

Lecture 9 Grain Boundary Cavitation

Accelerated tests. Subject to a stress at a high temperature, will a polycrystal creep continuously or rupture? We have talked about diffusional creep, and will now look at rupture. Let's say you want to design a component, with a new alloy, to last ten years. Nobody has done this before with this new alloy, so it's an innovation. But you don't know the levels of stress and temperature that the new alloy can sustain without rupture in ten years. You don't want to test it out in ten years, either. To *accelerate* the test, you subject the alloy to temperatures and stresses higher than the service conditions. Question: how should you use the data from such accelerated tests to *project* the rupture time under the service conditions?

The rupture time, t_r , is a function of the applied stress, σ , and the temperature, T . After several tests at high stress and temperature levels, which rupture the alloy in short times, you discover that the rupture times approximately takes the functional form:

$$t_r = A\sigma^{-n} \exp(q / kT).$$

Here A , n and q are the constants that best fit the experimental data; they are assumed to be independent of the stress and the temperature. The activation energy q is determined by the data at several temperatures at a constant stress, and the stress exponent n is determined by the data at several stresses at a constant temperature. The coefficient A is determined from either set of the data. On the basis of the data obtained in days or weeks, you decide that you will extrapolate the data to lower stress and temperature levels that *would* rupture the alloy in ten years. You hope that the empirical formula holds true in a stress-temperature regime that you have not tested.

Mechanistic models. Mechanistic models will answer the following questions. (1) Is the empirical formula good enough for extrapolation? (2) What is the physical significance of the fitting parameters?

Subject to a stress, the material spends its lifetime to first nucleate voids, and then grow them. Rupture occurs when voids coalesce. The nucleation process is poorly understood. It is entirely possible that voids exist in the material due to the manufacturing process. In any case, to be conservative, we simply neglect the time needed to nucleate the voids, and estimate the lifetime as the time needed for small voids to grow to coalesce. Our models will assume that initially the material contains voids of radius R_0 , separated by spacing 2λ . We set the lifetime to be the time for the voids to grow from radius R_0 to radius λ .

Cavitation by lattice diffusion. Let's start with the model in the previous lectures. Atoms only diffuse in the crystal lattice, and the void is in an infinite solid. Assume that the initial void size is so large that the effect of the surface tension is negligible. From Lecture 2 we know the void growth rate,

$$\frac{dR}{dt} = \frac{B\sigma}{R},$$

with $B = D_l \Omega / kT$, where D_l is the self-diffusivity of the lattice, and Ω the volume per atom.

Integrating, we have

$$\lambda^2 - R_0^2 = 2B\sigma t_r.$$

We can neglect R_0 if $R_0 \ll \lambda$. The rupture time is therefore

$$t_r = \frac{kT\lambda^2}{2D_l\Omega} \sigma^{-1} = \left[\frac{kT\lambda^2}{2D_{l0}\Omega} \right] \exp\left(\frac{q_l}{kT}\right) \sigma^{-1}.$$

Here D_{l0} and q_l are the pre-exponential factor and the activation energy of lattice diffusivity. This formula agrees with the empirical formula for the rupture time. If lattice diffusion is the dominant process, the fitting parameters in the rupture time formula have the following values: the stress exponent is $n = 1$, the activation energy is that of lattice diffusion, and A is given in the

above formula. Note that A varies with T linearly, but this variation is much weaker than the exponential function.

Cavitation by grain boundary diffusion. Hull and Rimmer (1959) studied grain boundary cavitation. Small voids were observed at grain boundaries, particularly those transverse to the applied tensile stress. Fracture results from the growth and coalescence of these voids. When a copper specimen was subject to a hydrostatic compression p in addition to the uniaxial tensile stress σ , rupture time was found to depend on $(\sigma - p)$. This indicates that the mechanism operates under tensile stress, and the shear stress has little effect.

The mechanism is as follows. The grain boundary acts as an *atomic sink*. Atoms *diffuse* from the cavity surface into the grain boundary, and *append* to either one of the grains. The tensile stress does work to move the two grains apart, making room for the arriving atoms. The atomic structure of the grain boundary remains unchanged: it doesn't get thicker over time!

Let 2λ be spacing between cavity nuclei. With our previous experience with grain boundary diffusion, we can readily modify the above rupture time. When grain boundary diffusion dominates, the rupture time scales as

$$t_r \approx \frac{kT\lambda^3}{\Omega D_b \delta_b} \sigma^{-1}.$$

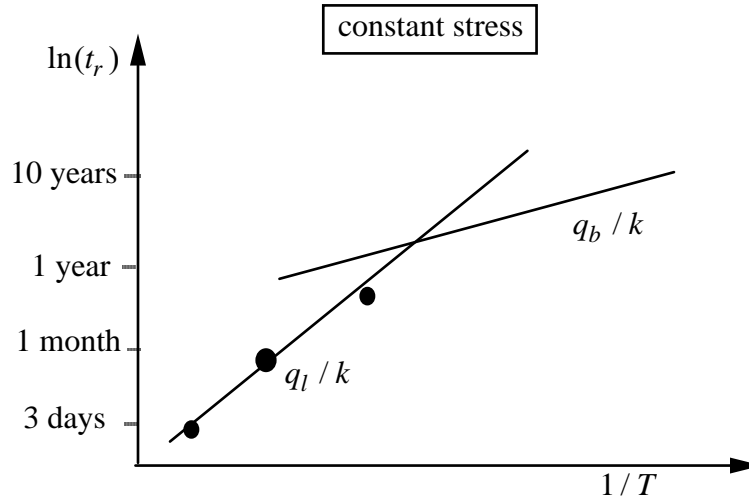
Note the different dependence on λ .

Lattice diffusion and grain boundary diffusion: regime of operation. By the 1950's, self-diffusivities have been measured for a few metals. One can check whether mass transfer is predominantly through lattice or on grain boundary. The ratio of the number of atoms transferred from the void to the grain boundary by lattice diffusion to that by grain boundary diffusion is roughly

$$\frac{D_l \lambda}{D_b \delta_b}$$

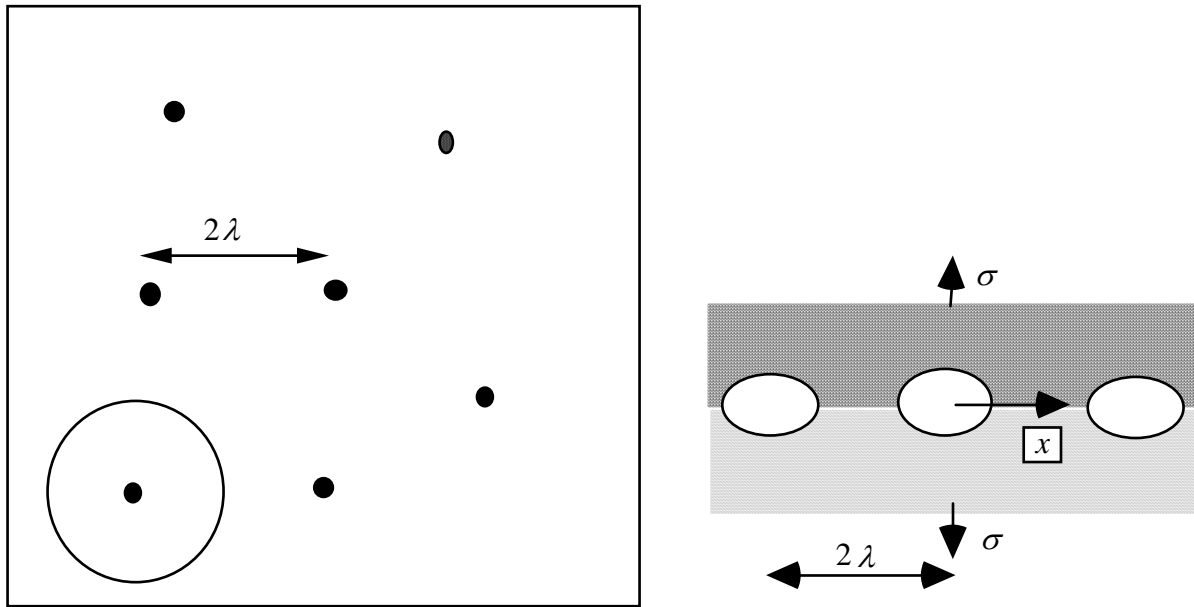
For silver at 500° C, $D_l \approx 2 \times 10^{-18} \text{ m}^2 / \text{s}$ and $D_b \delta_b \approx 3 \times 10^{-21} \text{ m}^3 / \text{s}$. Even at a quite large spacing, $\lambda = 10^{-4} \text{ m}$, the contribution from lattice diffusion is only 6% of the total, so that one is justified in neglecting it.

As the temperature increases, the lattice diffusivity increases faster than the grain boundary diffusivity due to the difference in the activation energies. Consequently, at a higher temperature, lattice diffusion may dominates over grain boundary diffusion. This mechanism switch is an important consideration in accelerated tests. The activation energy determined at very high temperatures corresponds to that of the lattice diffusion. It would overestimate the rupture time at lower temperatures.



Exact solution of the Hull-Rimmer model. The Hull-Rimmer model has been extended in many ways. The version discussed here was given in Chuang *et al.* (1979). Imagine that many cavity nuclei lie on a grain boundary. The spacing between the nuclei is 2λ . The plane view and the edge view are as follows. We will analyze a cylinder that contains only one cavity.

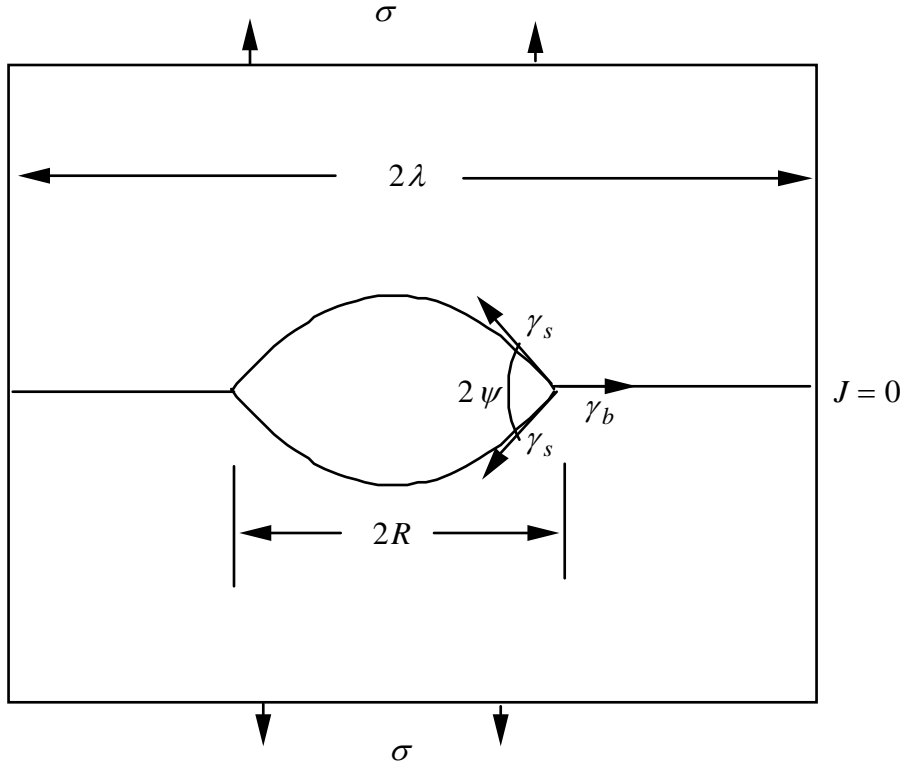
Grain boundary diffusion is taken to be the only rate process. Lattice diffusion is negligible when $D_l \lambda / D_b \delta_b \ll 1$, namely, when the temperature is low, and the length scale λ small. Creep due to dislocation motion in the lattice is negligible when the stress is low. Consequently, as atoms on a void surface diffuse into the grain boundary, the two grains drift apart like two rigid blocks. The effect of elastic deformation is often small, for the same reason as discussed in Lecture 1.



The triple junction. At the junction where the grain boundary meet with the two cavity surfaces, atoms flow from the cavity surfaces into the grain boundary. This process is much faster than the process to transport atoms on the grain boundary over a long distance. Consequently, we assume that the triple junction is in *local equilibrium*. This assumption has two consequences. The two caps make an angle 2ψ (i.e., the dihedral angle). The equilibrium between the grain boundary and the two surfaces requires that

$$\cos \psi = \gamma_b / 2 \gamma_s.$$

Furthermore, the local equilibrium requires that, at the junction, the chemical potential of the cavity surface equal that of the grain boundary.



The cavity surfaces. Often in solids surface diffusivity is much larger than grain boundary diffusivity. As atoms diffuse from the cavity surfaces to the grain boundary, the slow grain boundary diffusion is the rate-limiting step. Consequently, we assume that the cavity takes an equilibrium shape, consisting of two spherical caps. Denote the cavity radius by R . The volume and the surface area of the cavity are

$$V = \frac{4}{3} \pi R^3 h(\psi), \quad A = 4 \pi R^2 g(\psi),$$

with the shape factor

$$h(\psi) = \left(\frac{1}{1 + \cos \psi} - \frac{\cos \psi}{2} \right) \sin \psi, \quad g(\psi) = \frac{1}{1 + \cos \psi}.$$

Each cap is a part of a sphere, whose radius is

$$R_{\text{sphere}} = R / \sin \psi .$$

When the grain boundary energy is negligible compared to the surface energy, the dihedral angle approaches 180° , and the cavity becomes a sphere. Because the cavity is in an equilibrium shape, the chemical potential is uniform on the cavity surface, given by

$$\mu_s = -\Omega \frac{2\gamma_s}{R_{\text{sphere}}} = -\Omega \frac{2\gamma_s}{R} \sin \psi .$$

Recall this chemical potential is the free energy change when an atom is transferred from a large crystal to the cavity surface. The negative sign signifies a simple physical fact: the free energy of the combined system reduces when the transfer takes place. The surface energy tends to draw atoms from the crystal to fill the cavity.

Stress gradient as a driving force for self-diffusion. Atoms diffuse into the grain boundary because the grain boundary is under tension. For the atoms to diffuse on the grain, from the cavity toward the edge of the calculation cell, the tensile stress in the grain boundary $\sigma(r)$ must be an *increasing* function of r .

Let the reference system be a large single crystal under no stress. The given system is a polycrystal under a tensile stress σ normal to a grain boundary. When an atom is transferred from the reference system to the grain boundary, the atoms at the grain boundary adjust themselves to preserve the grain boundary structure. Assume that the grains are free to move, so that no elastic energy is generated inside the grains. The stress does work $\sigma\Omega$. Consequently, this transfer reduces the potential energy by $\sigma\Omega$. We say the chemical potential of each atom at the grain boundary under stress is

$$\mu_b = -\sigma(r)\Omega .$$

We have adopted the usual sign convention: a tensile stress is positive, and a compressive stress is negative. When no stress is applied, transferring an atom from the large

crystal to the grain boundary does not cause any change in the free energy of the combined system. The grain boundary structure is invariant, and the two grains drift apart to accommodate the space. *The net effect of this transfer is that one atom from the large crystal joins the lattice of either grain.* When a tensile stress is applied normal to the grain boundary, transferring an atom from the stress-free crystal to the grain boundary lowers the free energy of the combined free energy, and the chemical potential is negative. When a compressive stress is applied normal to the grain boundary, transferring an atom from the stress-free crystal to the grain boundary increases the free energy of the combined free energy, and the chemical potential is positive.

Now image that a grain boundary is under a nonuniform stress. When an atom moves from a position with a low tensile stress to a position of high tensile stress, the free energy of the system reduces. Thus, the driving force for atom to diffuse on a grain boundary is

$$F = -\frac{\partial \mu_b}{\partial x} = +\Omega \frac{\partial \sigma}{\partial x}.$$

Atoms move toward a position with a high tensile stress.

Force balance and local equilibrium. For the atoms to diffuse from the triple junction into the grain boundary, $\sigma_b(r)$ must increase with r . Force balance relates the distributed stress in the grain boundary, $\sigma_b(r)$, to the applied stress σ as

$$\pi(\lambda^2 - R^2)\sigma = \int_R^\lambda \sigma_b(r) 2\pi r dr. \quad (A)$$

The local equilibrium at the triple junction requires that the chemical potential be continuous across the junction, $\mu_s = \mu_b(R)$, so that

$$\sigma_b(R) = \frac{2\gamma_s}{R} \sin \psi.$$

The local equilibrium assumption sets a precise value of the stress in the grain boundary at the triple junction.

An unstable equilibrium state. All the above considerations assume that the grain boundary is not in an equilibrium state. In the special case, when the grain boundary *is* in an equilibrium state, the chemical potential in the grain boundary must be constant, independent of r . There is absolutely no free energy change when atoms transport from the cavity surfaces to anywhere on the grain boundary. Consequently, the entire grain boundary has a constant stress, given by

$$\sigma_b = \frac{2\gamma_s}{R} \sin \psi.$$

Substituting this into the force balance equation (A), we obtain the applied stress to maintain this equilibrium state:

$$\sigma_c = \left(1 - \frac{R^2}{\lambda^2}\right) \frac{2\gamma_s}{R} \sin \psi.$$

The physical significance of σ_c is as follows. Subject a bicrystal to a constant stress σ . If $\sigma > \sigma_c$, the cavity enlarges to reduce the free energy. If $\sigma < \sigma_c$, the cavity shrinks to reduce the free energy. We may compare this critical stress with the critical stress for a spherical cavity in an infinite single crystal, $\sigma_c = 2\gamma_s / R$. The factor $\sin \psi$ is due to the grain boundary energy. When the grain boundary energy is significant compared to the surface energy, the critical stress decreases. The factor $1 - (R/\lambda)^2$ is due to the finite radius of the cylinder.

Cavity growth rate. As the cavity grows, atoms from the cavity surface insert into the grain boundary. The two grains drift apart at velocity u . It relates to the cavity growth rate as $\pi(\lambda^2 - R^2)u = dV/dt$, namely,

$$u = \frac{4hR^2}{\lambda^2 - R^2} \frac{dR}{dt}.$$

Next examine the ring between r and λ . Denote the atomic flux on the grain boundary by J (i.e., the number of atoms diffusing across per unit length). It is in the radial direction, and is a function of the radius from the cavity center, r . The number of atoms moving into the ring at r per time is, $2\pi rJ(r)$, and no atoms move out of the ring at λ . The two grains drift apart, making a space of volume $\pi(\lambda^2 - r^2)\mu$ for the arriving atoms. Mass conservation requires that $\Omega 2\pi rJ(r) = \pi(\lambda^2 - r^2)\mu \frac{dR}{dt}$. These consideration relate the flux $J(r)$ to the cavity growth rate dR / dt :

$$J(r) = \frac{2hR^2}{\Omega(\lambda^2 - R^2)} \left(\frac{\lambda^2 - r^2}{r} \right) \frac{dR}{dt}.$$

Adopt the linear kinetic law,

$$J(r) = \Omega M_b \frac{d\sigma_b}{dr},$$

The mobility relates to the atomic diffusivity on the grain boundary, $M_b = D_b \delta_b / \Omega kT$.

Integrating the above equation from R to r , recalling that $\sigma_b(R) = 2\gamma_s \sin \psi / R$, we obtain the stress distribution in the grain boundary (**please check**):

$$\sigma_b(r) = \frac{2\gamma_s}{R} \sin \psi + \frac{hR^2}{M_b \Omega^2 (\lambda^2 - R^2)} \left(2\lambda^2 \ln \left(\frac{r}{R} \right) - r^2 + R^2 \right) \frac{dR}{dt}.$$

Inserting this stress distribution into the force balance equation (A), we obtain that

$$\frac{d\rho}{dt} = \frac{(1 - \rho^2) [1 - \Gamma(\rho^{-1} - \rho)]}{t_0 \rho^2 [\ln(1/\rho) - 0.25(3 - \rho^2)(1 - \rho^2)]}$$

where we have defined dimensionless quantities,

$$\rho = \frac{R}{\lambda}, \quad \Gamma = \frac{2\gamma_s}{\sigma\lambda} \sin \psi,$$

and a time scale,

$$t_0 = \frac{2h(\psi)\lambda^3}{M_b\Omega^2\sigma}.$$

Notice this is the same time scale as we have anticipated before on the basis of lattice diffusion.

Rupture time. Integrating the rate equation from the initial cavity radius $\rho_0 = R_0 / \lambda$ to the final radius $\rho = 1$, we obtain the rupture time

$$t_r = t_0 \int_{\rho_0}^1 \frac{\rho^2 [\ln(1/\rho) - 0.25(3 - \rho^2)(1 - \rho^2)]}{(1 - \rho^2)[1 - \Gamma(\rho^{-1} - \rho)]} d\rho.$$

The integral may be evaluated numerically; the result is a dimensionless number depending on Γ .

The exact solution gives the relaxation time in the same form as anticipated in the beginning of the lecture. It also gives the value of the coefficient, and its dependence on the initial radius, the dihedral angle, and the parameter Γ .

Further reading

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