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The activation energy for superplastic flow in Al–6 Cu–0.4 Zr

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A study of the activation energies for superplastic flow in an essentially single phase Al–6Cu–0.4Zr alloy has been made in the temperature range 430 to 490° C. Straight line Arrhenius plots for both Q_σ and $Q_{\dot\epsilon}$ were obtained in Regions I, II and III. In all cases the ratio $Q_{\dot\epsilon}/Q_\sigma$ corresponded well to the average strain rate sensitivity as determined by both change rate testing and from the slope of the $\ln \sigma$ versus $\ln \dot\epsilon$ curves. Values of Q_σ of 35.2, 19.0 and 20.1 kcal mol^{-1} were obtained in Regions I, II and III respectively. These values were expected to be close to the true activation energies, and corresponded to the measured lattice and predicted grain boundary diffusion activation energies. These energies, together with microstructural observations made on deformed material, were used to identify possible deformation mechanisms.

1. Introduction

There has been a sustained interest in measuring the activation energies associated with superplastic flow in order to explore the possible deformation mechanisms at each portion of the characteristic sigmoidal $\ln \sigma$ versus $\ln \dot\epsilon$ curves. The results so far obtained have been somewhat contradictory, as, for example, activation energies associated with both grain boundary and volume diffusion have been identified in the superplastic Region II, whilst other studies have yielded values inconsistent with either of these processes. These results have recently been reviewed by Edington *et al.* [1], Padmanahban and Davies [2] and Mohamed *et al.* [3]. In general, such studies have been restricted to microduplex alloys in which the small grain size required for superplasticity has been attained and retained by use of a eutectic or eutectoid mixture. Recently, there have been reported activation energies for superplastic flow in essentially single phase alloys, Al–Zn–Mg [4] and Cu–Al–Si–Co [5].

The ability to define an activation energy depends on the deformation following an empirical equation of the form

$$\sigma = \text{constant} \times \dot\epsilon^m \exp(Q/RT) \tag{1}$$

where σ is the flow stress, $\dot\epsilon$ the strain rate, m the strain rate sensitivity ($\mathrm{d}\ln\sigma/\mathrm{d}\ln\dot\epsilon$), Q the activation energy, R the gas constant, and T the absolute temperature. Alternatively this can be expressed as:

$$\dot\epsilon = \text{constant} \times \sigma^n \exp(-Q/RT)$$

where $n = 1/m$.

Padmanahban and Davies [2] have shown that the activation energies derived at constant stress and strain rate (Q_σ and $Q_{\dot\epsilon}$) will be different, and suggested that the discrepancies in the literature, where both lattice and grain boundary control have been reported, were due to a failure to distinguish between them. They showed that

$$mQ_\sigma = Q_{\dot\epsilon}, \tag{2}$$

where m is defined as before. As m is often about 0.5, which is also the usually measured ratio of grain boundary to lattice diffusion energies, such an argument is obviously appealing. However, Mohamed and Langdon [6] showed that this factor could not account for all the published

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discrepancies, and this question remains unresolved.

Recently, a new class of aluminium-based superplastic alloys, which are essentially single-phase, has been developed in which the fine grain size is first created by recrystallization and then retained by a fine dispersion of Al_3Zr [7]. Superplastic deformation in this alloy is shown, uniquely, to proceed by a process of dynamic recrystallization in the early stages (~ 50%) of deformation, although its continuing role is unclear. Therefore, a study of one such Al–Cu–Zr alloy was undertaken to provide more activation energy data from an effectively single-phase alloy, and to explore the effect of any continuing dynamic recrystallization on the energies measured. The attraction of such a single-phase system is that any activation energy can easily be compared to that for grain boundary or lattice self-diffusion, rather than having to consider the diffusion of a variety of species in a series of interfaces.

2. Experimental

Material of composition given in Table I was supplied in the form of $\frac{1}{4}$ in. plate from which tensile test specimens were cut in the finish rolling direction. Testing was carried out in a triple-wound furnace capable of sustaining a 200 mm zone of constant (± 2° C) temperature on a floor model Instron machine. In order to determine the activation energy for superplastic flow testing was carried out at 430, 450, 470, and 490° C; the material displaying the characteristic high strain rate sensitivity of the flow stress at all these temperatures. For each temperature the ln (stress) versus ln (strain-rate) curve and m values were determined by changing the imposed cross-head velocity incrementally, either from the fastest to slowest (change-down) or vice versa (change-up). The construction of $\ln \sigma$ versus $\ln \dot{\epsilon}$ curves and the determination of instantaneous m values depend on the assumption of uniform specimen deformation. It was found that this was not always the case in change-down tests, where large initial elongations were given in a region of low m, and necking could be observed. Such data was not recorded. However, in those cases where necking was not apparent, excellent agreement between the two modes of testing was given, and this demonstrates the structural stability of the material tested. This stability was attained by giving the specimens an initial strain of 50% with $\dot{\epsilon} = 10^{-3}\ \text{sec}^{-1}$ at each temperature, in order to break up the starting, directional microstructure, and to displace testing from the region where rapid structural changes are occurring. The $\ln \sigma$ versus $\ln \dot{\epsilon}$ curves were calculated from the maximum loads recorded at each strain rate and plots of m versus $\ln \dot{\epsilon}$ constructed from the load–time curves following the method denoted "C" by Hedworth and Stowell [8].

TABLE I The composition of the alloy studied in wt %

Al	Cu	Zr	Si	Fe
Balance	6.2	0.39	0.06	0.06

Thin foils for electron microscopy were prepared to examine any microstructural indications of a change in deformation mode with temperature. In an attempt to retain any dislocation substructure present, specimens were quenched into ice and water within 10 sec of the cessation of cross-head motion. Samples were examined from material deformed 100% with $\dot{\epsilon} = 10^{-3}\ \text{sec}^{-1}$ at 430, 450, 470 and 490° C.

3. Results

The $\ln \sigma$ versus $\ln \dot{\epsilon}$ curves for the material at the four temperatures studied are shown in Fig. 1.

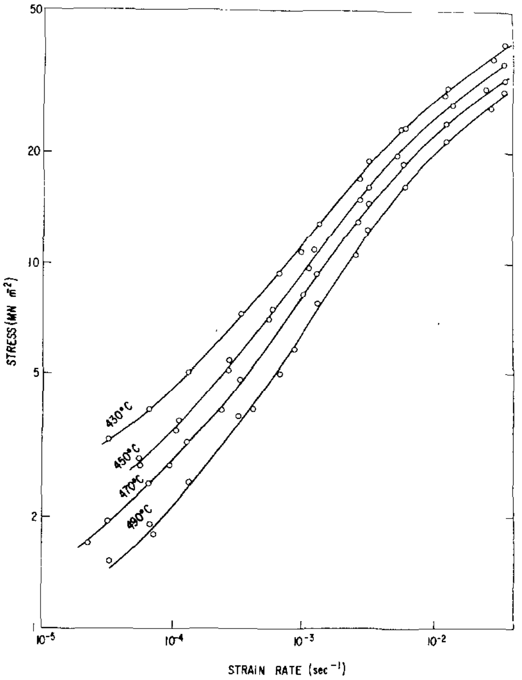

Figure 1 The ln (flow stress) versus ln (strain rate) curves for the material at the four test temperatures.

TABLE IIa The m values as measured from tangents constructed to the $\ln \sigma$ verus $\ln \dot{\epsilon}$ curves at the strain rates shown

Strain rate ($\sec^{-1}$)	Temperature (° C)				
	430	450	470	490	Average
10^{-2}	0.29	0.28	0.28	0.30	0.29
10^{-3}	0.47	0.50	0.52	0.56	0.51
10^{-4}	0.36	0.37	0.37	0.41	0.38

TABLE IIb The m values as measured from the change rate tests

Strain rate ($\sec^{-1}$)	Temperature (° C)				
	430	450	470	490	Average
10^{-2}	0.30	0.31	0.34	0.37	0.33
10^{-3}	0.43	0.45	0.47	0.49	0.46
10^{-4}	0.32	0.36	0.38	0.38	0.36

It can be seen that the classical sigmoidal curve associated with superplastic behaviour is given at each temperature and that the curves can be divided into Regions I, II, and III with the high strain-rate sensitivity being displayed in the intermediate Region II. It is possible that the m values may fall further in both Regions I and III, at strain rates which lay outside the range currently available. Tangents were constructed to each curve at strain rates of 10^{-2}, 10^{-3} and $10^{-4}\ \sec^{-1}$, and the strain rate sensitivities, m, obtained in this manner are given in Table IIa.

The m values obtained from load–time curves were plotted against the mean strain rate of the change, and a smooth curve drawn through the data points for each temperature (see Fig. 2). In this manner m values for each of the three chosen strain rates were obtained, and these are shown in Table IIb.

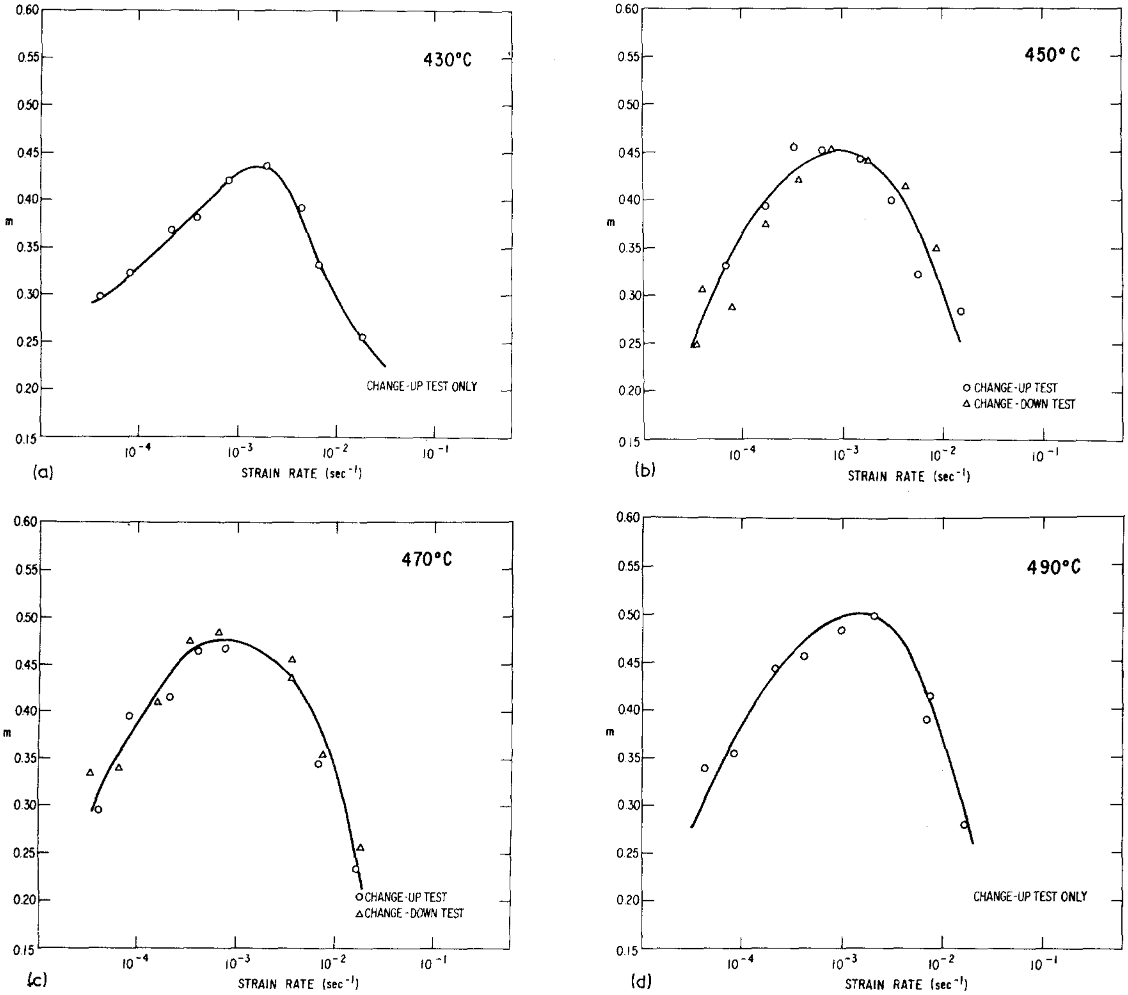

Figure 2 The plots of m against strain rate obtained at the four temperatures by change rate tests.

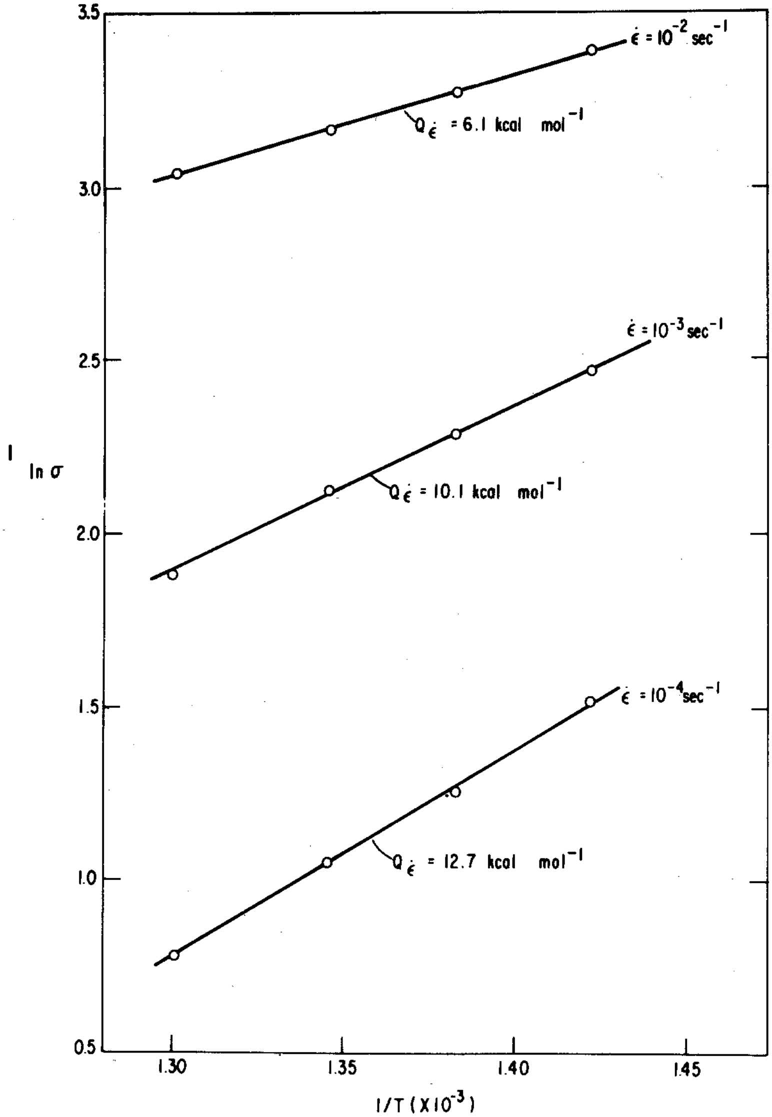

Figure 3 The Arrhenius plots used to determine activation energies at constant strain rate, $Q_{\dot{\epsilon}}$.

Activation energies at constant $\dot{\epsilon}$ were obtained from Fig. 1 by plotting ln (stress) against $1/T$ at the three selected strain rates. In all cases, linear plots (within the expected experimental errors) were obtained, and allowed the identification of a characteristic $Q_{\dot{\epsilon}}$ from the slope of the graphs, see Fig. 3. In order to compare these results obtained at constant $\dot{\epsilon}$ with those at constant σ, it is necessary to define a stress level corresponding to each strain rate. This was done by taking the mean stress position of the four curves at each strain rate; i.e., effectively the stress level for a 460° C curve. This gave ln σ values of 1.2, 2.2, and 3.2, or stresses of 3.3, 9.0, and 24.5 MN m^{-2}. The validity of this assumption of equivalent stress level is discussed in the next section. The Arrhenius plots at these equivalent stress levels are shown in Fig. 4, with the corresponding Q_σ indicated.

The microstructures observed after 100% superplastic deformation at $\dot{\epsilon} = 10^{-3}$ sec^{-1} (Region II) were remarkably similar at all temperatures. Fig. 5 shows an example of the microstructure observed after 100% elongation at 490° C. It can be seen that the structure is relatively equiaxed, but that the dislocation density varies greatly from grain to grain. Certain grains are essentially dislocation-free, whilst others show a large density of tangled dislocations. Fig. 6 illustrates a further class of grain which can be observed in which the dislocations are arranged in the form of sub-boundaries and networks. The configuration of the sub-boundary in this grain suggests it to be in a process of formation or dissolution.

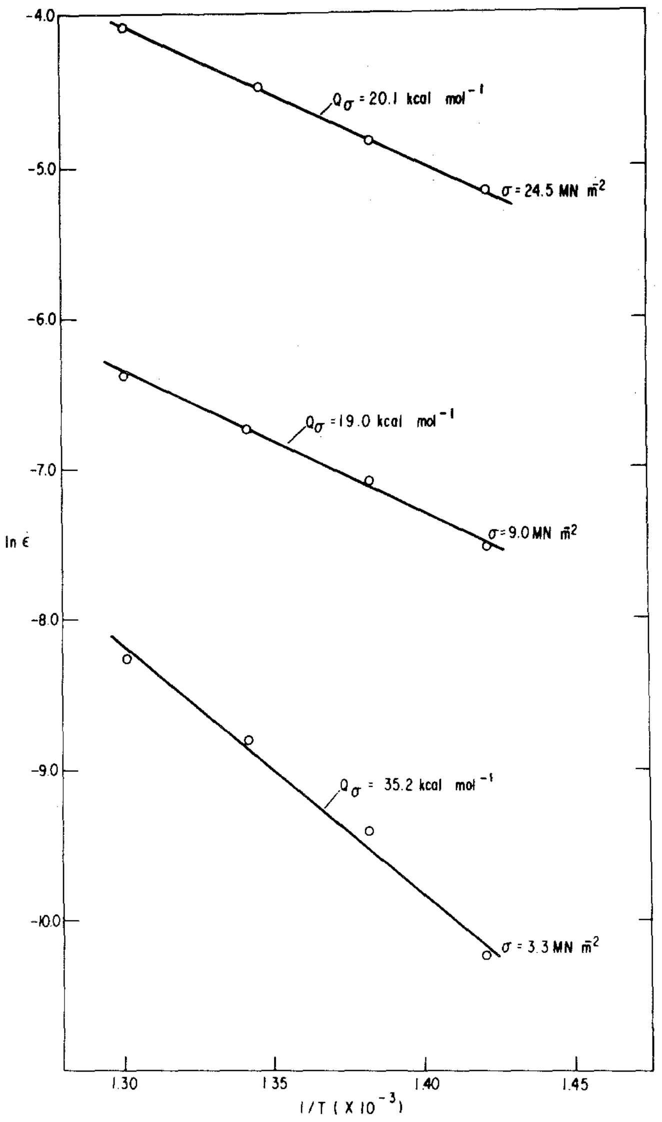

Figure 4 The Arrhenius plots used to determine activation energies at constant stress levels, Q_σ.

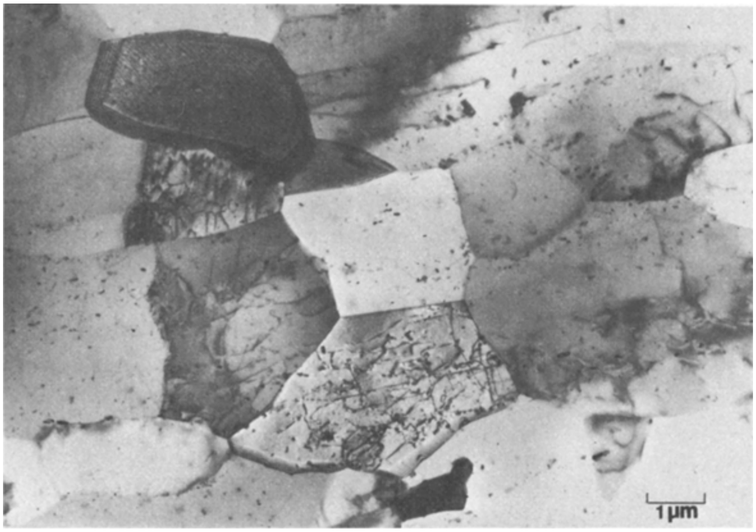

Figure 5 The microstructure observed after 100% superplastic deformation at 490° C, $\dot{\epsilon} = 10^{-3}$ sec^{-1} (Region II). It can be seen that the structure is relatively equiaxed, but with a highly variable dislocation density.

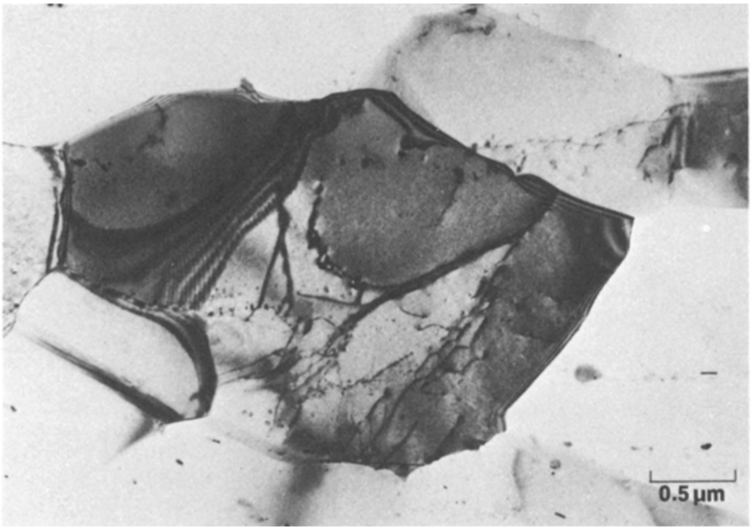

Figure 6 An example of a grain showing networks and sub-boundaries, deformed 100% at 430° C, $\dot{\epsilon} = 10^{-3}\ \text{sec}^{-1}$.

4. Discussion

4.1. Determination of activation energies from ln σ versus ln $\dot{\epsilon}$ plots

As was first pointed out by Padmanabhan and Davies [2] two characteristic activation energies can be measured for a superplastic deformation process, $Q_{\dot{\epsilon}}$ and Q_σ and these can be related by Equation 2. This analysis has recently expanded by Mohamed and Langdon [6], who further distinguished between a true and apparent activation energy, the true differing from the apparent in that a temperature compensated stress term is used. However, over the ranges involved any such correction will be small and the true activation energy can easily be identified with that measured at constant stress.

The validity of applying Equation 2 to experimental results depends on the constancy of the strain rate parameter, m. Gifkins [9] has pointed out the errors involved in Cahoon's work [10] on Al–17 wt% Cu when points at constant stress straddled Regions I to III and involved large changes in m. The changes in m with both strain rate and temperature which occur within any single Region have not been large enough to prevent straight line Arrhenius plots being obtained for $Q_{\dot{\epsilon}}$ and Q_σ, and have allowed the successful application of Equation 2 [2].

4.2. Analysis of the current results

The m values derived from the slope of the ln σ versus ln $\dot{\epsilon}$ curves average 0.29, 0.51, and 0.38 at the three strain rate levels chosen with spreads of ±0.01, ±0.04, and ±0.03, the higher values being consistently given at the higher temperatures. Despite such spread good straight line plots for $Q_{\dot{\epsilon}}$ were obtained and gave values of 6.1, 10.1, and 12.7 kcal mol^{-1} respectively, whilst corresponding Q_σ determinations yielded 20.1, 19.0 and 35.2 kcal mol^{-1}. These determinations were similarly made from linear plots at the higher stress levels, but at $\sigma = 3.3\ \text{MN m}^{-2}$ the worsening fit may be due to Region I not being fully entered. The relationship between $Q_{\dot{\epsilon}}/Q_\sigma$ and m is explored in Table III, for m determined both by change rate testing and from the slope of the curves. As experimental errors of ~0.02 in m determinations can be expected, the fit between the ratio $Q_{\dot{\epsilon}}/Q_\sigma$ and the average measured slope of the ln σ versus ln $\dot{\epsilon}$ curve is seen to be excellent, whilst that with the change rate data is acceptable allowing for the greater experimental difficulties involved. It can thus be seen that despite the changes in m within regions, straight-line Arrhenius plots can be constructed for both Q_σ and $Q_{\dot{\epsilon}}$, and that these yield ratios equal to the m as measured from the average slope of the curves.

Examination of the absolute values of Q_σ, which are expected to approximate to the true activation energy for the deformation process [6], shows that a virtually constant value of ~20 kcal mol^{-1} is obtained from both Regions II and III, rising to 35 kcal mol^{-1} in Region I. These values should be compared to the known activation energies for diffusion in aluminium. Lundy and Murdoch [11] obtained a value for Q_σ of 34 kcal mol^{-1} for self-diffusion in pure aluminium over the temperature range 456 to

TABLE III Comparison of $Q_{\dot{\epsilon}}/Q_\sigma$ and the average m values obtained from change rate testing and the slope of the $\ln \sigma$ versus $\ln \dot{\epsilon}$ curves. Data from Tables IIa and b

Strain rate; stress level	$Q_{\dot{\epsilon}}$ (kcal mol^{-1})	Q_σ (kcal mol^{-1})	$Q_{\dot{\epsilon}}/Q_\sigma$	m (change rate)	m (slope of $\ln \sigma$ versus $\ln \dot{\epsilon}$)
$\dot{\epsilon} = 10^{-2}$ sec^{-1}; $\sigma = 24.5$ MN m^{-2}	6.1	20.1	0.30	0.33	0.29
$\dot{\epsilon} = 10^{-3}$ sec^{-1}; $\sigma = 9.0$ MN m^{-2}	10.1	19.0	0.53	0.46	0.51
$\dot{\epsilon} = 10^{-4}$ sec^{-1}; $\sigma = 3.3$ MN m^{-2}	12.7	35.2	0.36	0.36	0.38

643° C, and this value was also found by Mehl *et al.* [12] for diffusion in Al–7% Cu in the 400 to 504° C range. Unfortunately, the situation with regard to grain boundary self-diffusion in aluminium is not so well defined, and no reported activation energy exists. Mukherjee [13] suggests the adoption of a value of approximately half the lattice diffusion activation energy; i.e., about 17 kcal mol^{-1}. This value is close to that measured in Regions II and III by the present study, which is also near to that of 23 kcal mol^{-1} measured for the diffusion of Cu in Al–AlCu$_2$ interfaces by Ho and Weatherly [14]. These observations suggest grain boundary diffusion to be the rate controlling process. Within Region II similar results have been obtained from a wide range of alloys [3–5, 15–17] and can be identified with a number of proposed mechanisms such as the local accommodation of grain boundary sliding [18], the climb of a dislocation from the head of a pile-up into a grain boundary [19], Coble creep [20], or Ashby–Verrall's model of superplasticity [21].

The similarity in microstructures noted throughout the temperature range in Region II supports the occurrence of a single deformation mode with a unique activation energy. The observed motion of sub-boundaries across grains could be taken as circumstantial support for climb into boundaries being the rate controlling step, and would lead to the observed activation energy.

The limited work [3–5, 15, 16] on Region III has indicated a value of Q_σ close to that for lattice diffusion, and this has been identified with an intragranular dislocation creep process. The current results suggest that this mechanism may still be controlled by boundary climb in the early part of Region III examined. The most closely corresponding superplastic alloys on which activation energy determinations have been made are an Al–17% Cu alloy [10] and an Al–6Zn–3Mg alloy [4]. The former study obtained a value of Q_σ of 39 kcal mol^{-1} throughout all the stress levels studied, which appeared to encompass Regions I, II, and III, whilst the latter obtained a value of 19 kcal mol^{-1} in Region II rising to 41 kcal mol^{-1} when grain growth occurred and Region III was entered.

The current activation energy obtained in Region I is exactly that expected for lattice diffusion, little dislocation activity is predicted at these stress levels, and a deformation process based on Nabarro–Herring creep [22, 23], or an Ashby–Verrall model [21] with volume diffusion predominating is suggested. Little previous work has been done on Region I, however Mohamed *et al.* [3] have reported a value of Q_σ equal to that for lattice diffusion in Zn–22 wt% Al within this region. In contrast, Vaidya *et al.* [16] have obtained a value corresponding to grain boundary diffusion in the same alloy, but their results were singular in also reporting an increase in m in this region. Activation energies corresponding to lattice diffusion in Region I have also been reported for PbSn [17] and a Cu alloy [5].

When considering the fact that no unusual activation energy effects were seen in this alloy, which may be undergoing a process of continuing dynamic recrystallization, it must be remembered that this recrystallization is not expected to be rate controlling under constant cross-head velocity testing, and that activation energies typical of diffusive processes would be expected for recrystallization.

5. Conclusions

(1) In the current Al–6Cu–0.4Zr superplastic alloy straight line Arrhenius plots for both Q_σ and $Q_{\dot{\epsilon}}$ are obtained from each region.

(2) The ratios $Q_{\dot{\epsilon}}/Q_\sigma$ agree well with the m values obtained from the slope of the $\ln \sigma$ versus $\ln \dot{\epsilon}$ curve, and to a reasonable degree with the less accurate change rate data.

(3) The activation energy, Q_σ, in both Region II and the start of Region III, for the 430 to 490° C range studied, corresponds to that expected for grain boundary diffusion.

(4) The activation energy, Q_σ, in Region I rises to that measured for bulk diffusion.

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References

1. J. W. EDINGTON, K. N. MELTON and C. P. CUTLER, *Prog. Mater. Sci.* **21** (1976) 61.
2. K. A. PADMANABHAN and G. J. DAVIES, *Phys. Stat.Sol. (a)* **18** (1973) 295.
3. F. A. MOHAMED, S. A. SHEI and T. G. LANGDON, *Acta Met.* **23** (1975) 1443.
4. R. H. BRICKNELL and J. W. EDINGTON, *Met. Trans* **7A** (1976) 153.
5. S. A. SHEI and T. G. LANGDON, *Acta Met.* **26** (1978) 1153.
6. F. A. MOHAMED and T. G. LANGDON, *Phys. Stat Sol. (a)* **33** (1976) 375.
7. B. M. WATTS, M. J. STOWELL, B. L. BAIKIE and D. G. E. OWEN, *Metal Sci.* **10** (1976) 186.
8. J. HEDWORTH and M. J. STOWELL, *J. Mater. Sci.* **6** (1971) 1061.
9. R. C. GIFKINS, *Scripta Met.* **10** (1976) 433.
10. J. R. CAHOON, *Metal Sci.* **9** (1975) 346.
11. T. S. LUNDY and J. F. MURDOCK, *J. Appl. Phys.* **33** (1962) 1671.
12. R. F. MEHL, F. A. RHINES and K. A. von den STEINEN, *Metals & Alloys,* **13** (1941) 41.
13. A. K. MUKHERJEE, *Mater. Sci. Eng.* **8** (1971) 83.
14. H. HO and G. C. WEATHERLY, *Acta Met.* **23** (1975) 1451.
15. F. A. MOHAMED and T. G. LANGDON, *Acta Met.* **23** (1975) 117.
16. M. L. VAIDYA, K. L. MURTY and J. E. DORN, *ibid.* **21** (1973) 1615.
17. F. A. MOHAMED and T. G. LANGDON, *Phil. Mag.* **32** (1975) 697.
18. R. RAJ and M. F. ASHBY, *Met Trans* **2** (1969) 1113.
19. H. W. HAYDEN and J. H. BROPHY, *Trans. ASM* **61** (1968) 542.
20. R. L. COBLE, *J. Appl. Phys.* **34** (1963) 1679.
21. M. F. ASHY and R. A. VERRALL, *Acta Met.* **21** (1973) 149.
22. F. R. N. NABARRO, Report on Conference on Strength of Solids, (Physical Society, 1948, London) p. 75.
23. C. HERRING, *J. Appl. Phys.* **21** (1950) 437.

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