MECHANISMS OF GAS BUBBLE EMBRITTLEMENT OF METALS

S. H. Goods and W. D. Nix*

INTRODUCTION

The presence of small holes at grain boundaries, whether they are voids, cavities due to creep, or gas bubbles, can produce serious degradation of the high temperature creep-rupture properties of metals. Interest in the nature of these deleterious effects has been increasing in recent years, especially in cases where the holes or gas bubbles are produced by the effects of high energy neutrons. It is well documented that neutron irradiation reduces the high temperature creep ductility of many alloys and it is generally accepted that the observed embrittlement is due to the presence of helium bubbles [1 - 5] which are present at grain boundaries as the result of (n, α) transmutation reactions with either impurity or matrix atoms. The processes by which helium bubbles are formed at grain boundaries are well understood, but how the presence of these bubbles affect the creep rupture properties is still being debated. In the present paper we report the results of a study of the effects of H_2O vapor bubbles on the creep rupture properties of polycrystalline Ag and compare these results to the rupture life predictions of various theoretical models found in the literature. A premise of this work is that gas bubble embrittlement does not depend on the nature of the gaseous specie within the cavity nor on how the grain boundary bubbles are formed and that neutron irradiation is but one way to create such structures.

MECHANISMS FOR CAVITY GROWTH

It seems likely that creep rupture of metals containing grain boundary bubbles is due to the growth and coalescence of these cavities. It remains therefore to determine the way in which these cavities can grow. One can immediately conceive of two possible mechanisms whereby a pre-existing grain boundary hole structure can lead to premature creep rupture. First, it seems plausible that these holes can grow by stress driven vacancy diffusion. Alternatively, the holes could possibly grow by plastic deformation of the surrounding matrix material.

Clearly, the bulk of the literature dealing with this problem has assumed the rate controlling process to be diffusional growth. Such a model as first proposed by Hull and Rimmer [6], involves stress driven vacancy diffusion to the hole surface via the grain boundary. Given an initial cavity size and spacing and assuming that the void spacing is large compared to the void radius, that there is no nucleation of new cavities during creep and that capillarity effects (which are important only for very small holes) may be neglected, the creep-rupture life is given approximately as

* Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, U. S. A.

$$t_r = KT\lambda^3/4(D_B\delta z)(\sigma - P)\Omega \qquad (1)$$

where

t_r = rupture life
D_B = grain boundary diffusivity
δz = grain boundary width
Ω = atomic volume
T = absolute temperature
k = Boltzman's constant
λ = cavity spacing
σ = tensile stress across grain boundary
p = hydrostatic pressure

Speight and Harris [7] and Dobes and Cadek [8] have modified this model by imposing different boundary conditions. Not withstanding these modifications, the resulting rupture time predictions remain inversely proportional to the applied tensile stress. A key assumption of all of these treatments is that the voids are initially spherical and that they remain spherical during growth. However, metallographic observation has shown that the grain boundary voids tend to be elongated in shape rather than spherical. Raj and Ashby [9] recently allowed for the initial lenticular nature of grain boundary cavities and arrived at an expression for the rupture life

$$t_r = \frac{3\sqrt{\pi}}{32}\frac{kT}{\Omega D_B\delta z}\frac{1}{\sigma\rho^{3/2}}\frac{F_V(\alpha)}{F_B^{3/2}(\alpha)}\int_{A_{max}}^{A_{max}} dA/f(A) \qquad (2)$$

where

ρ = number of voids per unit area
$F_V(\alpha)$ = void volume shape function
$F_B(\alpha)$ = grain boundary shape function
$f(A)$ = functional dependence of area fraction of voids in the grain boundary

Additional work by Dobes [10] on cavity growth showed that cavities in silver along the grain boundaries continue to elongate in the plane of the grain boundary during deformation. Thus describing the initial shape of the cavities may not be sufficient. Chuang and Rice [11] examined the shape of grain boundary cavities as they grow under an applied stress assuming that surface diffusion is the governing factor and Chuang [12] has extended the study to predict cavity growth rates. The results can be used to generate the following relation for the rupture lifetime:

$$t_r \approx \frac{kT\gamma_s^2}{D_s\Omega^{4/3}}\left(1 - \frac{\gamma_B}{2\gamma_s}\right)^{3/2} 4\sqrt{2}\,\frac{1}{\sigma^3}\,\lambda\left(.5 - \frac{a_o}{\lambda}\right)^4 \qquad (3)$$

where

a_o = initial cavity radius
γ_s = surface free energy
γ_B = grain boundary free energy
D_s = surface diffusivity

A prediction of this model is that the rupture lifetime is inversely proportional to the third power of the applied stress. All diffusion controlled models for creep rupture therefore result in a relatively small dependence of the rupture time on the applied stress. This can be contrasted to the more typical situation for creep of metals wherein the rupture life as given by the familiar Monkman-Grant relationship, $t_r\dot{\varepsilon}_{ss}$ = constant, is inversely proportional to the stress raised to a higher power, the stress exponent for creep.

There is some evidence which seems to indicate that rupture lifetimes can be much more sensitive functions of the applied stress [13, 14] than that indicated by diffusional hole growth models. It therefore appears that plastic creep deformation of the material surrounding the cavities could lead to hole growth and coalescence. In order for holes to exhibit net growth, they must be subjected to a triaxial stress state (neglecting hole-hole interactions), otherwise they will simply stretch in the direction of the applied stress and never link up. Such a triaxiality can be induced locally in a polycrystalline body subjected to uniaxial tension by the formation of wedge cracks at grain boundary triple junctions due to grain boundary sliding. The growth rate of holes for this type of mechanism would depend upon the stress dependence of the matrix strain rate and thus would account for the observed stress sensitivity of the rupture time. Such a model has been proposed [15]. It assumes that the holes or gas bubbles lie preferentially along grain boundaries and grow plastically in response to the applied stress as modified by wedge cracks. Each time the hole nearest the crack tip grows to the hole spacing, the crack tip moves forward by one hole spacing. The crack growth is therefore limited by the creep growth rate of the holes in the grain boundaries and fracture occurs when the wedge cracks have grown across a grain facet. The resulting rupture time prediction can be expressed as

$$t_r = \left\{\frac{(n^2-4)}{\sqrt{3}}\,\ell n\left(\frac{\lambda}{2a_o}\right)\right\}^{2/n+2}\left\{\frac{2\pi n^2}{9\sqrt{3}\xi}\right\}^{n/n+2}\left(\frac{\sigma}{E}\right)^{n/n+2}\left(\frac{\lambda}{L}\right)^{n-2/n+2}\left(\dot{\varepsilon}_{ss}\right)^{-1} \qquad (4)$$

where

n = power law creep stress exponent
ξ = fraction of creep strain due to grain boundary sliding
L = grain size
E = Young's Modulus

and the other quantities have been previously defined. The above expression predicts a rupture time which is more sensitive to the applied stress than predicted for diffusional hole growth. Owing to the presence of $(\dot{\varepsilon}_{ss})^{-1}$ in the equation, the stress dependence of the rupture time closely parallels the stress dependence for creep itself.

EXPERIMENTAL PROCEDURES

The material preparation and testing procedures are described elsewhere in some detail [16]. Briefly, a water vapor bubble microstructure is implanted in high purity (99.995%) polycrystalline silver by annealing creep samples at 800°C first in nitrogen, then in air and finally in hydrogen. Small silver coupons are also annealed along with the creep samples for metallographic observation of the bubble size and spacing. In this way a large stable grain size (≈ 0.3 mm) is formed with a uniform distribution of water vapor bubbles produced primarily along grain boundaries in relatively thick section specimens (≈ 1.7 mm). Constant stress creep tests were conducted in air at 400°C over a range of stress on material both with and without bubble microstructures.

RESULTS AND DISCUSSION

Figure 1 illustrates several of the important features of gas bubble embrittlement commonly observed. First, gas bubbles appear to have virtually no effect on the creep rate as evidenced by the superposition of creep curves for samples with and without bubbles. Clearly the major effect is seen in the rupture strain and time. The presence of a grain boundary hole structure causes premature fracture. Secondly, if the bubbles act simply as nuclei for creep cavitation, then the fracture surface should be intergranular with a dimple spacing roughly equal to the initial gas bubble spacing. Fractographic observations using scanning electron microscopy indicate this as shown in Figure 1. The appearance of coalescing bubbles along grain boundaries is also shown in Figure 1. The shape of these bubbles closely approximates those as proposed by Raj and Ashby and Chuang and Rice.

Figure 2 shows the rupture time for silver with bubbles as a function of the applied stress. The rupture life predictions for the models of cavity growth discussed above are also presented. It is clear that the data presented are in good agreement with the model proposed by Chuang and Rice. The failure of the creep model to correlate with the data is seen as being due to the fact that at the stresses and temperature of testing diffusion is the more efficient process. It should be noted that in many of the tests, especially in the low stress regime, there was essentially no strain to failure. Fracture occurred when the $H_2O(v)$ bubbles grew along the grain boundaries by diffusion in response to the applied stress until such time as the remaining cross section was reduced to the point where catastrophic plastic tearing of the ligaments between the cavities occurred.

Figure 3 contrasts the fracture surfaces for tension creep specimens of silver both with and without bubbles as seen in the SEM. For the material without bubbles there is substantial deformation of material adjoining the grain boundaries. While for silver with a pre-existing bubble microstructure the fracture surface appears much more brittle and the dimples are well defined. The plastic tearing of the ligaments between the cavities is clearly seen (Figure 3c).

The work to date suggests that hole growth and creep rupture in silver is apparently caused by stress assisted grain boundary diffusion. A key factor seems to be the accurate description of the cavity shape and thus the accurate formulation of the local stress state near the cavity tip giving rise to the resulting diffusion. Thus the assumption in the early models of cavity growth wherein the cavities are constrained to remain spherical

appears to have been in error. To date the most satisfactory treatment of this problem has been given by Chuang and Chuang and Rice as witnessed by the close agreement between the experimental data and predictions of their model.

ACKNOWLEDGEMENTS

This work was supported by the U.S. Energy Research and Development Administration under contract AT (04-3) 326 PA 17 from the Materials Science Program of the Division of Physical Research.

REFERENCES

1. HARRIES, D. R., J. Brit. Nucl. Energy, Soc., 5, 1966, 74.
2. McCOY, H. E., J. Nucl. Mater., 31, 1969, 67.
3. BARNES, R. S., Nature, 206, 1965, 1307.
4. GARR, K. R., KRAMER, D. and RHODES, C. G., Met. Trans., 2, 1971, 269.
5. SMITH, I. O. and RUSSELL, B., J. Nucl. Mater., 38, 1971, 1.
6. HULL, D. and RIMMER, D. E., Phil. Mag., 4, 1959, 673.
7. SPEIGHT, M. V. and HARRIS, J. E., Met. Sci. J., 7, 1967, 83.
8. DOBES, F. and CADEK, J., Scripta Met., 4, 1970, 1005.
9. RAJ, R. and ASHBY, M. F., Acta Met., 23, 1975, 653.
10. DOBES, F., Scripta Met., 7, 1973, 1231.
11. CHUANG, T. and RICE, J. R., Acta Met., 21, 1973, 1625.
12. CHUANG, T., Ph. D. Thesis, 1975, Brown University.
13. MATLOCK, D. K. and NIX, W. D., J. Nucl. Mater., 56, 1975, 145.
14. ERLICH, K., BÖHM, H. and WASSILEW, C., Irradiation Effects on Structural Alloys for Nuclear Applications, ASTM-STP 484, 495.
15. NIX, W. D., DIMELFI, R. J. and MATLOCK, D. K., (to be published).
16. GOODS, S. H. and NIX, W. D., Acta Met., (to be published).

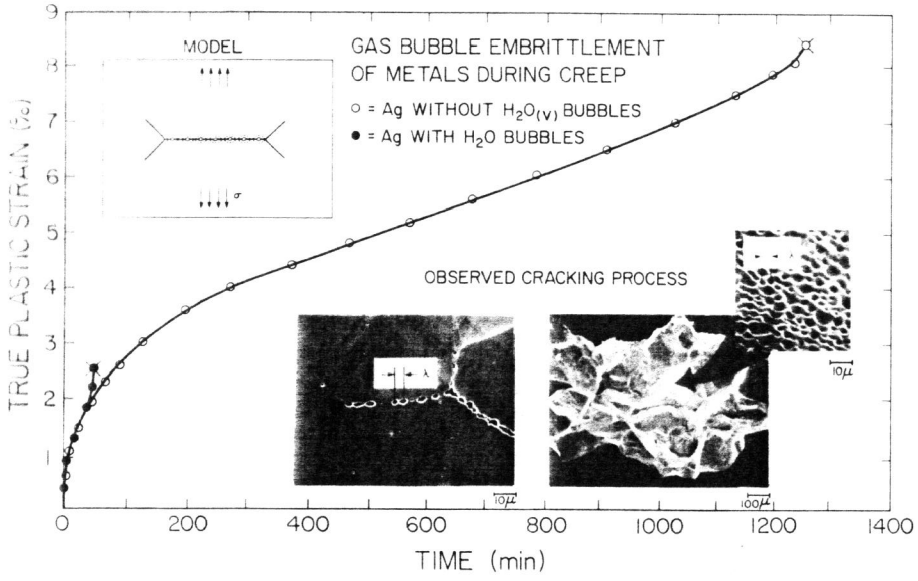

Figure 1 Effect of Grain Boundary Gas Bubbles on Creep Ductility of Polycrystalline Silver at 400°C and Observed Fracture Mode and Fracture Surface as Seen in Scanning Electron Microscopy

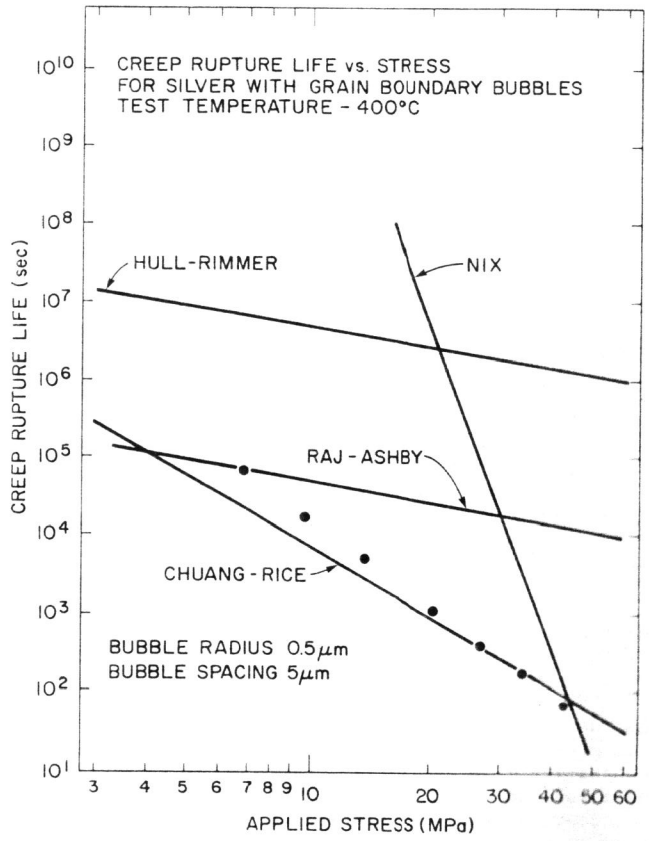

Figure 2 Time to Rupture at 400°C versus Applied Stress for Polycrystalline Silver with Water Vapor Bubbles at Grain Boundaries. The Solid Lines Indicate Predicted Lifetimes from the Models Discussed While Filled Circles are Actual Data Collected in this Study

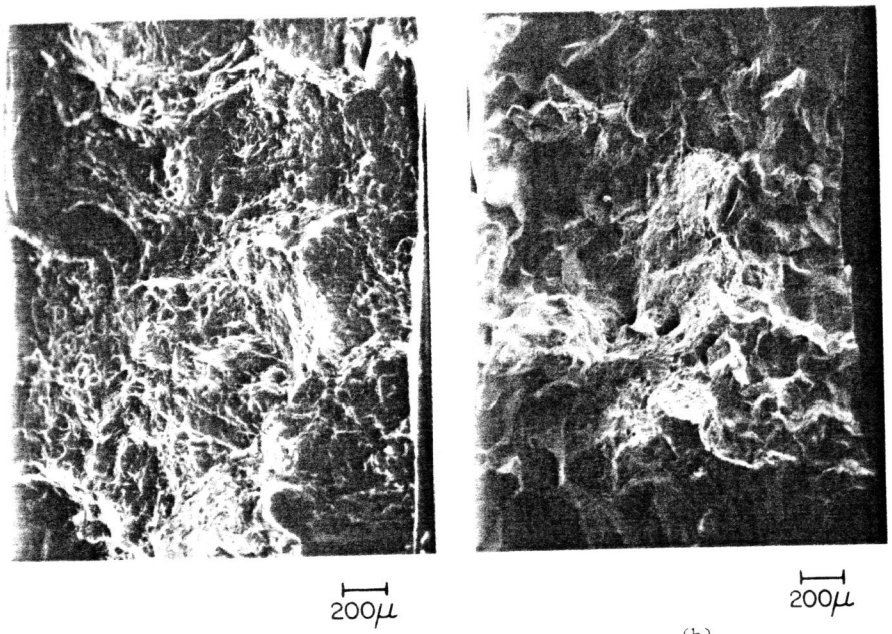

Figure 3 Observed Fracture Surfaces as seen in Scanning Electron Microscopy for Silver Crept at 400°C (a) Without Water Vapor Bubbles (b) and (c) With Bubbles