

Thermodynamics of Creep Rupture

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Synopsis

An earlier discussion of the entropy contributions to the well-known Zhurkov relationship for creep rupture is developed from a more rigorous basis. It is demonstrated that well-behaved Zhurkov materials (which follow his relationship closely) undergo quasistatic rupture (thermodynamically reversible). Other materials show modified Zhurkov behavior and can be described as undergoing nonquasistatic rupture, with an extra entropy term. By considering studies previously carried out in vacuum, this extra entropy has been attributed to surface phenomena.

INTRODUCTION

Recently a discussion was presented¹ on the well-known Zhurkov relationship² for creep rupture. The relationships and definitions of Zhurkov are

$$\tau = Ae^{-\alpha\sigma} \quad (\text{at constant temp}) \quad (1)$$

$$\tau = \tau_0 e^{U^*/kT} \quad (\text{at fixed } \sigma) \quad (2)$$

where τ = time to rupture, α = constant, A = constant, σ = applied uniaxial stress, τ_0 = constant, $U^* = U_0 - \gamma\sigma$ (energy), U_0 = an activation energy, γ = constant, k = Boltzmann's constant, and T = absolute temperature.

When experimental results of $\log \tau$ vs. stress σ , at several temperatures, are extrapolated to large stress they intersect at a common pole τ_0 at a critical stress σ_k . Well-behaved Zhurkov materials have poles near 10^{-13} s. Other materials show poles with $\tau_0 \gg 10^{-13}$ s. When these materials (i.e., $\tau_0 \gg 10^{-13}$ s) are studied in vacuum, a different behavior is observed. Earlier it was argued¹ that the common pole τ_0 and the critical stress σ_k were nonexistent. The development here shows that this assertion is probably not true and that the premature conclusion was based upon a too narrow range of temperature used in the vacuum studies. The earlier discussion showed that an entropy term, not present in well-behaved materials, could be justified by manipulation of the results obtained in air. The present discussion is a more rigorous development of the results and shows that the entropy term can be attributed to surface effects not apparent in the vacuum studies.

THE ENTROPY FUNCTION

The following abbreviated development is after Reif.³ For a macroscopic system characterized by one or more external parameters, the number of quantum states, Ω , in the energy interval between E and $E + \delta E$ depends not only on the energy but also on the particular values of the external parameters. For simplicity, for one external parameter $\Omega = \Omega(E, x)$, where x is some external

parameter. The energy of each state, E_n , depends on the value assumed by the external parameter; therefore, when the external parameter changes by dx , the energy of each state changes accordingly

$$dE_n = \frac{\partial E_n}{\partial x} dx = X_n dx$$

where for convenience

$$\frac{\partial E_n}{\partial x} \equiv X_n \quad (3)$$

It can be shown (see Reif) from the mean value of \bar{X} and by eq. (3) that

$$\bar{X} dx = \frac{\partial \bar{E}_n}{\partial x} dx = dW \quad (4)$$

is the mean increase in energy of the system which is the work dW done on the system when the external parameter is changed quasistatically, i.e., while the system remains arbitrarily close to equilibrium. In general, \bar{X} may have any dimensions and is called the mean generalized force on the system, conjugate to the external parameter x . Note that for the special case where the external parameter denotes a distance, \bar{X} has the dimensions of a force.

The change in the number of states, Ω , as a function of the work done on the system is given by

$$\left(\frac{\partial \ln \Omega}{\partial x} \right)_E = - \frac{\bar{X}}{kT}$$

With the Boltzmann defined entropy, $S = k \ln \Omega$, this becomes

$$\left(\frac{\partial S}{\partial x} \right)_E = - \frac{\bar{X}}{T} \quad (5)$$

which is the desired development for the present discussion.

“NORMAL” ZHURKOV MATERIALS

Zhurkov developed his well-known creep rupture relationship from the time dependence of strength under unidirectional tension. He successfully applied it to a variety of metals and nonmetals. Equations (1) and (2) may be combined to yield

$$\tau = \tau_0 e^{(U_0 - \gamma\sigma)/kT} \quad (6)$$

where the time to rupture, τ , is a function of the activation energy for the process, U_0 , less the work done, $\gamma\sigma$, on the system. The constant γ depends on the nature of the structure of the material. A simple manipulation of eq. (6) shows $U_0 = \gamma\sigma_k$. The τ_0 is considered to be $1/\nu$, where ν is a vibrational frequency of bonded atoms in the solid.

Work done at constant volume becomes a definite thermodynamic property of the system (i.e., a definite integral) so that the work done, $\gamma\sigma$, becomes, by eq. (4),

$$dW = \gamma d\sigma + \sigma d\gamma = \bar{X} dx$$

With γ being constant, eq. (5) can be written as

$$T \Delta S = \gamma(\sigma_k - \sigma) \quad (7)$$

From energy conservation the heat absorbed, dQ , by a system can be used to increase the internal energy, ΔE , and to do work. Therefore,

$$T \Delta S = dQ = \Delta E + \text{work}$$

In this quasistatic development the work may be taken as the negative of the work being done on the system, and from eq. (7)

$$T \Delta S = \gamma(\sigma_k - \sigma) = dQ = \Delta E - \gamma \sigma \quad (8)$$

This is just the Helmholtz "work function" relationship $\Delta A = \Delta E - T \Delta S$ when ΔA is taken as $\gamma \sigma$. With the Zhurkov defined $U_0 = \gamma \sigma_k$, substitution of $\sigma = 0$ or $\sigma = \sigma_k$ shows $U_0 = \Delta E$. In a given isothermal process ΔA is the maximum (reversible) work available. From eq. (8), when $\sigma = \sigma_k$, the process is adiabatic or the rupture of the specimen takes place before any absorption of heat from the reservoir. When there is no significant $P \Delta V$ work, such as with a solid, the Gibbs "free energy", $\Delta F = \Delta H - T \Delta S$, may be used for the Helmholtz relationship without loss of rigor. The association of U_0 with ΔH was shown earlier by a less rigorous development.¹

Thermodynamically Zhurkov's relationship can be written then as

$$\tau = \tau_0 e^{(U_0 - \gamma \sigma)/kT} = \tau_0 e^{\gamma(\sigma_k - \sigma)/kT} = \tau_0 e^{(\Delta H - \Delta F)/kT} = \tau_0 e^{\Delta s/k}$$

Thus at any stress level less than σ_k the time to rupture is determined by the entropy change in the solid.

MODIFIED ZHURKOV BEHAVIOR

For some materials the pole τ_0 is many orders of magnitude removed from $\tau_0 \sim 10^{-13}$ s as found for well-behaved Zhurkov materials. Celluloid⁴ has a $\tau_0 \approx 5 \times 10^{-4}$; Lucite and Delrin have τ_0 's of 5×10^{-3} and 2.5×10^{-3} s, respectively.^{5,6}

When the usual Zhurkov determination for γ is carried out, γ is not independent of temperature but rather is found to be $\gamma = aT + b$, where a and b are constants. For Lucite and Delrin, γ becomes zero at 350°K and 380°K, respectively, not unreasonable values for their glass temperatures (no information was found for T_g of Celluloid).

For these kinds of materials then, the entropy becomes

$$\Delta S = -a(\sigma_k - \sigma) + b(\sigma_k - \sigma)/T \quad (9)$$

Since the second term on the rhs has already been defined as for quasistatic process, the ΔS of eq. (9) is the entropy change for a nonquasistatic process. For a quasistatic process the entropy is given by

$$\Delta S = S_f - S_0 = \int_{qs}^f \frac{dQ}{T} \quad (\text{quasistatic})$$

and for a nonquasistatic process, empirically,

$$\Delta S = S_f - S_0 > \int_{nqs}^f \frac{dQ}{T} \quad (\text{nonquasistatic})$$

where T now refers to the temperature of the reservoir. If a quasistatic path is constructed for the nonquasistatic process, the entropy change can be determined as

$$\Delta S = \int \frac{dQ}{T} + \Delta S_i$$

as an analogue of

$$\Delta E = -\Delta W + \Delta Q$$

Then ΔS_i corresponds to ΔQ and is defined to be the discrepancy between $\int dQ/T$ and ΔS just as ΔQ is the difference between the work and the internal energy. For a quasistatic process $\Delta S_i = 0$, and $\Delta S_i > 0$ for a nonquasistatic process. Quasistatic processes are regarded as reversible and all other changes as irreversible. Reversibility means step-by-step as well as global reversibility. Thus eq. (9) is just

$$\int_{nqs} \frac{dQ}{T} = -\Delta S_i + \int_{qs} \frac{dQ}{T}$$

and the extra term in eq. (9) is the discrepancy between the quasistatic and nonquasistatic processes. Clearly for these kinds of materials the rupture process is fundamentally different from well-behaved Zhurkov materials, with the rupture process being inherently nonquasistatic.

For these materials the Zhurkov relationship can be written as

$$\tau = \tau_0 e^{-\Delta S_i/k} e^{\Delta S/k} = \tau_0' e^{\Delta S/k} = \tau_0' e^{(\Delta H - \Delta F)/kT} = \tau_0' e^{(U_0 - \gamma\sigma)/kT}$$

A similar result was found earlier.¹ There it was stated that the experimentally determined $\tau_0 \gg 10^{-13}$ s could be corrected by a fixed entropy term. That this cannot be strictly true is shown by the present development where it is found that the correction term ΔS_i is a function of σ . However, the a of the correction term is quite small (0.0134 for Celluloid, 0.074 for Lucite, and 0.037 for Delrin) so that the earlier contention of a fixed term is not entirely incorrect.

When Lucite and Delrin are studied under vacuum^{5,6} the slopes of $\log \tau$ vs. σ differ considerably from those obtained in air. It was argued earlier¹ that in vacuum the slopes, at various temperature, became parallel, i.e., no common τ_0 and σ_k . The development here shows that this is probably not true and that the premature conclusion was based upon a too narrow range of temperature used in the vacuum studies. From the development here it must be concluded that these materials must revert to well-behaved Zhurkov type materials, i.e., the finite ΔS_i found in air becomes zero in vacuum. With Lucite, at least, clearly visible surface cracking occurs during creep, and an obvious consideration is that the extra entropy term in air is a surface phenomenon associated with a difference in crack behavior of such materials in the presence of air.

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