Variations in activation energy for superplastic flow

The magnitude of the activation energy for superplastic flow has been a source of considerable confusion in recent times [1, 2]. It is conventional to define the activation energy as

$$Q_{\dot{\gamma}} = -\left(\frac{\partial \ln \dot{\gamma}}{\partial 1/kT}\right)_{\dot{\gamma}} \tag{1}$$

where $\dot{\gamma}$ is the shear strain rate, k is the Boltzmann's constant, T is the temperature of deformation on the absolute scale and τ, the shear stress, indicates that the estimation is done at constant stress conditions. However, it has been pointed out [3] that for superplastic flow the activation energy determined at constant strain-rate, namely,

$$Q_{\dot{\gamma}} = \left(\frac{\partial \ln \tau}{\partial 1/kT}\right)_{\dot{\gamma}} \tag{2}$$

is closer to the value predicted by the kinetics of the deformation process. This has necessitated the distinction between Q_{τ} and $Q_{\dot{\gamma}}$.

The difference in magnitude has been attributed to the strain-rate senstiivity index, m [3], and the relation

$$Q_{\tau} = (1/m) Q_{\dot{\gamma}} \tag{3}$$

holds good for superplastic flow. The general situation in which m is a variable has also been considered [4] and from the results, Equation 3 emerges as a special case when m is constant.

To date, the verification of Equation 3 has been undertaken only by Padmanabhan and Davies [3] using essentially the experimental data of Padmanabhan [5]. As a number of results are available in the literature, a case exists for their analysis. This will also provide broad-based justification for the theoretical predictions.

Further, the analysis is useful in verifying the applicability of the stress function proposed for superplastic flow [5, 6], i.e. in the equation

$$Q_{\text{app}} = Q_{\text{act}} - b\tau^{n} \tag{4}$$

or

$$Q_{\dot{\gamma}} = Q_{\dot{\gamma}\text{act}} - k_1 \dot{\gamma} \tag{5}$$

where Q_{app} is the observed activation energy, Q_{act} the activation energy for the deformation process in the absence of an applied stress and $b\tau^{n} (= f(\tau))$, a measure of the work done by the applied stress, is the amount by which the activation energy is lowered in the direction of stress. Equation 5 follows from Equation 4 because for superplastic deformation $Q_{\dot{\gamma}}$ is close to Q_{act} and $\dot{\gamma} \propto \tau^{n}$ [3, 5]. b, n and k_1 in these equations are constants.

Therefore, $Q_{\dot{\gamma}}$ versus $\dot{\gamma}$ should be linear at least over narrow domains, as b and n may vary over large ranges [6]. As τ and n are of the order of 1000 psi* and 1.5 to 3, respectively, use of Equation 4 will introduce large errors in the computed values of τ^{n} even if a small inaccuracy exists in the experimental evaluation of $n (= 1/m)$. Therefore, Equation 5 is to be preferred. Moreover, following Drucker [7], it has been assumed that the relations between the tensile stress, σ, and τ and the tensile strain rate, $\dot{\epsilon}$, and $\dot{\gamma}$, are linear. Thus in Equations 1 to 5, τ could be replaced by σ and $\dot{\gamma}$ by $\dot{\epsilon}$.

Data pertaining to Sn–Pb eutectic [8, 9], Zn–Al eutectoid [10] and Al–Cu eutectic [11] alloys were chosen for the present analysis.

From the superplasticity equation for constant grain size,

$$\dot{\epsilon} \propto \sigma^{n} \exp(-Q/kT), \tag{6}$$

the mean value of n, n_{mean}, could be estimated either as

$$n_{\text{mean}} = B_1 \log \dot{\epsilon}_{\text{mean}} + \frac{B_2}{T_{\text{mean}}} + B_3 \tag{7}$$

or as

$$n_{\text{mean}} \log \sigma_{\text{mean}} = C_1 + \frac{C_2}{T_{\text{mean}}} \tag{8}$$

depending on whether constant stress or constant strain-rate conditions are considered. In the above equations, B_1, B_2, B_3, C_1 and C_2 are constants and $\dot{\epsilon}_{\text{mean}}$, T_{mean} and σ_{mean} are the mean values of the strain-rate, temperature and stress, respectively. When the simultaneous changes in stress and/or strain-rate with n and T are ignored, both Equations 7 and 8 reduce to the form

$$n_{\text{mean}} = \frac{D_1}{T_{\text{mean}}} + D_2 \tag{9}$$

with D_1 and D_2 constants. n_{mean} evaluated from Equation 9 was extremely close to that obtained from Equation 7 or 8 and the difference was less than the experimental error [12]. Therefore, the simpler Equation 9 was employed in estimating

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*10^3 psi = 6·89 N mm^{-2}.

TABLE I

System	Authors	$\dot{\epsilon}$ (sec^{-1})	σ (psi)	$Q_{\dot{\epsilon}}$ (kcal 1 mol^{-1})	Q_σ (kcal 1 mol^{-1})	m_{mean} exptl	$\left(\frac{Q_{\dot{\epsilon}}}{Q_\sigma}\right)$ for equal m_{mean}
Sn–Pb	Cline and Alden [8]	1.7×10^{-5}		4.6		0.30	
		1.7×10^{-4}		6.1		0.50	
		1.7×10^{-3}		6.0		0.58	$\frac{6.1}{11.5} = 0.53$
			316.2		11.5	0.50	
			1000.0		10.6	0.58	
			3162.0		9.9	0.52	
	Zehr and Backofen [9]	10^{-4}		4.4		0.44	
	2.0 ± 0.2 μm	5×10^{-3}		4.2		0.44	
		10^{-2}		4.0		0.39	
			400		8.9	0.39	$\frac{4.2}{8.6} = 0.49$
			600		8.6	0.44	
			800		8.4	0.52	
			2000		8.1	0.50	
	7.5 ± 0.8 μm	5×10^{-4}		2.8		0.32	
		10^{-3}		2.7		0.30	
		10^{-2}		2.1		0.22	
			2000		12.2		
Zn–Al	Alden and Schadler [10]	1.7×10^{-5}		9.8		0.46	
		8.4×10^{-5}		8.3		0.46	
		1.7×10^{-4}		6.7		0.46	$\frac{9.8}{23} = 0.43$
		3.4×10^{-4}		6.6		0.46	
		1.7×10^{-3}		5.9		0.34	
			1000		23.0	0.45	$\frac{8.2}{23} = 0.36$
			2000		18.4	0.58	
Al–Cu	Holt and Backofen [11]	2×10^{-3}		23.8		0.57	
		5×10^{-3}		21.8		0.59	
		10^{-2}		18.7		0.57	$\frac{21.8}{43.6} = 0.50$
			800		46.1	0.51	
			1000		44.8	0.52	$\frac{23.8}{43.6} = 0.53$
			3000		43.6	0.60	

n_{mean} for use in Equation 3 ($n_{\text{mean}} = 1/m_{\text{mean}}$).

Table I summarizes the values of $Q_{\dot{\epsilon}}$, Q_σ and m_{mean} at various strain-rate and stress levels. It is evident that Q_σ is different from $Q_{\dot{\epsilon}}$ and that the former is of greater magnitude. Where applicable, Equation 3 is obeyed. Both $Q_{\dot{\epsilon}}$ and Q_σ decrease with increasing strain-rate and stress, respectively, and this is a consequence of Equation 4. However, for the data of Cline and Alden [8], at a strain-rate of 1.7×10^{-5} sec^{-1} the value of $Q_{\dot{\epsilon}}$ obtained is less than those estimated at higher strain-rates. As the scatter is of a small magnitude, much significance need not be attached to this single point of disagreement which may merely be due to experimental error. In passing, it is also mentioned that the present study is in agreement with the finding of Padmanabhan and Davies [3] that Q_σ depends on the stress level. On the other hand, their result that $Q_{\dot{\epsilon}}$ is independent of strain-rate is contradicted when wider ranges are considered.

Comparison of the results ($Q_\sigma = 16.2$ and $Q_{\dot{\epsilon}} = 9.8$ kcal mol^{-1}) for a grain size of 5.5 μm [3] with those of the present analysis using the data of Zehr and Backofen [9] indicates that perhaps the magnitude of both Q_σ and $Q_{\dot{\epsilon}}$ depends on the grain size. A more detailed analysis, however, is essential for unequivocal inference. Further, it is clear that the results of Holt and Backofen [11] and Padmanabhan and Davies [3] are in excellent agreement with the present study.

The magnitude and the systematic nature of the changes in Q_σ and $Q_{\dot{\epsilon}}$ indicate that the findings are genuine. The situation is comparable to that of a pseudo-plastic polymer ($m < 1$) like polyethylene [13]. Equations 4 and 5 predict that $Q_{\dot{\epsilon}}$ decreases with increasing strain-rate. This is

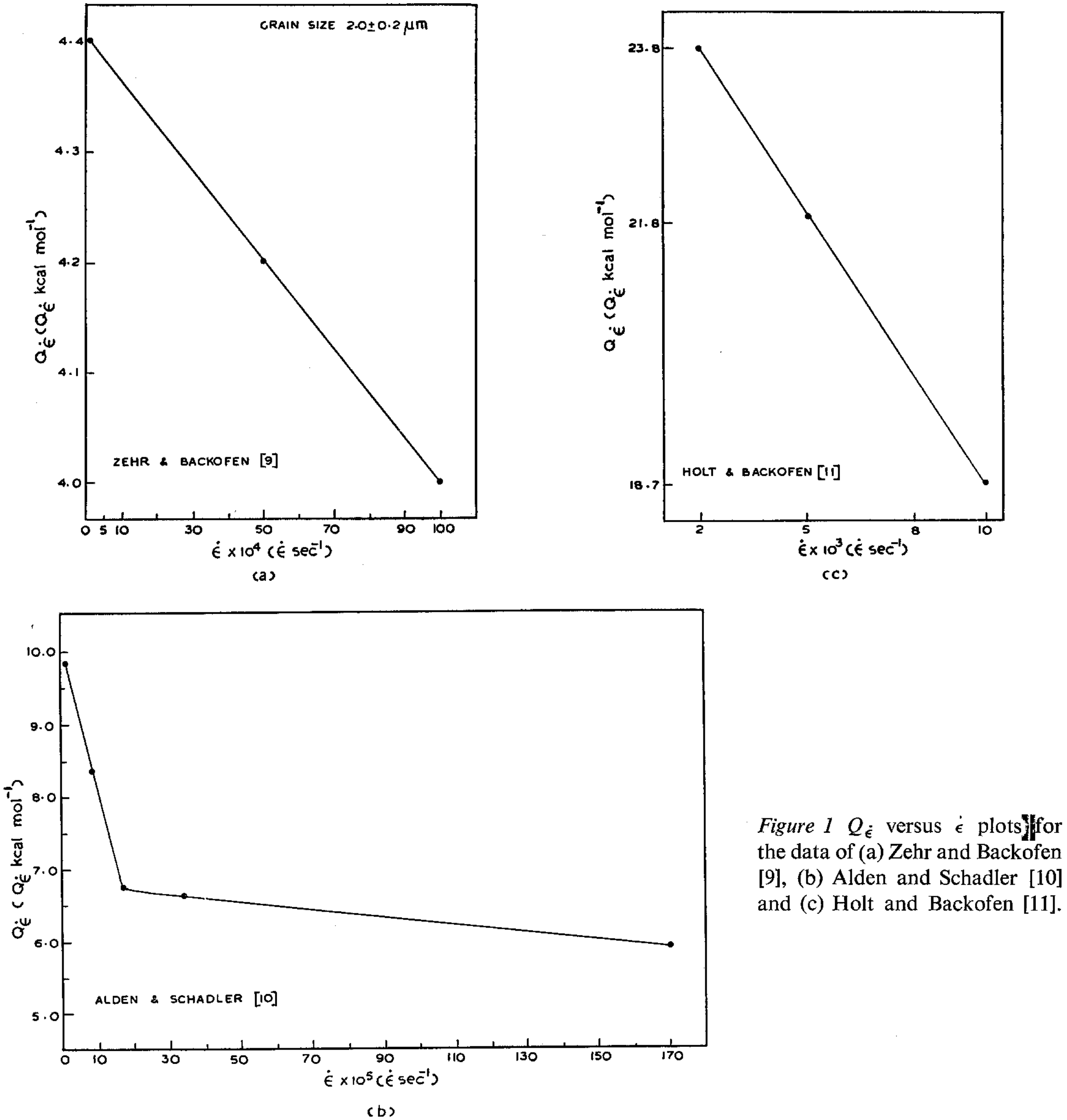

Figure 1 $Q_{\dot{\epsilon}}$ versus $\dot{\epsilon}$ plots for the data of (a) Zehr and Backofen [9], (b) Alden and Schadler [10] and (c) Holt and Backofen [11].

obeyed both by the superplastic alloys and polyethylene. However, the decrease in Q_σ with increasing stress recorded for the superplastic alloys conflicts with the finding in case of the polymer [13].

From Equation 3

$$dQ_\sigma = (1/m)\,[dQ_{\dot{\epsilon}} - Q_\sigma dm] \qquad (10)$$

(as m is a variable, strictly Equation 14 of [4] is to be considered. But the functional forms of the partial derivatives of m involved in the equation are not known either experimentally or theoretically).

Under optimal conditions, dm is positive for the superplastic alloy [1, 2, 14]. Therefore dQ_σ is always negative when a strain-rate increase is considered. For polyethylene dm is negative [13]. Thus dQ_σ is either positive or negative depending on the relative changes in $dQ_{\dot{\epsilon}}$ and dm. Evidently, for the results quoted by McKelvey [13], $Q_\sigma\,dm > dQ_{\dot{\epsilon}}$. However, at stresses greater than those for peak m, dm is negative for the superplastic alloys as well. In this range, considerations similar to those employed above for polyethylene will hold good.

In Fig. 1 $Q_{\dot{\epsilon}}$ is plotted against $\dot{\epsilon}$ and the linear relation obtained in all cases justifies Equation 5. For the results of Alden and Schadler [10], however, the significant drop (~ 40%) in the magnitude of the activation energy causes the entire region to be divided into two linear portions (Fig. 1b) consistent with earlier predictions [6].

It is emphasized that as the activation energy for superplastic deformation is a quantity estimated from an exponential relation involving macroscopic measurements it should not be looked upon as the sole proof for the validity of atomic mechanisms proposed. However, it could play a very useful role in providing further justification for conclusions reached from metallographic and rheological considerations. Viewed in this perspective, it is evident that the viscous boundary approach to superplasticity [5] assumes the correct form for the dependence of activation energy on applied stress.

Finally, it is noteworthy that the lowering of activation energy during superplastic deformation with stress and strain-rate is considerable compared to the results for high temperature creep [15-17] and hot working [18]. Whether this difference is due to the ultra-fine grain structure characteristic of superplastic alloys or to the unique mode of deformation in the superplastic range or to some as yet unidentified factor is not clear at this stage.

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Received 31 March
and accepted 21 April 1975

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