THERMODYNAMIC ANALYSIS AND MODELLING OF GRAIN-BOUNDARY VOID GROWTH UNDER HIGH TEMPERATURE

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An analytical model for void growth on grain-boundaries at high temperatures is addressed. The void volume accumulation is controlled by nucleation and diffusion of vacancies. A thermodynamic analysis of the chemical potential of vacancies yields to a boundary problem, a solution to which is found in explicit form.

INTRODUCTION

Creep fracture of most structural materials at elevated temperatures often is caused by accumulation of damage in the form of void nucleation, growth and coalescence. In many metals and alloys, void nucleation occurs at small strains. Here ductile mechanisms of cavitation have negligibly small effect and the voids grow mainly due to accumulation of vacancies, which nucleate and diffuse on grain boundaries. Void nucleate on grain boundary facets oriented perpendicularly (or slightly deviated) to the maximum normal stress.

Several models have been proposed for modelling the diffusion-controlled grain boundary void growth in creep (a brief overview is given by Skrypnyk and Nykyforchyn (1)). Most of them approximate voids as circular or elliptic-shaped holes in the grain boundary facets. However, these models assuming the accumulation of vacancies to be the leading mechanism of void growth do not incorporate

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directly this mechanism, while deriving the condition of thermodynamic balance on void surface. The present paper intends to include these effects into the modelling of the void growth.

THERMODYNAMICAL ANALYSIS

For a solid containing N atoms and n ($n<<N$) vacancies, which can be considered as the particles of another type, we can apply the form of Gibbs free enthalpy for a weak solution

$$G = N\mu_0 + kTn\ln\left({}^{n}\!/_{N}\right) + nU_f - \sigma_0(N+n)\Omega . \tag{1}$$

The chemical potential of vacancies in the system depends on the volume fraction c of the imperfections

$$\mu = \frac{\partial G}{\partial n} = U_f + kT\ln c - \sigma_0\Omega . \tag{2}$$

The equilibrium vacancy concentration is found by minimising G:

$$c_0 = \exp\left(\frac{U_f - \sigma_0\Omega}{kT}\right) . \tag{3}$$

Nabarro (2) has drawn attention that in tensile solid, the hydrostatic stress field is homogeneous. Thus the chemical potential is uniform, too, that is the condition of equilibrium and absence of any flow. Though in the solid, there is a vacancy flow resulting in diffusional creep. Therefore substitution of the hydrostatic stress σ_0 by the normal stress σ_z. was proposed (2). If such comparison is made, i.e., the flow is proportional to the gradient of chemical potential, the latter must have the form

$$\mu = U_f + kT\ln c - \sigma_z\Omega \tag{4}$$

and the equation for vacancy flow is (see, e.g., Schmidt (3))

$$J_b = -\frac{D_b}{kT\Omega}\operatorname{grad}\mu = -\frac{D_b}{c\Omega}\operatorname{grad}c + \frac{D_b}{kT}\operatorname{grad}\sigma_z . \tag{5}$$

Thus, in the system being in equilibrium state under the stress field, the spatial distribution of defects may exist.

From the equations (4)-(5) one can conclude that the knowledge of grain boundary stress distribution is insufficient to determine the vacancy flow and to evaluate the void growth and stability. It is necessary to account for spatial distribution of defects, i.e., system fluctuation from local equilibrium.

In analogy to chemical reaction-diffusion processes, the void formation due to diffusional mechanism is considered as nucleation of a new phase "vacancies' condensate" in "vacancies' solution". Then, we should account for the interface surface with specific energy γ_s. The increase of free energy of the system is

$$\partial F = -P_1 \partial V_1 - P_2 \partial V_2 + \mu \partial n + \gamma_s \partial s \qquad (6)$$

where indexes 1 and 2 mean the void and the lattice respectively.

Since $\gamma_s > 0$, the void surface tries to approach its minimum area. Therefore we consider a lattice including N atoms, n vacancies and a spherical void of radius r. To determine the equilibrium conditions for such system we let $\partial F = 0$. Taking the following relationships into account

$$P_1 \equiv 0;\ P_2 = -\sigma_0;\ V_1 + V_2 = \text{const};\ \partial V_1 = 4\pi R^2 \partial R;\ \partial V_2 = \Omega \partial n;\ \partial s = 8\pi R \partial R$$

we obtain:

$$\mu = \left({2\gamma_s}/{R} - \sigma_0 \right) \Omega . \qquad (7)$$

If substitute the equation (2) into the relationship (7), Thomson-Freundlich equation can be achieved:

$$\ln\left(\frac{c_s}{c_0}\right) = \frac{2\gamma_s}{R}\Omega \qquad (8)$$

describing the vacancy supersaturation near the void, that is necessary for system equilibrium. If let $\mu = 0$ in (7), the equation becomes:

$$\sigma_0 = {2\gamma_s}/{R} . \qquad (9)$$

This equation is often used to describe the thermodynamical balance in the area near the void surface (Speight and Harris (4) and Raj and Ashby (5)). At the same time the above relationships (9) is the partial cases of the equation (7) and describe the equilibrium of a two-phase system without imperfections (vacancies).

Analysis of equations (6)-(8) leads to the extension of concept of chemical potential of vacancies (Cadek (6)):

$$\mu = U_f + kT \ln c - \tilde{\sigma}\Omega \qquad (10)$$

$$\tilde{\sigma} = \begin{cases} \sigma_0 & \text{- if the body is considered;} \\ \dfrac{2\gamma_s}{r} & \text{- if the surface of curvature } \dfrac{1}{r} \text{ is considered.} \end{cases}$$

This allows to eliminate some ambiguities related with the existence of near-surface zone. They will appear only on the stage of evaluation of spatial distribution of vacancies $c(\vec{r})$.

The equation (10) shows, that the void will grow only when $\operatorname{grad} \mu|_{r=R} \neq 0$, i.e., when the system is beyond of the thermodynamic equilibrium state: $\mu|_{r=R} \neq 0$. Therefore in the model of balance type (Wirthman (7)) it is reasonable to accept the III-rd type boundary condition

$$\left(\alpha\mu+\frac{\partial\mu}{\partial r}\right)\bigg|_{r=R}=0 \tag{11}$$

VOID GROWTH MODEL PROBLEM

The boundary problem for void growth based on the above principles was formed earlier (1). The grain boundary was assumed to be a plate of a width δ_b and loaded by remote normal tension σ. The voids are circular holes of radius R in this plate and are spaced a distance 2λ apart at the grain boundary. Because of the symmetry, only a circular area of diameter 2λ can be considered. Similarly to Wirthman (7), we consider the diffusion equation

$$\frac{\partial c}{\partial t}=\frac{D_b}{kT}\frac{1}{r}\left(\frac{\partial}{\partial r}\left(r\frac{\partial\mu}{\partial r}\right)\right)+f(\mu,\sigma,\ldots). \tag{12}$$

Unlike Beere and Speight (8), we assume that generation of vacancies as well as their flow away from the boundary take place along the whole boundary and are proportional to the stress value and to the chemical potential μ respectively:

$$f(\mu,\sigma)=A\sigma-B\mu. \tag{13}$$

The diffusion of vacancies at $r=\lambda$ is absent because of the symmetry. Considering below only the steady state processes, we have a boundary problem:

$$\frac{D_b}{kT}\frac{1}{r}\left(\frac{\partial}{\partial r}\left(r\frac{\partial\mu}{\partial r}\right)\right)+A\sigma-B\mu=0,\quad\left(-\frac{\mu}{\delta_s}+\frac{\partial\mu}{\partial r}\right)\bigg|_{r=R}=0,\quad\frac{\partial\mu}{\partial r}\bigg|_{r=\lambda}=0. \tag{14}$$

By solving this problem we can evaluate the void growth rate $\dot{V}$ assuming it is proportional to vacancy flow through the area $2\pi R\delta_b$, i.e.

$$\dot{V}=\frac{2\pi RD_b\delta_b}{kT}\left(\frac{\partial\mu}{\partial r}\bigg|_{r=R}\right). \tag{15}$$

By substituting the equation $y=\mu-A\sigma/B$ into the relationships (14), we transform them into the linear uniform differential equation

$$\frac{1}{r}\left(\frac{\partial}{\partial r}\left(r\frac{\partial y}{\partial r}\right)\right)-C^2y=0 \tag{16}$$

with boundary conditions (here we assume $\delta_s\cong\delta_b$)

$$\left(\frac{\partial y}{\partial r}-\frac{y}{\delta_b}\right)_{r=R}=\frac{A\sigma}{B\delta_b};\quad\left(\frac{\partial y}{\partial r}\right)_{r=\lambda}=0;\quad C=\sqrt{\frac{BkT}{D_b}}. \tag{17}$$

The solution to the above problem is

$$y(r)=a_1I_0(Cr)+a_2K_0(Cr) \tag{18}$$

where

$$a_1=\frac{A\sigma K_1(C\lambda)}{BQ},\qquad a_2=\frac{A\sigma I_1(C\lambda)}{BQ}, \tag{19}$$

$$Q = K_1(C\lambda)\left[C\delta_b I_1(CR) - I_0(CR)\right] - I_1(C\lambda)\left[C\delta_b K_1(CR) + K_0(CR)\right].$$

Hence we obtain the equation for void growth rate:

$$\dot{V} = 2\pi R\delta_b A\sigma \frac{I_1(CR)K_1(C\lambda) - K_1(CR)I_1(C\lambda)}{CQ}. \qquad (20)$$

Taking into account that $\dot{V} = 4\pi R^2\, dR/dt$ and the C value is of the same order as $1/\delta_b$ and considering the void size $R > 10\delta_b$ we may approximate this expression by

$$\frac{dR}{dt} = K\frac{\sigma}{R}, \qquad (21)$$

where $K = \dfrac{A\delta_b}{2C(C\delta_b + 1)}$ is a constant, depending on the material properties and the temperature. This equation is similar to that of Hull and Rimmer (9), but it involves nucleation and diffusion of vacancies. Its solution gives a relationship for the void radius of the form

$$R = \sqrt{2K\sigma(t - t_n)}. \qquad (22)$$

USED SYMBOLS

A, B = empirical coefficients of the function $f(\mu, \sigma, \ldots)$

c = volume fraction of the vacancies

D_b = vacancy diffusion coefficient at grain boundary (m^2/s)

d = grain diameter (m)

$f(\mu, \sigma, \ldots)$ = the function of vacancy sources and fluxes at grain boundary

$I_{0,1}(x)$, $K_{0,1}(x)$ = the 0 and 1-t order modified Bessel functions of first and second type respectively

k = Boltzmann constant (J/K)

R = void radius (m)

T = absolute temperature (K)

t_n = the time of void nucleation.

U_f = vacancy nucleation energy (J)

γ_s = specific void surface energy (J/m^2)

$\delta_{b,}$ δ_b = grain boundary and surface layer widths respectively (m)

λ = distance between voids (m)

μ = chemical potential of vacancies (J)

σ_0 = mean stress (Pa)

σ_z = stress normal to grain boundary (Pa)

σ = remote tensile load (Pa)

Ω = atomic volume (m)

REFERENCES

(1) Skrypnyk, I.D. and Nykyforchyn, A.H., "Modeling of Crack Propagation in Damaged Material under Creep", "Materials Ageing and Component Life Extension", Vol. II, Edited by V. Bicego, A. Nitta, R. Viswanathan, EMAS, Warley, U.K., 1995.

(2) Nabarro, F.R. (1948). Deformation of crystals by the motion of single ions. Report on Conf. on Strength of Solids, Bristol, The Phys. Soc.

(3) Schmidt, R., "Ausscheidungsphänomene in Werkstoffen", Deutscher Verlag für Grundstoffindustrie, Leipzig, Germany, 1991.

(4) Speight, M.V. and Harris, J.E., Met. Sci. J., Vol. 1, 1967, pp. 83-85.

(5) Raj Rishi and Ashby, M.F., Acta Met., Vol. 23, No. 6, 1975, pp. 653-666.

(6) Cadek, J., Creep kovových materiálú, Academia, Prague, Czechoslovakia, 1984.

(7) Wirthman, J., Scripta Met., Vol. 1, 1979, pp. 1129.

(8) Beere, W. and Speight, M.V., Met. Sci., Vol. 12, No. 4, 1978, pp. 172-176.

(9) Hull, D. and Rimmer, D.E., Phil. Mag., Vol. 4, 1959, pp. 673-687.