

# The effect of the second-phase volume fraction on the grain size stability and flow stress during superplastic flow of binary alloys

ADI ARIELI

*Metals Research Laboratories, Olin Corp., New Haven, CT 06511, USA*

This paper considers to what extent the second-phase volume fraction in superplastic binary alloys affect the matrix grain size stability during deformation and, through it, the flow stress at constant temperature and strain rate. It is shown for five different superplastic binary alloy systems, that at constant temperature and strain rate the flow stress will increase with the deviation of the second-phase volume fraction in the alloys from that required for maximum matrix grain size stability. A new parameter ( $Z$ ) which quantifies these deviations has been introduced in this paper. The possible errors in determining the pertinent parameters in the rate equation for superplastic flow by testing alloys with  $Z$  is discussed.

## 1. Introduction

The stability of grain structure during superplastic deformation of metals and alloys is of paramount importance. The superplastic regime is confined to very fine grained structures ( $d \leq 10 \mu\text{m}$ ) and grain growth during deformation leads to the loss of superplastic behaviour [1] due to a reduction of the boundary area relative to the volume. In addition, it was shown that both the pre-exponential factor and the activation energy in the diffusivity expression are higher for a non-stationary boundary than for a stationary one [2]. Consequently, when grain growth takes place concurrently during superplastic deformation, a decrease in diffusivity might be expected leading to a decrease in strain rate at constant applied stress or an increase in the flow stress at constant imposed strain rate [1, 3].

As pointed out by Nicholson [4], there are two thermodynamic forces acting on grain growth during superplastic deformation: (a) due to consideration of reduction of surface energy, and (b) due to lowering of the stored strain energy term

arising from dislocation density due to deformation. The latter is related to the kinetics of grain boundary migration during deformation [5], which in turn is coupled to the kinetics of grain-boundary sliding [6], whereas the former will depend on the initial grain size, grain shape and diffusion. Second-phase particles (grains) will put an upper limit on the maximum grain size in a metal, i.e. the matrix size will be stabilized by a distribution of second-phase particles (grains). That seems to be the reason why superplastic behaviour is observed only in single-phase materials with second-phase particles uniformly distributed throughout the matrix or in two-phase alloys (microduplex alloys) [7, 8].\*

It is the purpose of this paper to examine the effect of second-phase particles (grains) on the matrix grain size stability and the measured flow stresses during superplastic flow of various alloys.

## 2. Theory

Recently, Beere [10] presented a computer model for grain size stability involving switching in micro-

\*Unusually high ductilities were observed in fine grained nickel [9] tested for short times. However, no superplastic behaviour *per se* was observed in this pure metal.

duplex alloys. His analysis indicates that in a perfect hexagonal array the minimum fraction of second-phase grains required to achieve grain stability is 0.25; whereas in an irregular grain structure it is  $\approx 0.28$ . The condition for this analysis to hold is that the grains of both phases should have the same average size. More complex expressions, which take into account the relative size of the two phases as well as the volume fraction of the second-phase, were proposed by Gladman [11], Edington [12] and Hellman and Hillert [13]. Corti [14] compared these expressions with data for  $\alpha + \beta$  Ti–Mn alloys and concluded that only the expression due to Hellman and Hillert [13] gives acceptable values of the stabilized matrix grain size.

According to Hellman and Hillert [13], the stabilized matrix grain size ( $d_\alpha$ ) is related to the second-phase grain size ( $d_\beta$ ) and volume fraction ( $X_\beta$ ) by the relation,

$$d_\alpha = \frac{4d_\beta}{9\beta'X_\beta}, \quad (1)$$

where  $\beta'$  is a correction factor.

The volume fraction of the second-phase required to stabilize the matrix grain size is then, according to Equation 1,

$$X_\beta = \frac{4}{9} \frac{1}{\beta'} \frac{d_\beta}{d_\alpha}. \quad (2)$$

Equation 2 indicates that  $X_\beta$  will be uniquely determined by the ratio of the second-phase grain size to the matrix grain size. This dependence is shown schematically in Fig. 1 for various values of  $\beta'$ . The plots in Fig. 1 suggest that relatively small volume fractions ( $X_\beta = 0.1$  to  $0.2$ ) of fine second-phase particles ( $d_\beta/d_\alpha = 0.2$  to  $0.3$ ) will stabilize the matrix grain size as effectively as large volume fractions ( $X_\beta = 0.4$  to  $0.50$ ) of large grained second-phase ( $d_\beta/d_\alpha = 0.9$  to  $1.0$ ).

It is of interest to calculate when the boundary of matrix grain will be able to sweep across a second-phase grain. The surface energy ( $E_\alpha$ ) of a spherical matrix grain is given by

$$E_\alpha = 4\pi r_\alpha^2 \sigma, \quad (3)$$

where  $r_\alpha$  is the radius of the matrix grain and  $\sigma$  is the surface tension of the boundary. Following Reed-Hill [15], the pull of boundary on the second-phase grain is a maximum at a contact angle between the boundary and the second-phase grain of  $45^\circ$  and is given by

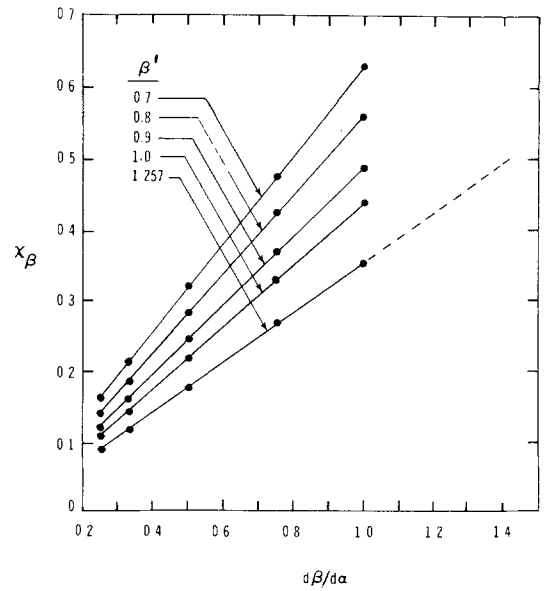


Figure 1 The variation of the volume fraction of the second-phase necessary to stabilize the matrix grain size with the ratio of second-phase to matrix grain size. The broken line represents the upper limit for the capability of the second-phase to hinder the matrix grain growth (see text).

$$F = \pi r_\beta \sigma, \quad (4)$$

where  $r_\beta$  is the radius of a spherical second-phase grain.

In order for the boundary to sweep the  $\beta$ -grain, the energy which must be provided is

$$E_\beta = FX2r_\beta = 2\pi r_\beta^2 \sigma. \quad (5)$$

Equating Equations 4 and 5 we obtain

$$\frac{r_\beta}{r_\alpha} = \frac{d_\beta}{d_\alpha} = 2^{1/2}. \quad (6)$$

Equation 6 indicates that there is an upper limit on the  $d_\beta/d_\alpha$  ratio of 1.41. Beyond this limit the second-phase will cease to hinder the matrix grain-boundary motion and rapid, abnormal matrix grain growth will occur. This condition is illustrated in Fig. 1 by the broken line for  $\beta' = 1.257$ . The volume fraction of second-phase needed at the limit is 0.5. At lower values of  $\beta'$  the volume fraction is higher than 0.5 and, therefore,  $\alpha$ -phase will play the role of the second-phase.

The deviation from the ideal volume fraction (as calculated from Equation 2) for a given  $d_\beta/d_\alpha$  ratio can be expressed as the ratio

$$Z = \frac{X'_\beta}{X_\beta}, \quad (7)$$

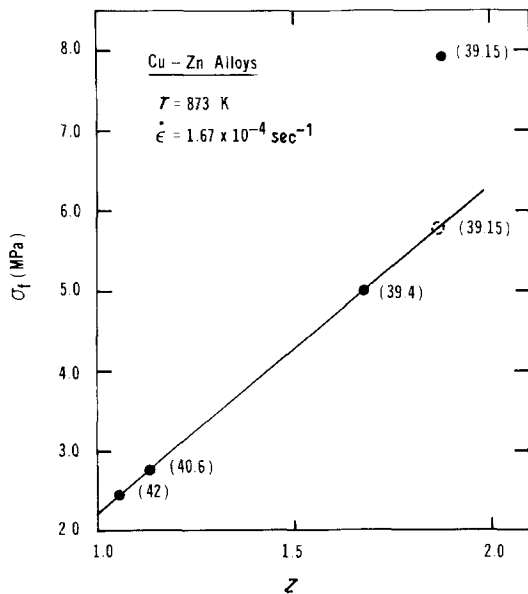


Figure 2 Variation of the flow stress with parameter  $Z$  for Cu-Zn alloys. The numbers in parentheses are the nominal percentage of Zn in the alloys. The open symbol shows the corrected  $\sigma_f$  for the Zn = 39.15 wt% alloy (see text).

where  $X'_\beta$  is the volume fraction determined from the applicable phase diagram.

### 3. Comparison with experiment

As mentioned earlier in this paper, most of the alloys which behave superplastically have a two-phase structure. For any binary or duplex alloy over the range of nominal compositions at one temperature, the chemical composition of each phase remains unchanged and only the volume fraction of the phases changes with the nominal composition. Therefore, any difference in mechanical behaviour of these alloys during superplastic deformation may be directly attributed to the difference in volume fractions of the two phases.

#### 3.1. Cu-Zn alloys

Suery and Baudalet [16] investigated four Cu-Zn alloys with Zn concentrations (wt%) between 39.15 and 42.0. The microstructure consisted of a mixture of  $\alpha$ -phase (Cu-Zn<sub>α</sub>) and  $\beta$ -phase (Cu-Zn<sub>β</sub>). At a constant temperature and strain rate the flow stress increased as the amount of Zn in the alloy increased. Their data are plotted in Fig. 2 as the flow stress at  $T = 873$  K and  $\dot{\epsilon} = 1.67 \times 10^{-4} \text{ sec}^{-1}$  against the ratio  $Z$ .

The experimental flow stress values are indicated by filled circles in Fig. 2. It is evident from

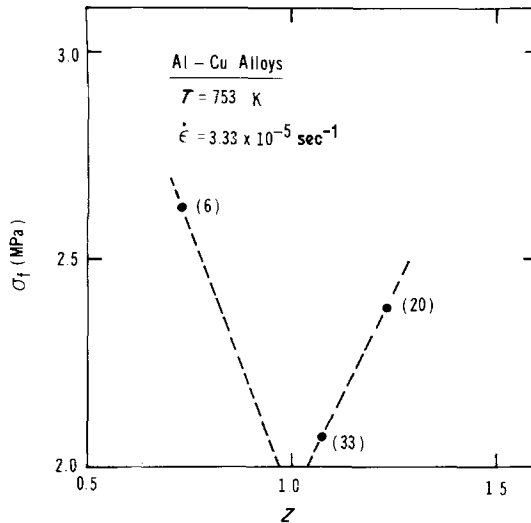


Figure 3 Variation of the flow stress with parameter  $Z$  for Al-Cu alloys. The numbers in parentheses represent the nominal percentage of Cu in the alloys.

Fig. 2 that there is excellent correlation between  $\sigma$  and  $Z$  for all but the alloy poorest in Zn. However, for this alloy the stress sensitivity coefficient was found to be equal to 2.5, whereas for the three other alloys the lower experimental value obtained was 2 [16]. If the stress flow for this alloy is corrected as  $\sigma^{2/2.5}$  the new stress value falls in line with the others (open symbols in Fig. 2).

#### 3.2. Al-Cu alloys

Matsuki *et al.* [17] investigated three Al-Cu alloys with nominal compositions of 6 wt% Cu, 20 wt% Cu and 33 wt% Cu, respectively. The Al-6 wt% Cu alloy consisted of a single-phase ( $\alpha$ -Al) with fine second-phase ( $\theta$ -Cu Al<sub>2</sub>) particles uniformly distributed throughout the matrix. The Al-20 wt% Cu and Al-33 wt% Cu have a duplex (two-phase) structure. At any test temperature and constant strain rate the flow stress decreased with increasing amount of Cu in the alloy. A plot of the flow stress at  $T = 753$  K and  $\dot{\epsilon} = 3.33 \times 10^{-5} \text{ sec}^{-1}$  against the parameter  $Z$  is shown in Fig. 3. The flow stress is minimum for  $Z$  values close to unity and increases at both higher and lower values. It is of interest to note that, although the alloys Al-6 wt% Cu and Al-20 wt% Cu have almost the same deviation from  $Z = 1$  ( $Z = 1.23$  and  $Z = 0.73$  for Al-20 wt% Cu and Al-6 wt% Cu, respectively), the flow stress is higher for  $Z$  values less than 1, i.e. the volume fraction of the second phase is lower than that given by Equation 2.

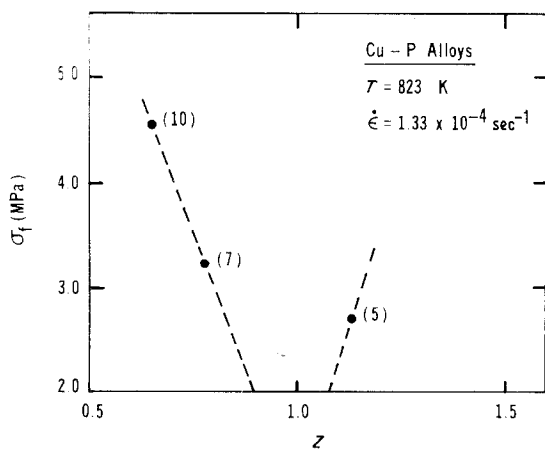


Figure 4 Variation of the flow stress with parameter  $Z$  for Cu-P alloys. The numbers in parentheses represent the nominal percentage of P in the alloys.

### 3.3. Cu-P alloys

Two hypoeutectic compositions (Cu-6 wt% P and Cu-7 wt% P) and one hypereutectic composition (Cu-10 wt% P) were studied by Herriot *et al.* [18]. The flow stress decreased (at constant test temperature and strain rate) with decreasing nominal composition of P in the alloys. This behaviour is apparently different from that described previously for Cu-Zn and Al-Cu alloys, where the flow stress decreased with increasing amount of the alloying element. However, the rationale for Cu-P alloys is the same as for the other alloys. When the flow stress is plotted against  $Z$  (Fig. 4), there is an increase in flow stress for  $Z$  value deviation from unity, both at higher and lower values.

### 3.4. Zn-Al alloys

Zn-Al alloys of compositions ranging from 0.4 wt% Al to 50 wt% Al were investigated by Kaybishev and co-workers [19]. The structure of

these alloys consists of two phases:  $\alpha$  which is Al-rich and  $\beta$  which is Zn-rich.

The behaviour of these alloys is different from those of the alloys studied until now in the sense that the flow stress at any constant temperature and strain rate within the superplastic regime passes through a minimum at some intermediate concentration of the alloying element (18 wt% Al at 423 K and 22 wt% Al at 523 K). The variation of the flow stress with the percentage additions of Al is shown in Figs 5a and 6a for  $\dot{\epsilon} = 1 \times 10^{-2} \text{ sec}^{-1}$  and  $T = 423$  and 523 K, respectively. Once again, the explanation for the stress variations with composition lies in the departure of the second-phase volume fraction in the alloys from those given by Equation 2, i.e.  $Z$  value (Equation 7). This is shown in Figs 5b and 6b. The behaviour of Zn-0.4 wt% Al at 523 K is very interesting (Fig. 6). At this temperature the alloy is single-phase, all the aluminium being dissolved in the Zn solid-solution. As a consequence, the flow stress increases rapidly (Fig. 6a) and cannot be correlated with the  $Z$  value (Fig. 6b).

### 3.5. High carbon steels

These alloys were investigated by Kayali [20], Caliguiri [21] and Walser and Sherby [22]. The variation of the flow stress with percentage carbon is similar to that for Zn-Al alloys, going through a minimum at 1.6 wt% C at  $T = 973 \text{ K}$  and  $\dot{\epsilon} = 10^{-4} \text{ sec}^{-1}$  (Fig. 7a).  $d_\alpha$  and  $d_\beta$  in Equation 2 were assumed to be the same for all alloys having values of 0.8 and  $0.5 \mu\text{m}$ , respectively [22]. Even with this approximation, the correlation between the flow stress and  $Z$  is exceedingly good (Fig. 7b).

## 4. Discussion

The relationship between the strain rate,  $\dot{\epsilon}$ , and the flow stress,  $\sigma$ , during steady-state superplastic flow is usually expressed by a non-dimensional rate

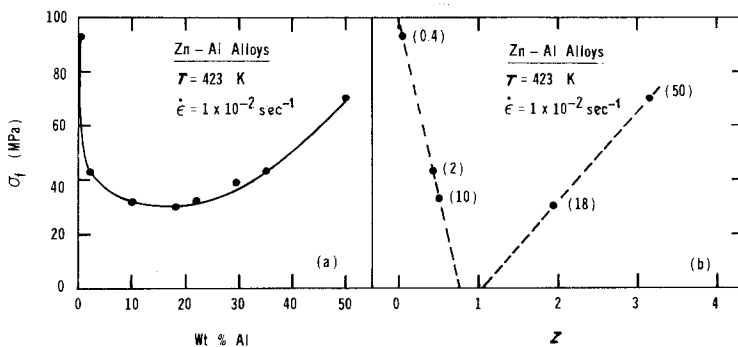


Figure 5 (a) The dependence of  $\sigma_f$  at 423 K on Al content in Zn-Al alloys; (b)  $\sigma_f$  against  $Z$  at 423 K for Zn-Al alloys. The numbers in parentheses show percentage Al in the alloys.

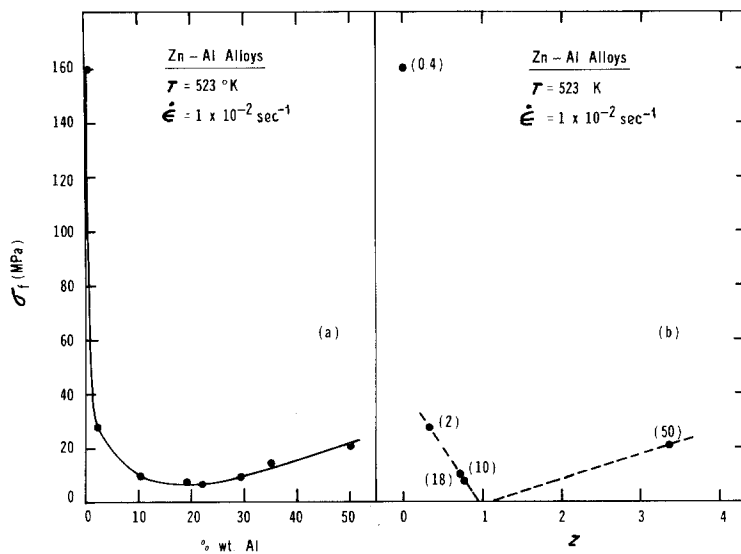


Figure 7 (a)  $\sigma_f$  against percentage C plot; (b) the variation of  $\sigma_f$  with parameter  $Z$  for Fe-C alloys. The numbers in parentheses show the nominal C content in the alloys.

equation of the form

$$\frac{\dot{\epsilon}kT}{DGb} = A \left(\frac{b}{d}\right)^p \left(\frac{\sigma}{G}\right)^n \quad (8)$$

where  $D$  is the diffusion coefficient for superplastic flow,  $G$  is the shear modulus,  $b$  is Burgers vector,  $d$  is grain size,  $k$  is Boltzman's constant,  $T$  is temperature,  $p$  is strain rate dependence on grain size coefficient,  $n$  is stress sensitivity and  $A$  is the substructure related parameter.

With the exception of  $k$ , which is a universal constant, the parameters incorporated in Equation

8 can be grouped into three categories: (i) material related properties ( $G$  and  $b$ ); (ii) experimentally imposed parameters ( $\dot{\epsilon}$ ,  $\sigma$ ,  $T$  and  $d$ ); and (iii) deformation mechanism related parameters ( $A$ ,  $D$ ,  $p$  and  $n$ ).\*

The complete form of Equation 8 can be determined in, say, constant strain rate tests where the flow stress is the measured parameter as follows.

#### 4.1. Determination of $n$ value

Specimens of constant average grain size are tested at the same temperature at several strain rates and

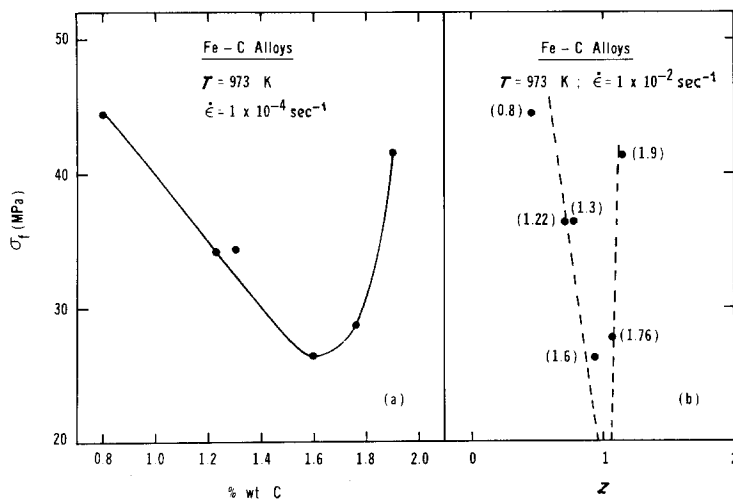


Figure 6 (a) Plot of the flow stress against composition at 523 K for Zn-Al alloys (b)  $\sigma_f$  against  $Z$  plot at 523 K. The numbers in parentheses are percentage Al in the alloys.

\*This classification is not exactly rigorous since some of the parameters belong to more than one category. For example, the  $G$  value will vary with temperature and  $D$  will vary with both temperature and alloy for the same deformation mechanism. Moreover, once we impose a certain strain rate while keeping  $d$  and  $T$  constant, the measured  $\sigma$  value will depend upon both alloy and deformation mechanism.

the flow stresses are measured. The stress sensitivity coefficient,  $n$ , will be given by the slope of the curve in the  $\ln \dot{\epsilon}$  against  $\ln \sigma$  plot or

$$n = \left. \frac{\partial(\ln \dot{\epsilon})}{\partial(\ln \sigma)} \right|_{d, T} \quad (9)$$

However, in the case of long testing times\* both second-phase and matrix grains coarsen and, unless their coarsening kinetics are identical,  $X_\beta$  will change during the test, resulting in a  $Z$  dependence on testing time (or strain). The grain growth data reported by Sammelson *et al.* [24] for Zn–40 wt% Al alloy show that the grain growth kinetics are different in the  $\alpha$ - and  $\beta$ -phases, respectively. The same should be true for other alloy systems due to differences in diffusivities, size (i.e. surface energy) and rate of dislocation accumulation between the phases present in the alloys. Therefore, even for small variations in the average grain size, the variation in  $Z$  value with strain rate (i.e. testing time) can be quite large, leading to an apparent dependence of  $n$  on strain rate. Since the testing time increases with decreasing strain rate,  $n$ , apparently, will decrease with decreasing strain rate within the superplastic range.

#### 4.2. Determination of $p$

Specimens of different average grain sizes (obtained by giving the alloy different thermomechanical treatments) are tested at constant temperature and strain rate. The parameter  $p$  is determined from the slope of the curve in the  $\ln \sigma$  against  $\ln d$  plot or

$$p = n \left. \frac{\partial(\ln \sigma)}{\partial(\ln d)} \right|_{\dot{\epsilon}, T} \quad (10)$$

where  $d$  is the average grain size and is given by

$$d \simeq (1 - X'_\beta) d_\infty + X'_\beta d_\beta \quad (11)$$

It is evident from Equation 11 that if an alloy is prepared with two average grain sizes  $d_1$  and  $d_2$  by, say different annealing treatments, Equation 10 will yield a true  $p$  value only if both phases respond identically to the annealing treatments, i.e.  $d_1/d_2 = d\alpha_1/d\alpha_2 = d\beta_1/d\beta_2$ . In any other case  $d\beta_1/d\alpha_2 \neq d\beta_2/d\alpha_2$  and  $Z_1 \neq Z_2$  and Equation 10

\*For example, Mohamed *et al.* [23] reported that the flow stress value at  $\dot{\epsilon} = 1.67 \times 10^{-5} \text{ sec}^{-1}$  ( $d = 2.5 \times 10^{-4} \text{ cm}$  and  $T = 523 \text{ K}$ ) has been obtained after  $\simeq 15 \text{ h}$ .

†The same average grain size can be, conceivably, obtained by (i) cold working and subsequently annealing for a short time or (ii) by annealing for a long time without any previous cold working. However, the phases present in the alloy will react differently to these two treatments.

yields an apparent  $p$  value which will depend upon the thermomechanical treatments given to the alloys to result in different grain sizes.† It is also self-evident that if concurrent grain growth takes place during deformation, the deviations of  $p$ , determined in such experiments, will increase from the true value (i.e.  $Z = 1$ ).

#### 4.3. Determination of the activation energy for deformation

The diffusion coefficient in Equation 8 is given by

$$D = D_0 \exp\left(-\frac{Q}{RT}\right), \quad (12)$$

where  $D_0$  is the pre-exponential factor,  $Q$  is activation energy for deformation and  $R$  is the gas constant.

Testing several specimens of constant average grain size at constant strain rate and various temperatures,  $Q$  can be determined from the slope of the curve of the  $\ln(\sigma^n G^{n-1} T)$  against  $(1/T)$  or,

$$Q = R \frac{\partial \ln(\sigma^n G^{n-1} T)}{\partial(1/T)} \quad (13)$$

It is evident from Fig. 2 that  $X'_\beta$  will vary with temperature and, hence, for a given structure at room temperature, a different  $Z$  value will be taken at each test temperature. Therefore, because of the strong dependence of  $\sigma$  on  $Z$ ,  $Q$  values determined at constant average grain size will be in error regardless of the specific experimental method used for its determination (e.g. tensile tests, creep tests, rapid temperature variations, etc.). In this case, again, concurrent grain growth during deformation will compound the error. An additional complication arises in the case of  $Q$  determination because the chemistry of the phases present in the alloy will change with temperature and so does their diffusivity [25].

From the foregoing discussion it becomes evident that the rate equations experimentally determined for superplastic alloys might be seriously in error when only the average grain size is considered. Careful consideration should be given to alloy selection for laboratory studies and only alloys which can be prepared to result in  $Z$  values close to unity should be used. In such a

way maximum grain size stability during subsequent mechanical testing is ensured. Furthermore, the thermomechanical treatments used to obtain various average grain sizes in the alloy should be designed in such a way to yield also, identical or very close  $Z$  values. Additional care is required to make sure that, by using different thermomechanical treatments, a subtle difference in texture and/or other substructural features are not produced in the microstructure [3, 25]. Finally, it should be pointed out that for reasons discussed above all the methods currently used for  $Q$  evaluation are erroneous. The problem can be eventually circumvented by determining the activation energies for deformation over a narrow temperature range and selecting an alloy system for the investigation which will show only minute variations in the volume fraction and chemistry of the phases within the narrow temperature range.

## 5. Summary and conclusions

It was shown in this paper that when the chemistry of the phases in superplastic binary alloys remains the same over a range of nominal alloy compositions, the flow stress at a constant test temperature and strain rate is determined by the matrix grain size and its stability. The matrix grain size stability is determined, in turn, by the volume fraction of the second phase present in the alloy.

Analysis of the data published in the literature for five alloy systems shows that the volume fraction of the second phase necessary to stabilize the matrix grain size can be calculated by an expression (Equation 2) developed by Hellman and Hillert [13]. The values taken by the flow stress at constant temperature and strain rate for each nominal alloy composition can be correlated extremely well with a parameter  $Z$  (Equation 7) which indicates the deviation of the second-phase volume fraction in alloy from that required for matrix grain size stabilization.

Without taking into account  $Z$  values for various testing conditions, the experimentally determined parameters in the rate equation for superplastic flow (Equation 8) might be different from their true values (i.e. at  $Z = 1$ ) and can differ from investigation to investigation even when the same nominal composition, average grain size, testing methods and conditions are used.

Finally, it was suggested that careful consider-

ation be given to alloy selection and thermo-mechanical treatments used for alloy preparation before actual testing in order to ensure maximum grain size stability and comparable  $Z$  values for all the testing conditions.

## References

1. J. W. EDINGTON, K. N. MELTON and C. P. CUTLER, *Prog. Mater. Sci.* **21** (1976) 61.
2. K. SMIDODA, C. GOTTSALK and M. GLEITER, *Acta Met.* **26** (1978) 1833.
3. A. ARIELI and A. K. MUKHERJEE, in "Micro-mechanisms for Plasticity and Fracture in Engineering Solids" edited by D. M. R. Taplin (Pergamon Press, Oxford, 1981).
4. R. B. NICHOLSON, in "Electron Microscopy and Structure of Materials", edited by G. Thomas (University of California Press, Berkeley, 1972) p. 689.
5. A. ARIELI and A. K. MUKHERJEE, *Mater. Sci. Eng.* **45** (1980) 61.
6. M. F. ASHBY, *Surface Sci.* **31** (1972) 498.
7. A. K. MUKHERJEE, *Ann. Rev. Mater. Sci.* **9** (1979) 191.
8. T. H. ALDEN, in "Treatise on Materials Science and Technology", Vol. 6, edited by R. J. Arsenault (Academic Press, New York, 1975) p. 226.
9. S. FLOREEN, *Scripta Met.* **4** (1967) 19.
10. W. BEERE, *Scripta Met.* **12** (1978) 337.
11. T. GLADMAN, *Proc. Roy. Soc. A* **294** (1966) 298.
12. J. W. EDINGTON, *Met. Tech.* **3** (1976) 138.
13. P. HELLMAN and M. HILLERT, *Scand. J. Metall.* **4** (1975) 211.
14. C. W. CORTI, *Scripta Met.* **12** (1978) 65.
15. R. E. REED-HILL, "Physical Metallurgy Principles", (Van Nostrand Co., New York, 1964).
16. M. SUERY and B. BAUDELET, *Phil. Mag.* **41** (1980) 41.
17. K. MATSUKI, K. MINAMI, M. TOKIZAWA and Y. MURAKAMI, *Met. Sci.* **8** (1979) 619.
18. G. HERRIOT, B. BAUDELET and J. J. JONAS, *Acta Met.* **24** (1976) 687.
19. O. A. KAYBISHEV, I. V. KAZACHOV and B. V. RODIONOV, *Fiz. Metal. Metalloved.* **39** (1975) 338.
20. S. KAYALI, PhD Dissertation, Stanford University (1976).
21. R. D. CALIGUIRI, PhD dissertation, Stanford University (1977).
22. B. WALSER and O. D. SHERBY, *Met. Trans.* **10A** (1979) 1461.
23. F. A. MOHAMED, M. M. I. AHMED and T. G. LANGDON, *Met. Trans.* **8A** (1977) 933.
24. L. C. A. SAMUELSSON, K. N. MELTON and J. W. EDINGTON, *Acta Met.* **24** (1974) 1017.
25. A. ARIELI and A. K. MUKHERJEE, presented at AIME Fall Meeting, Pittsburgh, PA, October 1980; also, *Met. Trans. A*, in press.

Received 2 December 1980 and accepted 23 March 1981.