the size of region II. The local displacement velocity between grains in region I due to vacancy creation is $\beta_1 \Omega$, where Ω is the atomic volume. Assuming equilibrium between normal boundary stress and vacancy concentration the one-dimensional differential equation relating normal stress and displacement velocity is given by

$$\frac{\mathrm{d}^2 \sigma_1}{\mathrm{d} x_1^2} + \beta_1 \frac{kT}{D_{\mathsf{g}} \delta} = 0, \ 0 \leqslant x_1 \leqslant b_1, \qquad (1)$$

where σ_1 is the normal boundary stress and β_1 the creation rate of vacancies in region one, x_1 the distance along the boundary measured from the pore surface, D_g the grain-boundary diffusion coefficient, δ the grain boundary width, and kT the thermal energy.

Initially it is assumed that the vacancy source and sink immediately outside the precipitate are of equal strengths. Hence the vacancy flux between regions I and II is zero

$$\left. \frac{\mathrm{d}\sigma_1}{\mathrm{d}x_1} \right|_{b_1} = 0. \tag{2}$$

The normal boundary stress matches the surface tension restraint at the cavity

$$\sigma_1(x=0) = \gamma/a_1 \tag{3}$$

where γ is the surface tension. The solution of Equation 1 subject to the Conditions 2 and 3 is

$$\sigma_1 = \frac{\gamma}{a} + \beta_1 \frac{kT}{D_g \delta} \left(b_1 x_1 - \frac{x_1^2}{2} \right).$$

Initially it is assumed that stress is concentrated over the precipitate and extends onto the boundary a short distance. Reference to Fig. 2b

shows that the second derivative $(d^2\sigma/dx^2)$, is initially negative near the cavity but must change sign in the region where the stress increases sharply. On approaching the precipitate the second derivative reverts to a negative value again. The latter condition is necessary because vacancies are not created on the precipitate and the vacancy flux $(\alpha d\sigma/dx)$ is zero at the precipitate. The form of the vacancy creation rate around the precipitate is not known but the consequences of the argument can be discussed semi-quantitatively by assuming a simple form for the vacancy creation rate. The fluxes in region II can be localized by assuming a vacancy creation rate of the form $\beta_2 x_2 (x_2 - x_2)$ $(b_2/2)(x_2 - b_2)/(b_2/2)^3$, where x_2 is measured from the precipitate. This ensures that the stress undergoes inflections at the points $x_2 = 0$, $b_2/2$, b_2 . The creation rate is symmetric about x = $b_2/2$ and the vacancies created in the region $0 \le x_2 \le b_2/2$ are exactly annihilated in the region $b_2/2 \leq x_2 \leq b_2$. The maximum and minimum vacancy creation rates are at $x_2 = (1 \pm 1/\sqrt{3})b_2/2$ at which points the value is $\pm 2\beta_2/3\sqrt{3}$. The differential equation is

$$\frac{\mathrm{d}^2 \sigma_2}{\mathrm{d}x_2^2} + \beta_2 \frac{kT}{D_{\mathrm{g}}\delta} \frac{8x_2(x_2 - b_2/2)(x_2 - b_2)}{b_2^3} = 0,$$
$$0 \le x_2 \le b_2$$

and the solution subject to the conditions

$$\frac{\mathrm{d}\sigma_2}{\mathrm{d}x_2}\Big|_{b_2} = 0$$

$$\sigma_2(x_2 = b_2) = \sigma_1(x_1 - b_1)$$

is given by

$$\sigma_{2} = \frac{\gamma}{a_{1}} + \beta_{1} \left(\frac{kT}{D_{g}\delta}\right) \frac{b_{1}^{2}}{2} + \beta_{2} \left(\frac{kT}{D_{g}\delta}\right) \left(-\frac{2b_{2}^{2}x_{2}^{3}}{3} + b_{2}x_{2}^{4} - \frac{2x_{2}^{5}}{5} + \frac{b_{2}^{5}}{15}\right) \frac{1}{b_{2}^{3}}.$$
(4)

The stress over the plating zone and around the precipitate must equal the applied load. If σ is the externally applied tensile stress and the boundary is normal to this stress, then balancing forces gives the equation below.

$$(a_1 + b_1 + a_2 + b_2)\sigma - \gamma = \int_0^{b_1} \sigma_1 \, dx_1 + \int_0^{b_2} \sigma_2 \, dx_2 + a_2 \sigma_2(0).$$

The stress over the particle has been considered where σ_0 is a threshold stress given by constant. Integration gives the result

$$c\left(\sigma - \frac{\gamma}{a_{1}}\right) = \beta_{1} \left(\frac{kT}{D_{g}\delta}\right) \left(\frac{b_{1}^{3}}{3} + \frac{b_{1}^{2}b_{2}}{2} + \frac{b_{1}^{2}a_{2}}{2}\right) + \beta_{2} \left(\frac{kT}{D_{g}\delta}\right) \left(\frac{b_{2}^{3}}{30} + \frac{b_{2}^{2}a_{2}}{15}\right).$$
(5)

Initially region II is arbitrarily confined to the zone $b_2 = 2a_2$. Equation 5 then reduces to

$$c\left(\sigma - \frac{\gamma}{a_1}\right) = \beta_1 \left(\frac{kT}{D_g \delta}\right) \left(\frac{b_1^3}{3} + \frac{3b_1^2 b_2}{4}\right) + \beta_2 \left(\frac{kT}{D_g \delta}\right) \frac{b_2^3}{15}.$$
(6)

The excess stress over the precipitate must be capable of driving the dislocation creep process at a rate commensurate with the vacancy creation rate on the boundary. The displacement rate next to the precipitate now has a maximum value of $2\beta_2 \Omega/3\sqrt{3}$. The rapid increase in stress on approaching the particle can increase the rate considerably above the value $\beta_1 \Omega$ nearer the cavity. If the material deforms by a power law process of the type $\dot{\epsilon} = B\sigma^n$ then the displacement rate by power law creep equals the displacement rate by vacancy creation when the following applies:

$$\left(\frac{b_2}{2}\right)B\left(\sigma_2(0)-\sigma_2(b_2/2)\right)^n\approx\frac{2}{3\sqrt{3}}\beta_2\Omega.$$
 (7)

The decrease in stress on moving from $x_2 = 0$ to $x_2 = b_2/2$ can be found from Equation 4. Putting b_2 equal to $2a_2$ then from Equations 4 and 7 the vacancy creation rate in region II is given by

$$\beta_2^{n-1} \approx \frac{2}{3\sqrt{3}} \frac{\Omega}{a_2 B} \left(\frac{15 D_g \delta}{2k T a_2^2} \right)^n. \tag{8}$$

The growth rate of the cavity dA/dt is given by

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \beta_1 \Omega(a_1 + b_1). \tag{9}$$

When the precipitate is small compared to the precipitate/cavity spacing, c is approximately equal to b_2 . Then from Equations 6, 8 and 9 the growth rate is given by the equation

$$\frac{\mathrm{d}A}{\mathrm{d}t} \approx 3 \frac{D_{\mathrm{g}} \delta \Omega}{kTc} \left(\sigma - \frac{\gamma}{a_{1}} - \sigma_{\mathrm{o}} \right),$$

$$\sigma_0 \approx \frac{4}{c} (a_2)^{(n-4)/(n-1)} \left(\frac{5}{\sqrt{3}} \frac{D_{\rm g} \delta \Omega}{BkT} \right)^{1/(n-1)} . (10)$$

The above formulae have been calculated by matching the upward displacement in the region $b_2/2 > x_2 > 0$ (Fig. 2) due the vacancy creation with dislocation creep over the particle. Further away from the particle the displacement is reversed, and material on adjacent sides of the boundary is moving together. This displacement is not matched by dislocation creep since compressive forces would be required. The conclusion is that the negative displacement at the vacancy sink causes the stress to rise in the interval $b_2 >$ $x_2 > b_2/2$. Since the integrated stress must equal the applied load, the stress over the precipitate drops and the stress concentration broadens.

Compressive forces cannot develop on the boundary since they would be unstable. Consider, for instance, a third region between regions I and II in which the second derivative of stress is positive (vacancy sink) and the stress is compressive. Now let the compressive stress decrease slightly. This will decrease the vacancy sink displacement rate in an approximately linear fashion. The dislocation creep displacement rate decreases faster for a typical material with a high creep exponent. The mismatch between the two rates is in the direction that decreases the compressive stress still further. Eventually the stress becomes tensile and the stress concentration broadens as argued previously.

The threshold stress calculated previously (Equation 10), was based on the initial assumption of a local stress concentration around the precipitate. It has been argued that the concentration profile tends to broaden. The maximum broadening occurs when region II occupies the whole of the available boundary (Fig. 3). The cavity growth rate in this extreme will be zero since diffusive fluxes are directed solely to accommodating plastic flow around the precipitate. The applied stress can be found by letting b_2 increase to a value $(c - a_1 - a_2) \sim c$. The analysis can be repeated in an analogous way to obtain the applied stress when the dislocation creep rate balances the vacancy creation rate over the region $b_2/2 > x_2 > 0$. This applied stress is given by

$$\sigma - \frac{\gamma}{a_1} = 2 \left(\frac{40}{\sqrt{3}} \frac{D_g \delta \Omega}{BkTc^3} \right)^{1/(n-1)}$$



The latter stress is larger than the previous value (Equation 10). However, the problem of a stable stress distribution has still not been solved since the vacancy sink will still tend to increase the stress in the region $b_2/2 < x_2 < b_2$. If the tensile stress is allowed to increase further then a situation is eventually reached in which the second derivative of normal boundary stress with distance changes sign. The boundary is then no longer a vacancy sink and the second derivative is everywhere negative. This is now the situation envisaged in the *Introduction* when describing the changeover

between vacancy diffusion and dislocation creep control (Fig. 4). It was argued that on decreasing the applied stress the diffusion-controlled zone increased in size until the precipitate was encountered. On lowering the stress still further the dislocation creep displacements could only be matched with vacancy creation rate displacements if some form of stress concentration was allowed over the precipitate. However, the stress concentrations have been found to be unstable. Rapid vacancy diffusion tends to even out inflections in the grain-boundary stress profile.



Figure 4 The stress profile when the entire boundary acts as a vacancy source. This situation depicts the minimum applied stress for which a solution 'is available for the combined diffusion/dislocation creep problem.

Figure 3 The stress concentration over the particle can be broadened until limited by the necessary stress $(2\gamma/a)$ adjacent to the cavity.

4. Mechanisms of vacancy creation in the boundary

The analysis has considered coupled grain-boundary diffusion and dislocation creep processes operating in the region of a cavity and a precipitate. The only stress distribution found to be stable was one which always had a negative second derivative of normal boundary stress with distance. This implies that the boundary is everywhere a vacancy source. In addition, a localized stress concentration cannot exist anywhere on the boundary. The dislocation creep displacement rate can be matched with the vacancy creation displacement rate only above a certain applied stress. On lowering the applied stress the critical stress is reached when the diffusive plating zone, extending from the cavity, closely approaches the precipitate. Below the critical stress no stable solutions were found to the coupled diffusion/dislocation creep model. Many different types of stress profile were tried but are not reported here. Clearly this does not constitute a proof that a solution does not exist, but the arguments regarding the positive values of the second derivative can be made quite general. The analyses always led to the conclusion that the two deformation processes could not be coupled below a critical stress.

Obviously stress distributions across the boundary do exist below the threshold stress but the initial set of assumptions embodied in the analysis do not allow a description. The initial assumptions were assessed. The likely candidate to be invalidated in the present application is the condition of equilibrium on the boundary. This maintains that the excess vacancy concentration is proportional to the normal tensile stress. This has been validated in pure materials by diffusion creep experiments. However, in precipitate-hardened materials diffusion creep can be inhibited. In this case it is likely that the boundaries are not perfect sources of vacancies. The mechanism of inhibition is unlikely to involve areas of a boundary which behave perfectly containing small particles acting as poor vacancy sources. This leads to stress concentrations above the particles. Rapid vacancy diffusion, even by volume diffusion, will tend to flatten out the stress profile as discussed earlier.

Alternatively, the entire area of boundary may be a poor source of vacancies. This situation can be envisage if vacancies need to be created at a line source with dislocation character. The motion of the dislocations in the boundary will, in general, involve a combination of glide and climb. The velocity of a dislocation climbing along the boundary depends on the *net* stress acting on the dislocation. If an edge dislocation moves in a pure climb mode along the boundary, the rate of working by the applied forces per unit length of dislocation must equal the energy dissipated as heat when the dislocation moves. If the dislocation is one of an array climbing along the boundary, forces are balanced by the equation

$$\frac{V'}{B'} = \sigma b - \sum_{i} \sigma_{i} b - \frac{kTb}{\Omega} \ln\left(\frac{c}{c_{0}}\right) \qquad (11)$$

where B' is the mobility of the dislocation, c is the vacancy concentration, c_0 the concentration at an unstressed boundary acting as a perfect source, and the summation represents the interaction stresses between dislocations in the array. In the absence of obstacles the dislocation array climbs uniformly, the dislocation spacings are equal, and the summation is zero. Experimentally observed interfacial effects are small in singlephase materials. Hence (V'/B') is small and from Equation 11 the normal boundary stress is given by the usual form $\sigma = (kT/\Omega) \ln (c/c_0)$.

Precipitates impede the motion of the dislocations in the boundary. Continued dislocation climb can be achieved by bowing round the precipitates leaving behind dislocation loops around the precipitate. The continued operation of dislocation climb in the boundary depends on the removal of the dislocation loops around the precipitate. Many loops form a dislocation pile up but the stresses at the head will be relaxed by matrix plasticity below the stresses calculated for elastic dislocation pile ups. The summation term in Equation 11 will now be significant and the "equilibrium" vacancy concentration will be below the value for a "perfect" boundary.

If the stress at the particle is sufficiently large, the dislocation loops may be removed by loop punching or alternatively by dislocation climb in the particle/matrix interface. Quantifying this type of model is difficult because the relationship between normal boundary stress and excess vacancy concentration is now not known. The stress over the particle, the vacancy concentration in the boundary and the dislocation configuration in the boundary are all intimately connected.

An alternative approach is to consider the number of dislocations entering the boundary

from the matrix due to dislocation creep. Observations suggest that lattice dislocations can enter the boundary where they may form partials or combine with other dislocations before climbing in the boundary plane [19, 20]. In steady state the density of boundary dislocations remains constant. Later it is shown that dislocations must re-enter the lattice elsewhere. This model is similar to one proposed earlier but has been quantified and modified to incorporate the effect of precipitates [21].

Creep control of vacancy creation/ annihalation in boundaries

Dislocation creep in the matrix inevitably results in some dislocations entering grain boundaries where they may climb a short distance before being re-emitted into the matrix. The problem is to quantify the vacancy production rate in the boundary for a given plastic strain in the matrix.

Consider a block of material containing dislocations having their glide plane parallel to the 1-axis (Fig. 5). During creep dislocations glide until their motion is impeded by an obstacle. The dislocation may climb a small amount to release itself before repeating the glide step. Although the creep may be controlled by the climb process the bulk of the plastic deformation is glide. Ignoring the smaller climb contribution, the strain rate in the square block (Fig. 5) due to dislocations of density, ρ , with Burger's vector, \boldsymbol{b} , moving at an average velocity, V, is

$$\dot{\boldsymbol{\epsilon}}_{12} = \rho \boldsymbol{V} \boldsymbol{b}.$$

All other strains in the block are considered negligibly small. If the block is orientated at an angle θ to the specimen axes the specimen strains

are given by

$$\dot{\epsilon}_{2'2'} = \dot{\epsilon}_{12} \sin \theta \cos \theta$$
$$\dot{\epsilon}_{1'2'} + \dot{\epsilon}_{2'1'} = \dot{\epsilon}_{12} (\cos^2 \theta - \sin^2 \theta).$$

The material will have more than one operative glide plane and for m glide planes we have

$$\dot{\epsilon}_{2'2'} = \sum_{i}^{m} \rho_{i} V_{i} \boldsymbol{b}_{i} \sin \theta_{i} \cos \theta_{i}$$

$$\dot{\epsilon}_{2'1'} + \dot{\epsilon}_{1'2'} = \sum_{i}^{m} \rho_{i} V_{i} \boldsymbol{b}_{i} (\cos^{2} \theta_{i} - \sin^{2} \theta_{i})$$
(12)

In the matrix, volume is conserved hence $\dot{e}_{2'2'} + \dot{e}_{1'1'} = 0$ and since rotations are not considered, only the symmetric form of the strain tensor need be used. Thus at least two independent glide systems are needed to satisfy Equations 12. (In three dimensions at least five independent glide systems are needed to satisfy the five equations as required by the Von Mises condition.)

When lattice dislocations enter the boundary they may dissociate. The climb of all the dissociated dislocations produces the same net translation as the original dislocation. Hence to find the net translation we need only consider the nature of the dislocations entering the boundary. This ignores the motions of internally generated grain-boundary dislocations. The precipitates are assumed to block the dislocation generation mechanism in the boundary. The sum of the normal components of dislocation Burger's vectors entering the boundary can be shown to be nonzero. In steady state the dislocation density remains constant, hence dislocations are also re-emitted from the boundary.



Figure 5 Dislocation in the matrix enter the boundary (shown dashed) during the course of creep. In the boundary the dislocations climb a distance l before being re-emitted into the matrix. If dislocations in the boundary climb a distance l before being re-emitted, then on average, in time dt, half the dislocations in the parallelogram of sides l and Vdt (Fig. 5) will pass through the point x. The other half share the same glide plane but move in the opposite direction. Since an equal number enter the boundary from above, the normal motion of the boundary at the point x is

$$\dot{n} = \sum_{0 < \theta < \pi}^{m} \rho |V| b l \sin^2 \theta.$$
 (13)

The positive value of V is taken to sum correctly the contributions from different climb directions in the boundary. The resolved shear stress on the dislocations is given by

$$\sigma_{12} = (\sigma_{2'2'} - \sigma_{1'1'}) \sin \theta \cos \theta + \sigma_{1'2'} (\cos^2 \theta - \sin^2 \theta).$$

Thus for uniaxial deformation $(\sigma_{1'1'} = \sigma_{1'2'} = 0; \sigma_{2'2'} = \sigma)$, V is positive in the interval $0 < \theta < \pi/2$ and negative in the interval $\pi/2 < \theta < \pi$.

Equations 12 and 13 may be simplified by taking average values for the angles of the glide planes. In the case of uniaxial strain, the velocity V changes sign as discussed above and the geometrical terms in the summation for the shear strain rate (Equation 12), becomes zero as required. The average values for the uniaxial strain rate (Equation 12), and the normal velocity (Equation 13), become

$$\dot{\epsilon}_{2'2'} = \frac{2}{\pi} \rho |V| \boldsymbol{b}$$
$$\dot{\boldsymbol{n}} = \frac{1}{2} \rho |V| \boldsymbol{b} l.$$

Putting $\dot{e}_{2'2'} = \dot{e}'$ the strain rate immediately above the boundary, the normal motion of the boundary is given by

$$\dot{n} = \frac{\pi}{4} \dot{\epsilon}' l. \tag{14}$$

The average values for the summations may also be found for a matrix deforming in pure shear. In this case the normal boundary motion is found to be zero. Similarly a boundary parallel to the stress direction during tensile deformation is a vacancy sink.

6. Cavity growth

The previous section calculated the normal motion of the boundary resulting from dislocation climbcreating vacancies. The vacancies were produced solely by dislocations entering the boundary from the matrix and climbing a short distance before being re-emitted. Dislocations created internally in the boundary will also be capable of climbing and creating vacancies but in boundaries decorated with precipitates it is assumed, at least for the present, that this mechanism is blocked. It will also be assumed that the matrix dislocations on entering the boundary climb on average a distance equal to the precipitate spacing 2λ before being re-emitted. The validity of the assumptions will later be checked by comparison with experiment.

The rate of increase in volume of cavities $\dot{\nu}$, is given by the change in volume associated with an area of boundary πc^2 , where c is the cavity half-spacing.

$$\dot{\nu} = \pi c^2 \dot{n}$$
$$= \frac{\pi^2}{2} c^2 \lambda \dot{\epsilon}'. \qquad (15)$$

The creep rate required in Equation 15, $\dot{\epsilon}'$, is local to the boundary. It will differ from the far field creep rate due to the effect of the porosity.

If σ is the applied stress and σ_l the average stress local to the boundary, balancing forces gives

$$\sigma c^2 = \sigma_l (c^2 - a^2) + 2a\gamma \qquad (16)$$

where a is the cavity radius, γ the surface energy, and c the cavity half-spacing. Rearranging Equation 16 gives

$$\sigma_l - \frac{2\gamma}{a} = \left(\frac{c^2}{c^2 - a^2}\right) \left(\sigma - \frac{2\gamma}{a}\right).$$

The relationship between the far field creep rate $\dot{\epsilon}$ and the local creep rate $\dot{\epsilon}'$ will be

$$\dot{\epsilon}' \approx \dot{\epsilon} \left(\frac{c^2}{c^2 - a^2}\right)^n \left(1 - \frac{2\gamma}{a\sigma}\right)^n,$$
 (17)

where n is the creep exponent for power law creep. Finally the rate of change of volume from Equations 15 and 17 is

$$\dot{\nu} \approx \frac{\pi^2}{2} c^2 \lambda \dot{\epsilon} \left(\frac{1 - 2\gamma/a\sigma}{1 - a^2/c^2} \right)^n.$$
(18)

7. Discussion

Equation 18 describes the growth rate of a cavity due to lattice dislocations entering the grain boundary and climbing a short distance before being re-emitted. The rate-limiting step is taken to be the supply rate of dislocations from the creep process in the matrix. The cavity grows by



the agglomeration of vacancies but the vacancy supply is controlled by dislocation creep. Vacancies created during dislocation climb diffuse rapidly to the cavities. The latter requirement will be true provided the diffusion-controlled vacancy growth rate is faster than the creep-limited creation rate. The diffusion-limited rate has been calculated by many authors for the case of grain boundaries acting as perfect sources of vacancies. However, in this form of diffusion control the boundaries will have a slightly reduced efficiency for vacancy creation. The models for perfect source behaviour are a useful upper bound for diffusion ratecontrolled growth and will be used in a comparison of growth rates. Several very similar expressions have been derived for the latter growth rate and the following is used solely from familiarity [22],

$$\dot{\nu}_{\rm d} = \frac{8\pi D_{\rm g} \delta \Omega(\sigma - 2\gamma/a)}{kT (4 \ln (c/a) - (1 - a^2/c^2)(3 - a^2/c^2)},$$
(19)

Figure 6 The cavity growth rate predicted for four mechanisms operative in a copper silica alloy at 500° C.

where $\dot{\nu}_{d}$ is the diffusion controlled growth rate, D_{g} the grain-boundary diffusion coefficient, δ the grain-boundary width and Ω the atomic volume.

At higher stresses the growth rate is again controlled by plastic deformation of the matrix. This time the growth is solely by plastic strain and does not involve vacancy agglomeration. The rate of change of cavity radius for this process is given by $\dot{a} \sim a\dot{e}/2$ [23]. Incorporating approximately the effect of cavity interaction gives the equation

$$\dot{\nu}_{\mathbf{p}} \approx 2\pi a^{3} \dot{\epsilon} \left(\frac{1 - 2\gamma/a\sigma}{1 - a^{2}/c^{2}} \right)^{n}.$$
 (20)

Finally, cavity growth can be controlled by geometrical creep constraint of surround grains [11]. The following expression describes the constrained growth rate for power law creep [12]

$$\dot{\nu}_{\rm c} = 2\lambda^2 d\dot{\epsilon} \exp\left(\frac{(n-1)\ln 10}{5}\right),$$
 (21)

where d is the grain size.



Figure 7 The cavity growth rate predicted for four mechanisms operative in a copper silica alloy at 700° C.

The four mechanisms described by Equation 18 to 21 were compared for a copper/silica alloy [5]. The creep rates employed in the calculations were taken from the experimental data. The precipitate sizes and spacings were known. The grain-boundary diffusion coefficient was taken from an analogous study of cavity sintering [24].

Fig. 6 shows the calculated growth rate for a copper-silica specimen crept at 500° C. Small cavities are predicted to grow by the creepcontrolled vacancy growth process at low stresses. This process is very stress sensitive and at higher stresses the climb rate of boundary dislocations becomes limited by vacancy diffusion. The control mechanism now changes to diffusion-controlled vacancy growth. The two vacancy growth processes are sequential and the slower controls. Increasing the stress further changes the control mechanism from diffusion to plastic growth as has been discussed previously. The latter two mechanisms behave like independent mechanisms and the faster is rate controlling.

Closer examination of the vacancy diffusion

and plastic growth mechanism reveals considerable interaction, and in the changeover region the growth rate is faster than the sum of the two rates [8]. Since in the present discussion the interaction effects are not known, none of the growth rates are summed, although the true growth rate will have a smooth transition between control mechanisms.

When cavities are large and interacting, cavity growth is controlled by geometrical creep constraint. This mechanism acts in a sequential manner with the other growth mechanisms. The approximations in the growth rates Equations 18 to 21 are least satisfactory for large closely spaced cavities. The extent of the constrained region is subject to some uncertainty.

The correct choice of growth control mechanism does not depend on the fastest mechanism since the mechanisms share mixed sequential/ independent type relationships between each other. The correct choice can be made by first considering the two sequential-type processes: creep-controlled vacancy growth and diffusion-



Figure 8 The predicted ducility for various creep exponents and initial pore sizes is compared with the experimental data.

controlled vacancy growth. The slower of the two need only be considered further. Next compare this rate with the vacancy-independent plastic growth rate. These act independently and the faster of the two is considered. Finally, the three direct growth mechanisms act sequentially with geometrical creep constraint. One of the direct growth mechanisms will be rate controlling provided the geometrical creep constraint mechanism is faster.

The cavity growth rate in the copper/silica alloy has also been calculated for a higher temperature (Fig. 7). The operative regions assigned to each mechanism remain roughly the same although the absolute growth rate increases. Also indicated in Figs. 6 and 7 is the stress range open to experimentation. At lower stresses observations are inconveniently long and at higher stresses other failure mechanisms become operative.

The calculations indicate that in the experimental region much of the growth is controlled by the creep-controlled vacancy growth mechanism. Diffusion-controlled vacancy growth and plastic growth will be operative for a short time near fracture. At lower stresses control can change from creep-controlled vacancy growth directly to geometrical constraint. In this case the component will spend almost its entire life in the creepcontrolled vacancy growth region. The strain to failure et_f , where t_f is the lifetime, can be found by integrating Equation 18

$$\dot{\epsilon}t_{\rm f} = \frac{8}{\pi} \int_{a_0}^{c} \frac{a^2}{c^2} \left(\frac{1-a^2/c^2}{1-2\gamma/a\sigma}\right)^n \frac{\mathrm{d}a}{\lambda} \,.$$

This assumes that all cavities are initially present and of size a_0 . The above formula has been applied to the copper/silica data and is illustrated in Fig. 8. Cavities were produced by prestraining prior to creep. The value of a_0/λ has been put equal to the ratio of the precipitate radius to spacing. The creep exponent varied with temperature and has a considerable effect on the lifetime. The experimental observations and the theoretical predictions show similar trends. The observed variation of lifetime with a_0/λ and n is predicted by theory to change in a similar fashion.

The creep-controlled vacancy growth mechanism outlined in the present paper may prove useful in assessing cavity growth in creep-resistant alloys. Calculating the vacancy production rate depends on relating the plastic strain local to the boundary with the specimen strain. In bicrystal experiments, unconstrained sliding on the grain boundary may result in an excess vacancy production and a growth rate limited by diffusion. In addition, creep-controlled vacancy generation mechanism does not include other grain-boundary dislocation sources. If, for instance, the boundary is free of precipitates and the climb distance l in Equation 14 is put equal to the grain size, the vacancy production rate is too low to observe diffusion creep. In this case the dislocation sources in the boundary are not blocked by precipitates and can supply dislocations. The present theory could be modified to incorporate specific effects but this is probably unwarranted until further comparisons have been made with experiments.

One present difficulty in interpreting the copper/silica rupture data [5] lies in assigning initial values to the cavity size and spacing immediately after nucleation. The observed trend in life-time was predicted by assuming cavity nuclei equal in size to the particles although this relationship may not be exact. Also the operation of the creep-controlled vacancy growth mechanism requires that some part of the precipitate remains in contact with the boundary. This could be achieved by the cavity growing solely to one side of the precipitate or for some precipitates to be free of cavities.

If the precipitates are all associated with cavities such that they are attached to part of the cavity surface not containing the grain boundary then the creep-controlled vacancy mechanism is inoperative. In this case pore growth is likely to be limited by geometrical creep constraint in dispersion-hardened materials. An interesting situation can now develop in such a material containing a crack. Rapid grain-boundary diffusion tends to decrease the normal stress acting across boundaries containing pores thus increasing the effective crack size. The crack is expected to propagate rapidly down cavitated boundaries in a brittle fashion. The sensitivity to crack propagation may prove a useful method of assessing cavity growth mechanisms which inhibit vacancy diffusion in precipitate-hardened materials.

8. Conclusions

(1) At intermediate stresses, cavities on grain boundaries acting as perfect vacancy sources and containing precipitates can grow by vacancy agglomeration. Boundary displacements resulting from vacancy creation can be matched with dislocation creep displacements in the matrix around the boundary precipitates.

(2) Below a threshold stress, this model cannot describe boundary diffusion. If vacancies are created solely at dislocations climbing in the boundary, precipitates will impede dislocation motion. In this case boundaries will be imperfect sources of vacancies. At sufficiently low stresses the arrival rate of vacancies at the cavities depends not on the diffusion rate from the dislocations but on the availability of climbing dislocations.

(3) Dislocations moving in the matrix as a result of creep intersect the grain boundary. In the boundary the lattice dislocation dissociates and climbs a distance roughly equal to the precipitate spacing before being re-emitted to the matrix. This process releases vacancies on boundaries under normal tension.

(4) In the creep-controlled vacancy growth regime, the growth rate of cavities of radius a, half-spacing c, is given by

$$\dot{\nu} \approx \frac{\pi^2}{2} c^2 \lambda \dot{\epsilon} \left(\frac{1 - 2\gamma/a\sigma}{1 - a^2/c^2} \right)^n,$$

where λ is the precipitate half-spacing, $\dot{\epsilon}$ the distant creep rate, γ the surface energy and σ the applied stress. The strain to failure is given by

$$\dot{\epsilon}t_{\mathbf{f}} = \frac{8}{\pi} \int_{a_0}^c \frac{a^2}{c^2} \left(\frac{1-a^2/c^2}{1-2\gamma/a\sigma} \right)^n \frac{\mathrm{d}a}{\lambda} \,.$$

The strain to failure is sensitive to the creep exponent, n, and the initial cavity size after nucleation a_0 .

(5) Four cavity growth control mechanisms were discussed for a copper/silica alloy. At low stresses the operative mechanism for small cavities is creep-controlled vacancy growth. The growth of larger cavities is controlled by geometrical creep constraint of neighbouring grains.

At higher stresses growth becomes limited by vacancy diffusion or plastic deformation without vacancy fluxes.

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