Letters

On the evaluation of the activation energy for superplastic flow

A number of reviews [1–6] have concluded that the best description of superplastic flow in a material of constant grain size is given by the empirical equation

$$\dot{\epsilon} \propto \sigma^{1/m} \exp(-Q/kT), \qquad (1)$$

where $\dot{\epsilon}$ is the strain rate, σ is the applied stress, k is Boltzmann's constant, T is the absolute temperature of deformation, m is the strain-rate sensitivity index (which is a function of temperature, grain size and stress/strain rate) and Q is the activation energy.

A recent theoretical treatment [7–9] leads to an equation of flow analogous to Equation 1. Thus, physical meaning can be assigned to an activation energy obtained from Equation 1, provided that the temperature and stress/strain rate dependence of m is taken into account. (The grain-size dependence poses no problem because the analysis is always carried out in a material of constant grain size.)

For the determination of the activation energy at constant stress, Q_σ, Equation 1 is approximated as

$$\dot{\epsilon}|_\sigma \propto \exp(-Q_\sigma/kT). \qquad (2)$$

Evidently Equation 2 ignores the strain rate and temperature dependence of m.

Occasionally an activation energy at constant strain rate, $Q_{\dot{\epsilon}}$, is determined from an equation of the type

$$\sigma|_{\dot{\epsilon}} \propto \exp(Q_{\dot{\epsilon}}/kT). \qquad (3)$$

Although it has been shown (last paragraph, Section 1 of [10]) that both Equations 2 and 3 are consistent with Equation 1 for the limiting case $m = 1$, Gifkins and Langdon [11] have recently stated that Equations 2 and 3 cannot be reconciled.

In our approach [9, 10, 12–14] there is only one real activation energy, Q. This quantity, however, is different from both the apparent activation energies Q_σ and $Q_{\dot{\epsilon}}$. The relations between Q, Q_σ and $Q_{\dot{\epsilon}}$ have also been deduced. The relation between Q and $Q_{\dot{\epsilon}}$ was obtained from the limiting case $m = 1$ for which Equation 3 is consistent with Equation 1 [10]. All the other relationships, as well as the prediction that Q_σ decreases parabolically with the applied stress [9] (which has experimental support [9]), have been derived from the theoretically meaningful Equation 1.

Alternatively, an activation energy can be obtained from the equation [15–22]

$$\dot{\epsilon} = (AG\mathbf{b}/kT)(\mathbf{b}/L)^p(\sigma/G)^{1/m} \exp(-Q/kT), \qquad (4)$$

where G is the modulus of rigidity, **b** is the Burgers vector, L is the grain size and A and p are constants.

This is, of course, a popular equation in creep, first introduced by Dorn and co-workers (see, for example, [23]). This equation is "largely empirical" and systematizes the dependence of the flow rate on the experimental variables [23].

It should be noted that the pre-exponential temperature term in Equation 4 makes it incompatible with conventional Arrhenius kinetics. This is because in the "Arrhenius plots" involving "temperature-compensated" strain rates [18] both the x- and y-axes contain temperature terms. Nevertheless, the technique has proved useful in the case of high-temperature creep because (a) the range of temperature involved is relatively small and so the "temperature compensation" often introduces only small changes in the flow rate, (b) the stress exponent n ($= 1/m$) is a constant, and (c) the apparent activation energy is virtually independent of the applied stress. (Only then will Q_σ always be equal to Q). The last two conditions, which are related, are not met during superplastic flow.

No doubt this problem can be overcome by dividing the optimal range into linear portions [15–22] and assuming values for n based on experimental results (which are, in turn, attributed to as yet unidentified mechanisms). The popular view [1–6, 24–26], however, is that the transition from conventional to superplastic modes of flow is gradual and that the microstructural and the topological features of deformation do not change suddenly at a fixed strain rate.

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(The striking differences in the microstructural features of regions I and II, shown by Gifkins and Langdon [11] and Vatsava and Langdon [27], are confined to the presence of measurable normal boundary displacements in region I (which are practically absent in region II). If grain-boundary sliding is also due to diffusional flow parallel at every point to the boundary curvature [7–9], then the varying amounts of parallel and normal (boundary) displacement contributions in regions I and II can be traced to the different stress gradients present in the two regions. This point, which is beyond the scope of the present paper, is discussed in detail in a very recent book [28].)

Perhaps it is not also correct to claim [11] that the analysis of Langdon and co-workers [15–22] is based on an equation analogous to those deduced in some of the theories of structural superplasticity [24–26, 29]. While these theories assign specific values to n, and where applicable predict its variation with the experimental conditions [25, 26], in the analysis of Langdon *et al.* [15–22] n has been used as an adjustable empirical parameter. More significantly, Langdon and co-workers have not yet identified the mechanisms responsible for regions I and II.

In another context [9] four limitations of the analysis based on Equation 4 [15–22] were noted, namely:

(1) Arrhenius kinetics requires that when $m = 1$, $Q_\sigma = Q_{\dot{\epsilon}} = Q$ [10]. But the analysis of Mohamed and Langdon [18] predicts that when $m = 1$, $Q_\sigma < Q$. (This discrepancy can be traced to the pre-exponential temperature term in Equation 4; see above also);

(2) Dividing the optimal range into two linear portions resulting from different (but unidentified) mechanisms, is perhaps unrealistic. (See earlier portions as well);

(3) Equation 4 is "largely empirical" [23]. The value of n assumed for each region also has no theoretical basis;

(4) An "activation energy" derived from an equation that has no physical basis is a meaningless quantity, even if its magnitude is close to that of some physically significant parameters.

The following additional limitations are also inherent:

(5) The modulus of rigidity enters Equation 4 to account for "dislocation interactions" [23]. But dislocation models are inadequate for understanding superplastic flow [3–9, 25, 30]. On the other hand, following the later view [11], if Equation 4 is taken to represent diffusion-controlled flow, the question "what is the diffusional mechanism which predicts value for n well in excess of unity?" would arise. In our opinion, only our model [7] does this; although Langdon and co-workers [11, 18, 31] do not share this view. In any case, in the viscous boundary approach [7] n is not a constant (as required by the analysis).

(6) Within each region n has been assumed to be temperature-independent despite experimental evidence [3–7, 25] to the contrary.

(7) For obtaining numerical values of G, linear corrections have been applied to low temperature data. The modulus of rigidity of an alloy, on the other hand, is assumed to be related to those of the constituent elements through the rule of mixtures. These approximations may give rise to sizeable errors in the subsequent calculations.

(8) Langdon himself has noted [20] that the same data could either be presented as a smooth curve or as comprising three linear regions. Therefore, the division of the $\log \sigma - \log \dot{\epsilon}$ plots into linear portions to assign a different mechanism for each of the (linear) regions may not be realistic. In any case, it is conceivable that the slope of the $\log \sigma - \log \dot{\epsilon}$ plot could change even during the operation of a single mechanism [7].

(9) Measured strain rates in region I are greater than even those predicted by the (grain-boundary diffusion based) Coble creep model [19]. Yet the analysis predicts an activation energy of the order of that for volume diffusion for region I. This paradox has been explained only by postulating the presence of an as yet unidentified mechanism. On the contrary, in the analysis based on Equation 1 [9, 10] the increase in the activation energy in region I is an apparent effect arising from the (predictable) increase in the magnitude of n with decreasing stress.

Thus it would appear that the use of Equation 4 to derive an activation energy for superplastic flow is not completely justified.

References

1. R. B. NICHOLSON, "Plasticity and Superplasticity" (Institution of Metallurgists Review Course, Ser. 2

(3), London, 1969) p. 19.

2. R. H. JOHNSON, *Met. Rev.* 15 (1970) 115.
3. G. J. DAVIES, J. W. EDINGTON, C. P. CUTLER and K. A. PADMANABHAN, *J. Mater. Sci.* 5 (1970) 1091.
4. R. B. NICHOLSON, "Electron Microscopy and Structure of Materials", edited by G. Thomas (University of California Press, Berkeley, 1972) p. 689.
5. P. M. HAZZLEDINE and D. E. NEWBURY, "Grain Boundary Structure and Properties", edited by G. A. Chadwick and D. A. Smith (Academic Press, London, 1976) p. 107.
6. J. W. EDINGTON, K. N. MELTON and C. P. CUTLER, *Prog. Mater. Sci.* 21 (1976) 61.
7. K. A. PADMANABHAN, *Mater. Sci. Eng.* 29 (1977) 1.
8. R. K. YADAVA and K. A. PADMANABHAN, *ibid.* 37 (1979) 127.
9. K. A. PADMANABHAN, *ibid.* 40 (1979) 285.
10. G. PADMANABHAN and K. A. PADMANABHAN, *Phil. Mag.* 33 (1976) 371.
11. R. C. GIFKINS and T. G. LANGDON, *Mater. Sci. Eng.* 40 (1979) 293.
12. K. A. PADMANABHAN and G. J. DAVIES, *Phys. Stat. Sol. (a)* 18 (1973) 295.
13. K. A. PADMANABHAN, *ibid.* 22 (1974) K95.
14. P. MAULIK and K. A. PADMANABHAN, *J. Mater. Sci.* 10 (1975) 1646.
15. F. A. MOHAMED and T. G. LANGDON, *Acta Met.* 23 (1975) 117.
16. F. A. MOHAMED, S. SHEI and T. G. LANGDON, *ibid.* 23 (1975) 1443.
17. F. A. MOHAMED and T. G. LANGDON, *Phil. Mag.* 32 (1975) 697.
18. *Idem. Phys. Stat. Sol. (a)* 33 (1976) 375.
19. *Idem, Scripta Met.* 11 (1977) 575.
20. T. G. LANGDON, Proceedings of the Fifth New Zealand Science of Materials Conference, Wellington, 1977 (Department of Scientific and Industrial Research, Lower Hutt, New Zealand, 1977) p. 11.
21. S. SHEI and T. G. LANGDON, *Acta Met.* 26 (1978) 639.
22. *Idem, ibid.* 26 (1978) 1153.
23. A. K. MUKERJEE, J. E. BIRD and J. E. DORN *Trans. ASM* 62 (1969) 155.
24. A. BALL and M. M. HUTCHISON, *Met. Sci. J.* 3 (1969) 1.
25. M. F. ASHBY and R. A. VERRALL, *Acta Met.* 21 (1973) 149.
26. J. H. GITTUS, *J. Eng. Mater. Technol.* 99 (1977) 244.
27. R. B. VATSAVA and T. G. LANGDON, *Acta Met.* 27 (1979) 251.
28. K. A. PADMANABHAN and G. J. DAVIES, "Superplasticity" (Springer Verlag, Berlin, 1980).
29. A. K. MUKHERJEE, *Mater. Sci. Eng.* 8 (1971) 83.
30. T. H. ALDEN, *Acta Met.* 17 (1969) 1435.
31. R. C. GIFKINS and T. G. LANGDON, *Mater. Sci. Eng.* 36 (1978) 27.

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Evaluation of the kinetic parameters in a reaction with a solution of the type $y = A \exp(-t/\tau_1) + B \exp(-t/\tau_2)$

Kinetics of the type

$$y = A \exp(-t/\tau_1) + B \exp(-t/\tau_2) \qquad (1)$$

are characteristic of many competitive and consecutive reactions [1]. Determination of the parameters of Equation 1 from individual experimental data points requires the solution of a system of transcendental equations which must be more than four generally, because the mean square error should be minimized. As the solution is cumbersome, a mathematical method which employs the experimental curve as a whole and not just discrete points on it, is developed here.

By using the well known integral

$$\int_0^\infty t^n \exp(-t/\tau)\, \mathrm{d}t = n!\, \tau^{n+1}, \qquad (2)$$

by multiplication of Equation 1 by t^0 (= 1), t^1

TABLE I Fitted parameters using Equations 4 to 7. (The bracketted values of τ_1 and τ_2 are taken from Trieb and Veith [2])

	S (min)	M (min)^2	J (min)^3	T (° C)	A	τ_1 (min)	τ_2 (min)
Cu–15 at % Al	13.9	279.0	13.1	245	0.6	6.3 (6.2)	25.2 (25.3)
Cu–18 at % Al	−11.0	−450.4	−26.4	260	1.58	3.5 (3.7)	28.4 (28)

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