

Activation energies for the deformation of superplastic alloys and their phases derived from hot microhardness studies

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Activation energies for two superplastic alloys (Zn78–Al22 and Cu60–Zn40) and their individual phases have been determined by plotting H/E against T_m/T and utilizing the relationship $H/E = G' \exp(Q/nRT)$. Hot hardness measurements were made with a microhardness tester and Young's modulus values were obtained over the appropriate temperature range using the Rayleigh vibration technique. The activation energies obtained are compared, wherever possible, with those reported in the literature and are found to be in reasonably good agreement. These data help in the understanding of the mechanisms of superplasticity in these alloys.

1. Introduction

In superplastic alloys, most of which consist of two or more phases, it seems likely that the flow behaviour of the phases, at some fixed temperature, will differ. It is also possible that this difference is responsible for the cavitation behaviour which many superplastic alloys exhibit [1, 2]. In this work, Zn78–Al22 and Cu60–Zn40 have been chosen for study, because the former is not generally prone to cavitation, while the latter is. Hot microhardness measurements were chosen to determine activation energies for flow, and, as superplastic grains are too small for the hardness of individual phases to be measured *in situ*, alloys were prepared to represent the compositions of the individual phases and these were tested appropriately.

Hot hardness testing has been used to determine activation energies for creep in many pure metals [3–5], but in order to compare strictly the hot hardness data with the corresponding creep data, it is necessary to define the stress, strain and strain rate associated with the indentation and to be able to vary them at will. Usually, the hot hardness data are obtained using a constant load and a constant time of loading at different temperatures. In a hardness test, the indentation stress decreases and the strain rate increases with increasing temperature. The effect of a change in strain rate will be a minimum if the time of loading is

kept short and this approach was used by Larsen-Badse [3], which enabled him to interpret his results in terms of a steady-state creep equation

$$H = A \exp(2Q'/RT) \quad (1)$$

where Q' is the "apparent activation energy for indentation hardness" and R and A are constants. Larsen-Badse determined Q' for 23 metals, and concluded that Q' was proportional, but not equal, to the activation energy for steady-state creep (Q_c) or self-diffusion (Q_L).

Sherby and Armstrong [4] showed the necessity of taking into account the variation of Young's modulus with temperature and derived the following relationship:

$$H/E = G' \exp(Q_c/nRT) \quad (2)$$

where n is the stress exponent ($n = 1/m$, m being the strain-rate sensitivity index) and has a value between 5 and 7 for most pure metals. Equation 2 is used in this work to calculate the activation energies both for the two-phase superplastic alloys and also for their individual phases.

2. Experimental procedure

2.1. Materials

The composition of the alloys tested is shown in Table I. A series of alloys was produced of

TABLE I Composition of alloys

| Alloy | Denoted by | Actual composition (wt %) | Phase represented in superplastic alloy | Temperature range (°C) |
|-----------|-------------------|---------------------------|---|------------------------|
| Al-78Zn | $A_{\alpha\beta}$ | Al-77.4Zn-0.09Fe | | |
| Al-22Zn | A_{α} | Al-21.8Zn | α | 230 to 270 |
| Al-99.5Zn | A_{β} | Al-98.5Zn | β | 20 to 270 |
| 60Cu-Zn | $B_{\alpha\beta}$ | 59.6Cu-Zn | | |
| 62Cu-Zn | B_{α} | 61.4Cu-Zn | α | 300 to 700 |
| 55Cu-Zn | B_{β} | 54.6Cu-Zn | β | 300 to 700 |

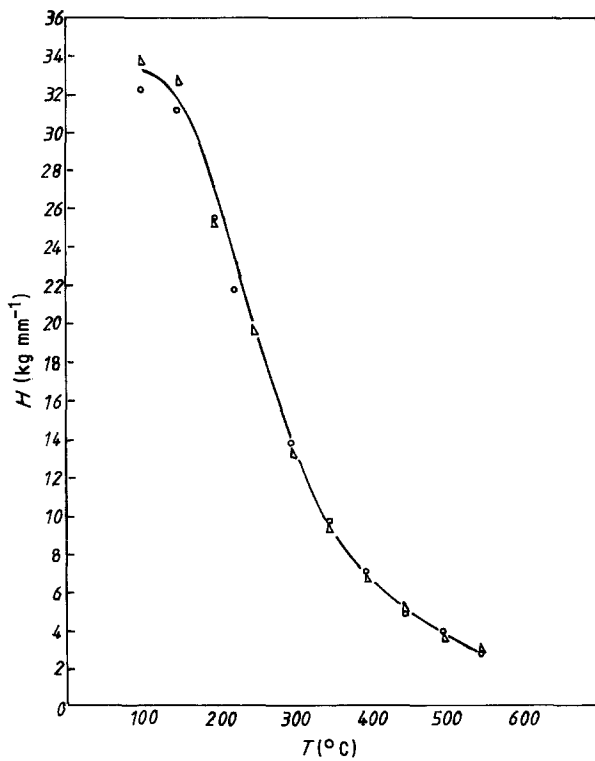


Figure 1 Hardness against temperature curve for commercially pure aluminium: (○) cooling, (Δ) heating. Load, $L = 10$ g, time, $t = 15$ sec.

compositions corresponding to those of the alpha and beta phases in Zn-22Al and Cu-40Zn alloys at their optimum superplastic temperatures. These alloys were in the form of extruded bars of about 2.5 cm diameter.

2.2. Microhardness testing

A hot microhardness tester of Gove [6] design was used and the design and construction of the instrument are described in this reference. Details of the mode of operation of this machine are given elsewhere [7].

2.3. Determination of Young's modulus

For the determination of Young's modulus (E) at various temperatures, a vibration technique based on the Rayleigh principle was used. E was found from the following equation:

$$f_0^2 = \frac{(4.73)^4 E a^4}{16\pi m l^3} \quad (3)$$

where a , l , m and f_0 are the radius, length and mass of the rod, and characteristic frequency of the first mode of vibration, respectively. All materials were centreless ground to the form of cylindrical rods of 0.50 cm diameter, which dimension was constant along the length to within ± 0.005 cm. The specimens were annealed to relieve any residual stresses, and the length of each rod was 10.795 cm. The samples were cleaned ultrasonically in a solution of Gramosol, washed with alcohol and dried before weighing. The total error in determining modulus by this technique is not more than 2%.

3. Results

Hot hardness tests were conducted on commercial purity aluminium and the results are shown in Fig. 1. Using Young's modulus data from Fine [8], a modulus-compensated hardness, H/E , against T_m/T is plotted in Fig. 2. With $n = 5$, an activation energy value of 31 ± 2 kcal mol⁻¹ (130 kJ mol⁻¹) was obtained at $\sim 0.8 T_m$ and this agrees with $Q = 34$ kcal/mol⁻¹ determined from diffusion studies by Lundi and Murdock [9].

The $\ln(H/E)$ against T_m/T curves for all alloys are shown in Figs 3-6. Using Equation 2, Q values were calculated appropriately in the superplastic temperature range (of the model alloys) from the slope of each of these curves and these are given in Table II. All the relationships between hardness and temperature and Young's modulus and temperature are given by Sohal [7], but E against temperature is shown in Figs 7 and

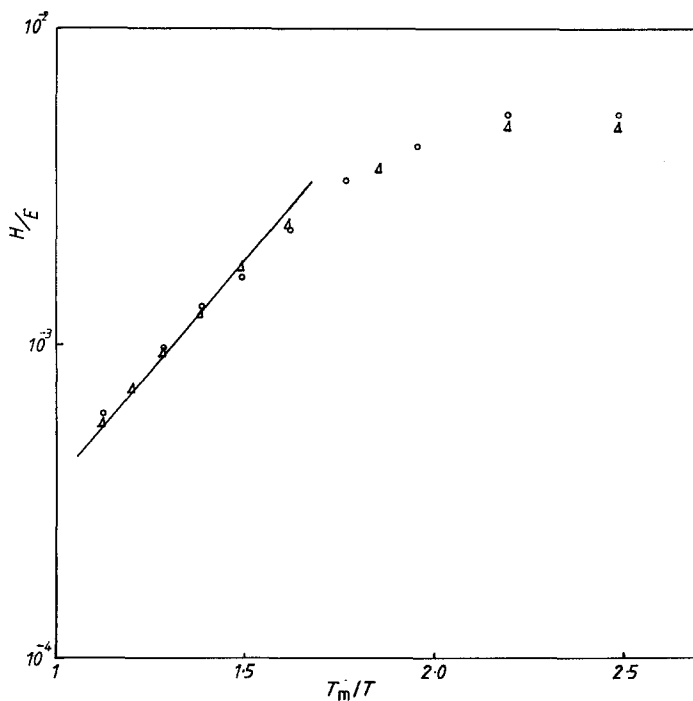


Figure 2 H/E against T_m/T for commercially pure aluminium: (○) cooling, (Δ) heating. Modulus data from Fine [8]. $L = 10$ g, $t = 15$ sec. From straight-line portion $Q = 31$ kcal mol⁻¹ (130 kJ mol⁻¹).

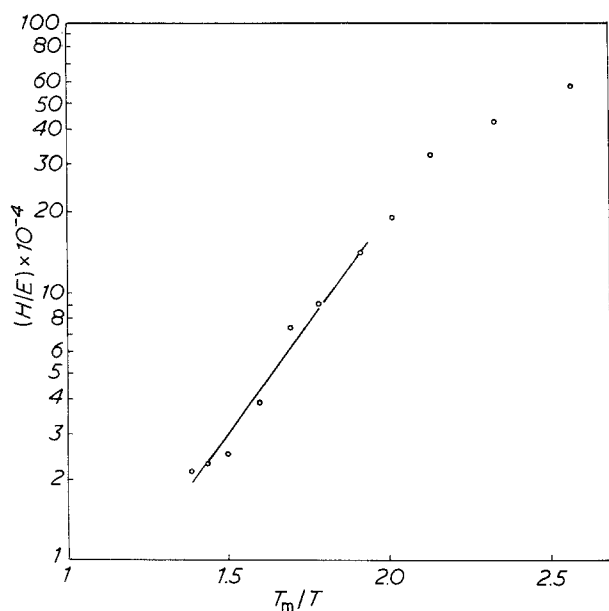


Figure 3 H/E against T_m/T for Zn-Al eutectoid (superplastic Zn78-Al22). From straight-line portion $Q = 11.3 \text{ kcal mol}^{-1}$ (47 kJ mol^{-1}).

8, together with the values predicted from an empirical relation, $E(AB) = N(A)E(A) + N(B)E(B)$, where $N(A)$ and $N(B)$ are the atomic fractions, and $E(A)$ and $E(B)$ are the Young's modulus values for the elements A and B, respectively. Temperature measurements are accurate to within $\pm 2.5^\circ \text{C}$. The total error in determining the Young's modulus was $\pm 2\%$ in the temperature range 0.6 to $0.9 T_m$. The total error in the determined Q values here is $\pm 2 \text{ kcal mol}^{-1}$ (8 kJ mol^{-1}).

4. Discussion

Reported Q values for superplastic deformation,

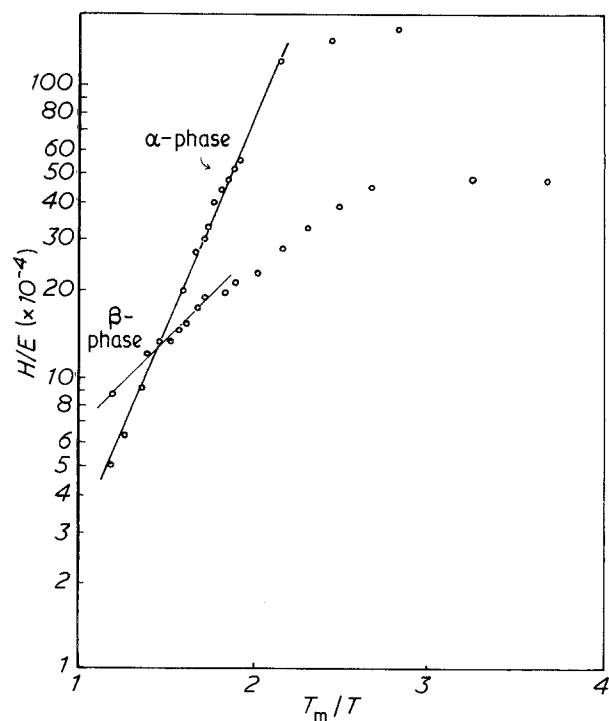


Figure 4 H/E against T_m/T for α and β phases of Zn-Al eutectoid. $Q_\alpha = 29.9 \text{ kcal mol}^{-1}$ (125 kJ mol^{-1}), $Q_\beta = 19.5 \text{ kcal mol}^{-1}$ (82 kJ mol^{-1}).

TABLE II Activation energy values for the alloys

| Alloy | Activation energy, Q (kcal mol^{-1}) | Temperature range | Value of n used in Equation 2 |
|--------------|---|---------------------|---------------------------------|
| $A_{z\beta}$ | 11.3 ± 2 | 0.5 to $0.7 T_m$ | 2 [1, 12] |
| A_z | 29.9 ± 2 | 0.5 to $0.8 T_m$ | 5* |
| A_β | 19.5 ± 2 | 0.7 to $0.9 T_m$ | 5* |
| $B_{z\beta}$ | 21.2 ± 2 | 0.67 to $0.8 T_m$ | 2 [1, 12] |
| B_z | 42.2 ± 2 | 0.6 to $0.8 T_m$ | 5* |
| B_β | 43.0 ± 2 | 0.5 to $0.7 T_m$ | |
| | 22.0 ± 2 | 0.7 to $0.8 T_m$ | 3.5 [18] |

*Data not available. However, it appears that for a large fraction of alloys investigated, the value of n is the same as for pure metals, i.e. $n = 5$ [17].

together with measured values for diffusional processes, are collected for a number of materials by Davies *et al.* [10]. Q values generally fall into two categories: one where the same value is observed as for creep for dislocation-climb (Q_L for self-diffusion), and the other where the values are lower and can be identified as Q for grain-boundary diffusion. A number of workers have determined the Q value for superplastic flow in the Zn-Al eutectoid and the results are summarized by Mohammed *et al.* [11]. A Q value of $15.4 \text{ kcal mol}^{-1}$ (64 kJ mol^{-1}) was obtained by Ball and Hutchison [12] and 13 to 20 kcal mol^{-1} (54 to 84 kJ mol^{-1}) by Naziri *et al.* [13]. It was pointed out that these workers did not correct their Q values for the temperature dependence of the shear modulus, and by doing so Mohammed *et al.* [11] obtained $Q = 17.9 \text{ kcal mol}^{-1}$ (75 kJ mol^{-1}) for the Zn-Al eutectoid. They used an empirical relation of the type $G = N(\text{Zn})G(\text{Zn}) + N(\text{Al})G(\text{Al})$ to calculate the shear modulus G of the alloy, where $N(\text{Zn})$ and $N(\text{Al})$ are the atomic fractions and $G(\text{Zn})$ and $G(\text{Al})$ are the values of the shear modulus for the pure zinc and aluminium, respectively. Fig. 7 shows that the calculated Young's modulus of the eutectoid from such a relationship is markedly different from the actual modulus values, and suggests that the averaging approach of Mohammed *et al.* is not correct.

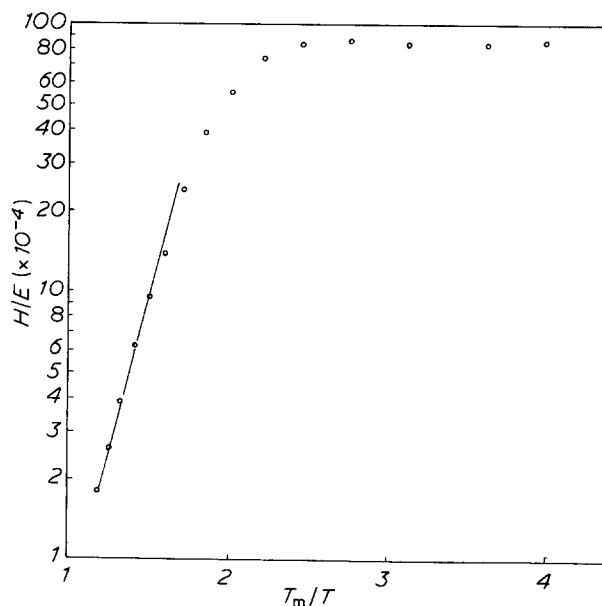


Figure 5 H/E against T_m/T for superplastic 60/40 brass. From straight-line portion $Q = 21.2 \text{ kcal mol}^{-1}$ (89 kJ mol^{-1}).

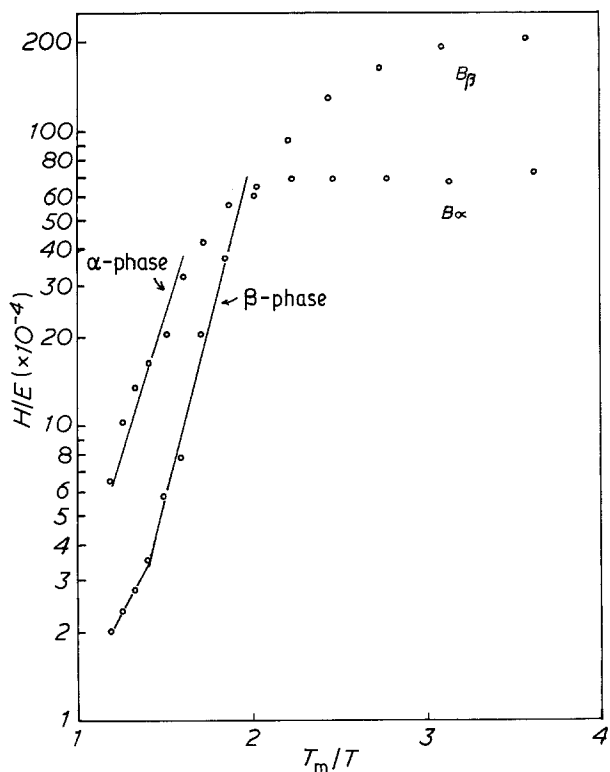


Figure 6 H/E against T_m/T for α and β phases of 60/40 brass. $Q_\alpha = 42 \text{ kcal mol}^{-1}$ (176 kJ mol^{-1}); $Q_\beta = 22 \text{ kcal mol}^{-1}$ (lower portion) and 43 kcal mol^{-1} (upper portion) (92 and 180 kJ mol^{-1}).

In the present study, experimental values of modulus at various temperatures were determined and used and a Q value of $11.3 \pm 2 \text{ kcal mol}^{-1}$ ($47 \pm 8 \text{ kJ mol}^{-1}$) obtained from Fig. 3. At the superplastic temperature of 250°C , Q values as found from the slope in Fig. 4 and using Equation 2 are 29.9 ± 2 and $19.5 \pm 2 \text{ kcal mol}^{-1}$ (128 ± 8 and $82 \pm 8 \text{ kJ mol}^{-1}$) for the alpha phase and beta phase, respectively. The H values of the alpha phase, beta phase and that of the

alloy itself at 250°C are 18, 15 and $1.3 H_v$, respectively. Based on the data presented here and those on the mechanical properties of the individual phases it is suggested [14] that the accommodation of grain-boundary sliding may be occurring in the alpha phase predominantly by dislocation glide, whereas in the beta phase, diffusion may be more important. The Q value for the eutectoid is close to the Q value for grain-boundary diffusion in zinc, and indicates the important role played by the beta phase in the superplastic deformation of the alloy, as suggested by Naziri and Pearce [15].

From their work on the effect of order-disorder transformation upon diffusion in Cu-Zn, Funamizu and Watanabe [16] showed that Q for interdiffusion in the disordered beta phase (above 453°C) was $22.6 \text{ kcal mol}^{-1}$ (95 kJ mol^{-1}). Griffiths and Hammond [17] quoted $Q = 24 \text{ kcal mol}^{-1}$ (100 kJ mol^{-1}) for beta brass (47.7% Zn) at $0.8 T_m$. In this work, at 600°C , data from Figs 5 and 6 give

$$Q_\alpha = 42.2 \pm 2 \text{ kcal mol}^{-1} (177 \pm 8 \text{ kJ mol}^{-1})$$

$$Q_\beta = 22.0 \pm 2 \text{ kcal mol}^{-1} (92 \pm 8 \text{ kJ mol}^{-1})$$

$$Q_{\alpha\beta} = 21.2 \pm 2 \text{ kcal mol}^{-1} (89 \pm 8 \text{ kJ mol}^{-1})$$

It seems reasonable to suppose, then, that in superplastic flow in Cu-40Zn, the accommodation mechanism is bulk diffusion of the beta phase [14].

Incidentally, the hardness (at 600°C) of the phases and the alloy are

| | |
|-------------------|-----------|
| α phase | $8.5 H_v$ |
| β phase | $1.1 H_v$ |
| $B_{\alpha\beta}$ | $3.1 H_v$ |

5. Conclusions

1. It has been shown that activation energies for two-phase superplastic alloys and for their individual

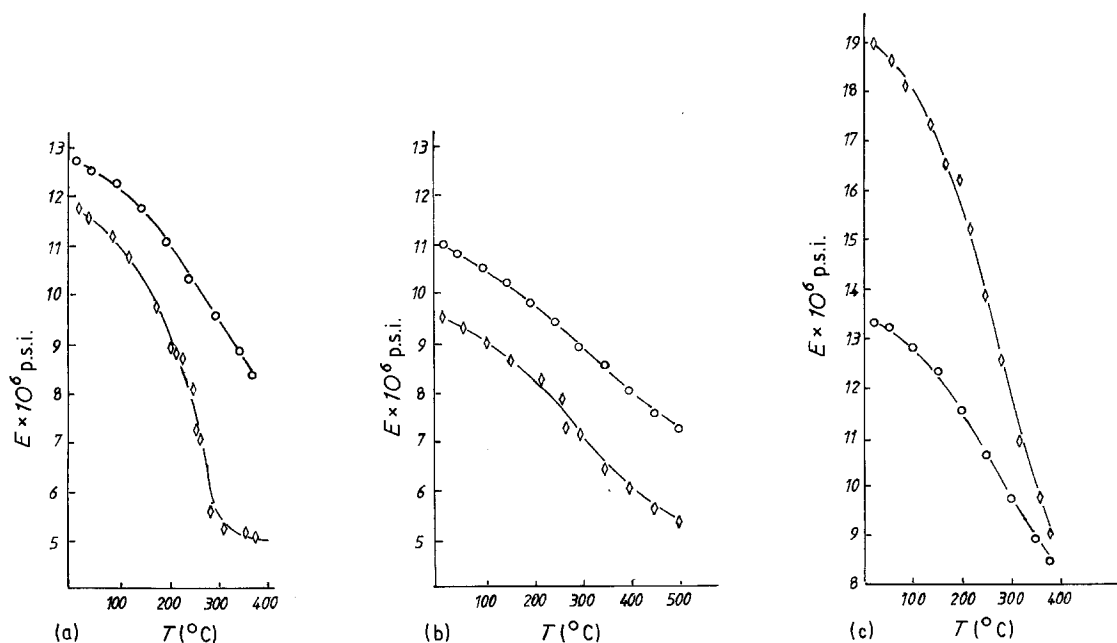


Figure 7 Young's modulus at various temperatures for (a) Zn-Al eutectoid ($A_{\alpha\beta}$) and (b) its α -phase (A_α) and (c) its β -phase (A_β): (\diamond) experimental, (\circ) calculated from an empirical relation $E_{ZnAl} = (E_{Zn}N_{Zn} + E_{Al}N_{Al})/(N_{Zn} + N_{Al})$. E data on pure elements from Fine [8]. 1 p.s.i. = 6.895 kPa .

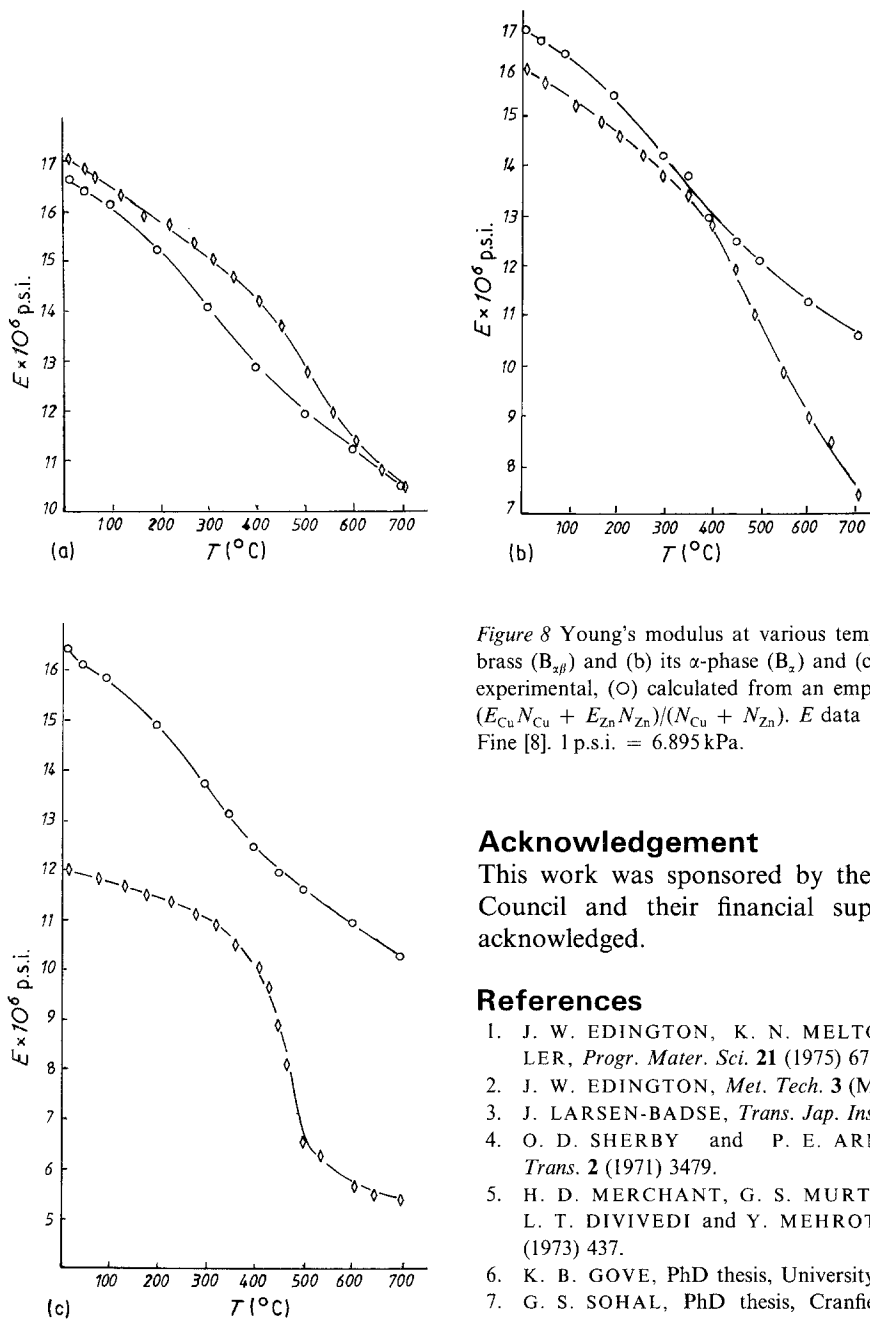


Figure 8 Young's modulus at various temperatures for (a) 60/40 brass ($B_{\alpha\beta}$) and (b) its α -phase (B_{α}) and (c) its β -phase (B_{β}): (\diamond) experimental, (\circ) calculated from an empirical relation $E_{CuZn} = (E_{Cu}N_{Cu} + E_{Zn}N_{Zn})/(N_{Cu} + N_{Zn})$. E data on pure elements from Fine [8]. 1 p.s.i. = 6.895 kPa.

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phases may be determined from a hot microhardness study.

2. The Q values reported here, derived from hot microhardness measurements, are compared wherever possible with those reported in literature and are in reasonably good agreement.

3. These Q values fit in with certain of the mechanisms proposed for the superplastic deformation of these alloys [14]:

(a) The Q value for the Zn–Al eutectoid is close to the activation energy of grain-boundary diffusion in zinc, indicating the important role played by the beta phase ($\alpha:\beta = 28:72$ at 250°C) in the superplastic deformation of this alloy.

(b) The Q value for the Cu–40Zn duplex alloy is similar to the activation energy for its beta phase ($Q_{\beta} = 22.0 \pm 2 \text{ kcal mol}^{-1}$ ($92 \pm 8 \text{ kJ mol}^{-1}$)), indicating the important role played by the beta phase (its hardness at 600°C is $1.1 H_v$) in the superplastic deformation of this alloy.

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