Plastic flow of MgO: analysis in the case of ΔG-T plots of increasing slope

In a recent paper, Srinivasan and Stoebe [1] described some experiments concerning the plastic flow of MgO crystals and presented activation enthalpy-temperature (ΔH–T) and activation free energy-temperature (ΔG–T) plots which were both convex towards the T-axis. These results are, however, in some conflict with the principles of thermally activated glide [2-5] and it is the purpose of the present note to consider some of the implications of their experimental results and to suggest a method of overcoming the difficulties of analysis.

The present authors have recently analysed [5] the inter-relationship between the curvatures of the constant strain rate ΔH–T and ΔG–T diagrams constructed for the purpose of identifying the rate controlling obstacles involved in low temperature deformation. The ΔG–T plot can, in principle, be either straight or exhibit a convex or concave curvature towards the temperature axis. We concluded that a *concave* ΔG–T curve, signifying an increase in the pre-exponential factor with effective stress, is typical of thermally activated plastic flow, although a constant or nearly constant, pre-exponential factor (linear ΔG–T) may sometimes result when single crystals are deformed in easy glide. A decrease in the pre-exponential factor with stress was considered to be extremely unlikely as such a stress dependence is inconsistent with any of the rate controlling mechanisms advanced to date. A convex ΔG–T plot, corresponding to the above situation, has nevertheless been observed experimentally by several authors. In the following, we discuss a possible explanation for this behaviour.

In view of the expression:

$$\Delta G = kT \ln(\dot{\epsilon}_0/\dot{\epsilon}) \qquad (1)$$

where $\dot{\epsilon}_0$ is the pre-exponential factor and $\dot{\epsilon}$ is the strain rate, ΔG must be zero at 0 K. Inasmuch as the activation entropy is also zero at 0 K, it follows that the activation enthalpy must equally be zero at 0 K. When the ΔH and ΔG curves of Fig. 8 in [1] are extrapolated to 0 K, however, non-zero values are obtained for these two parameters. Nevertheless, it is possible, by means of the procedure that follows, to calculate ΔG values from which the required intercept can be estimated. This was done in the present instance by substituting the experimental τ^*–T data of [6] and the V_{exp}–τ^* data of [1] into Equations 2 and 3 below:

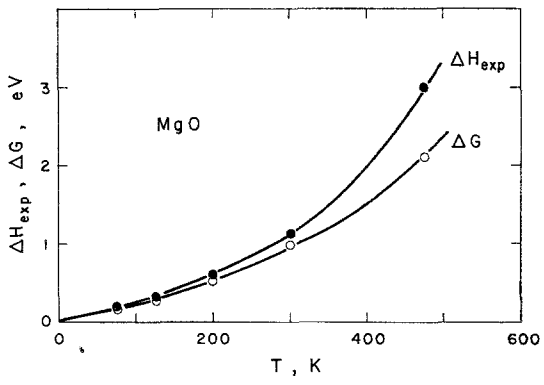

Figure 1 Temperature dependence of ΔH_{exp} and ΔG for the plastic flow of MgO

$$\Delta H_{exp} = -V_{exp} T \frac{\Delta \tau^*}{\Delta T} \qquad (2)$$

$$\Delta G = \frac{\Delta H_{exp} + (V_{exp}\tau^*)\left(\frac{T}{\mu}\frac{d\mu}{dT}\right)}{1 - \left(\frac{T}{\mu}\frac{d\mu}{dT}\right)} \qquad (3)$$

Here, V_{exp} is the experimentally determined activation volume, τ^* is the effective stress and μ is the shear modulus†. It is important to note [4] that Equation 3 is only valid if $\dot{\epsilon}_0$ is either a constant or a function of modulus-reduced stress (τ^*/μ) alone.

The results of this calculation are shown in Fig. 1, and it should be emphasized that the *effective stress notation* was used exclusively in the preparation of this diagram. It is apparent from the figure that the extrapolated values of ΔH_{exp} and ΔG pass through the origin, in agreement with thermodynamic considerations. An important aspect of Fig. 1 requires further comment. It is clear from the non-linearity of the ΔG–T plot that $\dot{\epsilon}_0$ is not constant. Thus the use of Equation 3 cannot be justified on the basis of a fixed $\dot{\epsilon}_0$. It follows from the conditions under which Equation 3 is valid that Fig. 1 is a rigorous representation of the data only if the pre-exponential factor is some function of τ^*/μ. As will be discussed in more detail below, such is unlikely to be the case.

We turn now to the observation that the

†The shear modulus data of [7] were employed for these calculations.

ΔG–T curve of Fig. 1 exhibits a pronounced upward curvature, which corresponds to a *decrease* in the pre-exponential with stress by about ten orders of magnitude in the experimental range. Such a large variation cannot easily be accounted for by any normal dislocation-obstacle interaction. A natural inference is that the pre-exponential must have a pronounced temperature dependence in addition to the usual τ^*/μ dependence, and that this can be attributed, for example, to a rapid increase in the density of activatable sites with temperature. This could arise, in the present instance, if the density of activatable sites depends on the concentration of point defects, particularly vacancies. For the case of dislocation-point defect interaction in MgO, the pre-exponential factor includes the defect concentration due to the presence of impurities and due to non-stoichiometry. At low temperatures the thermal vacancy concentration is too small to affect $\dot{\epsilon}_0$ to any significant extent. As a result, the ΔG–T curve will be either straight or concave in this temperature range. The thermal point defect concentration becomes larger at higher temperatures, however, and the ΔG–T curve can then be expected to exhibit progressively increasing upward curvature as the temperature increases. It is precisely at the higher temperatures (298 to 473 K) in the case of the MgO data of Fig. 1 that the curvature of the ΔG–T plot is the most pronounced.

In order to extract the temperature dependence of $\dot{\epsilon}_0$ from experimental data, the temperature dependence of ΔG *at constant effective stress* τ^* (or the ΔG–τ^* dependence *at constant* T) must be known. In addition, suitable correction terms must be added to Equation 3 to allow for the temperature dependence. As τ^*–T data for MgO are not available at different strain rates, it was not possible in the present case to determine the functional form of $\dot{\epsilon}_0$. It can nevertheless be concluded that the upward curvature of ΔG–T plots in MgO and similar materials can have a physical basis, and that this is likely to involve a rapid increase in the pre-exponential factor with temperature. The latter, in turn, is probably associated with the increase in vacancy concentration, and therefore in the density of activatable sites, that accompanies the increase in temperature.

The authors are indebted to Atomic Energy of Canada Limited and to the National Research Council of Canada for financial support.

References

1. M. SRINIVASAN and T. G. STOEBE, *J. Mater. Sci.* **8** (1973) 1567.
2. G. B. GIBBS, *Mat. Sci. & Eng.* **4** (1969) 313.
3. T. SUREK, M. J. LUTON and J. J. JONAS, *Phil. Mag.* **27** (1973) 425.
4. T. SUREK, L. G. KUON M. J. LUTON and J. J. JONAS, in "Rate Processes in Plastic Deformation", Proceedings of the John E. Dorn Memorial Symposium, Cleveland, Ohio (ASM. Metals Park, Ohio, 1972) in press.
5. D. H. SASTRY, M. J. LUTON and J. J. JONAS, to be published.
6. M. SRINIVASAN and T. G. STOEBE, *J. Mater. Sci.* **9** (1974) 121.
7. O. L. ANDERSON and P. ANDREATCH, JUN, *J. Amer. Ceram. Soc.* **49** (1966) 404.

Received and accepted 26 September 1974

D. H. SASTRY*
M. J. LUTON
J. J. JONAS
Department of Mining and Metallurgical Engineering, McGill University, Montreal, Canada

*On leave from Department of Metallurgy, Indian Institute of Science, Bangalore, India.

The relation between linear and non-linear viscoelasticity of polypropylene

At present there exists no description of non-linear viscoelastic behaviour of solids under multiaxial loading, which is of proven validity and also fruitful in suggesting physical origins of the non-linearity. In these respects the following extension of the theory of linear viscoelasticity is attractive. For a creep experiment in which the stress tensor $\boldsymbol{\sigma}$ is applied at time $t = 0$, define the mean stress σ_m and deviatoric stress tensor $\boldsymbol{\sigma}'$

$$\sigma_m \equiv \tfrac{1}{3}Tr\boldsymbol{\sigma}\,,\quad \boldsymbol{\sigma}' \equiv \boldsymbol{\sigma} - \mathbf{I}\sigma_m$$

where $\mathbf{I}$ is the unit matrix. An isotropic linear viscoelastic solid with shear compliance function $J(t)$ and compressibility function $B(t)$ then deforms at $t > 0$ with strain tensor $\boldsymbol{\epsilon}(t)$ given by

$$\boldsymbol{\epsilon}(t) = \frac{J}{2}(t)\boldsymbol{\sigma}' + \frac{B}{3}(t)\sigma_m\mathbf{I}\,. \qquad (1)$$