

# Evaluation of activation energy in sintered samples

K. M. R. ACHARI

Loyola Academy, Alwal, Secunderabad 10, Andhra Pradesh, India

M. B. REDDY

A.V. College, Dhomalguda, Hyderabad 29, Andhra Pradesh, India

R. B. RAMACHANDER

Department of Physics, Osmania University, Hyderabad 500 007, Andhra Pradesh, India

The neck curvature obtained in sintering two spherical particles is related to the neck radius of the contact area and the radius of the particles. The radius of the neck curvature, when expressed in terms of the fractional shrinkage, leads to an elegant method of evaluating the activation energy corresponding to the operating mechanism at different stages of sintering. The calculated values of activation energy confirm the diffusion mechanisms operative at different temperatures and different sintering durations.

## 1. Introduction

In the sintering of copper powders, spherical particles are brought in contact by pressing the copper powder in a die [1]. The compacts when sintered at different temperatures for different durations develop neck contacts and neck curvatures between any two particles. Kingery and Berg [2] have shown that the radius of neck curvature  $\varrho$ , when two spheres are in contact as in Fig. 1, is given by

$$\varrho = x^2/2r \quad (1)$$

where  $x$  is the radius of the neck contact area and  $r$  is the radius of the particles (Fig. 1). Further, Lee [3] has shown that

$$\varrho = \text{constant} \times \left(\frac{t}{T}\right)^m D_v^m \quad (2)$$

in his studies on self-diffusion in sintering. Here  $m = n/(2n + 1)$  and  $n$  takes a value equal to 2, in the case of spherical particles;  $t$  is the duration of sintering,  $T$  the sintering temperature and  $D_v$  the volume diffusion coefficient. The shrinkage  $\Delta L$  depends on  $\varrho$  and  $D_v = D_0 e^{-Q_v/kT}$ .

The fractional shrinkage  $(L_0 - L)/L_0 = \Delta L/L_0 = f$  is expressed as

$$f = \text{constant} \times \left(\frac{t}{T}\right)^m e^{-Q_v/kT} \quad (3)$$

where  $Q_v$  is the activation energy. By plotting  $\ln f$  against  $\ln t$  at a given temperature, we obtain a straight line. The slope gives the value of  $m$  and thus slopes of a plot of  $\{[(\ln f)/m] + \ln T\}$  against  $1/T$  at a given time can be used to evaluate activation energies.

## 2. Experimental details

Nearly 0.4 g of copper powder of particle size  $100 \mu\text{m}$  is pressed into pellets of 13.10 mm diameter ( $L_0$ ). The

thickness of the samples is about 0.5 mm. These pellets are sintered in a furnace for different durations. The diameters ( $L$ ) of the samples are measured after sintering. The shrinkages are calculated and also fractional shrinkages ( $f$ ) are determined at different times.

A plot of  $\ln f$  against  $t$  using the values of fractional shrinkages and duration of sintering is made (Fig. 2). This is linear for a given temperature. From the linearity of the plots the value of  $m$  is found to be 0.46, which is in conformity with the value reported by Lee [3] for spherical particles. The experimental values are given in Table I. Plots of  $\{[(\ln f)/m] + \ln T\}$  against  $1/T$  are also shown in Fig. 3.

## 3. Results and discussion

Corresponding to the slopes of the segments of each plot, different types of effective mechanism can be associated with the respective intervals of temperature. It has been widely confirmed that sintering in copper is mainly by diffusion mechanisms [4]. For all the curves it is seen that the value of  $\{[(\ln f)/m] + \ln T\}$  varies sharply with  $1/T$  and with sintering duration. For the samples of 1 to 3 h duration the curve decreases up to 1173 K and then rises with respect to the abscissa. Using the slopes, the calculated

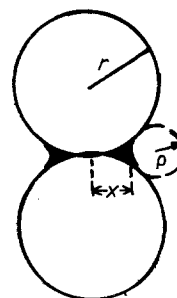


Figure 1 Two spheres in contact.

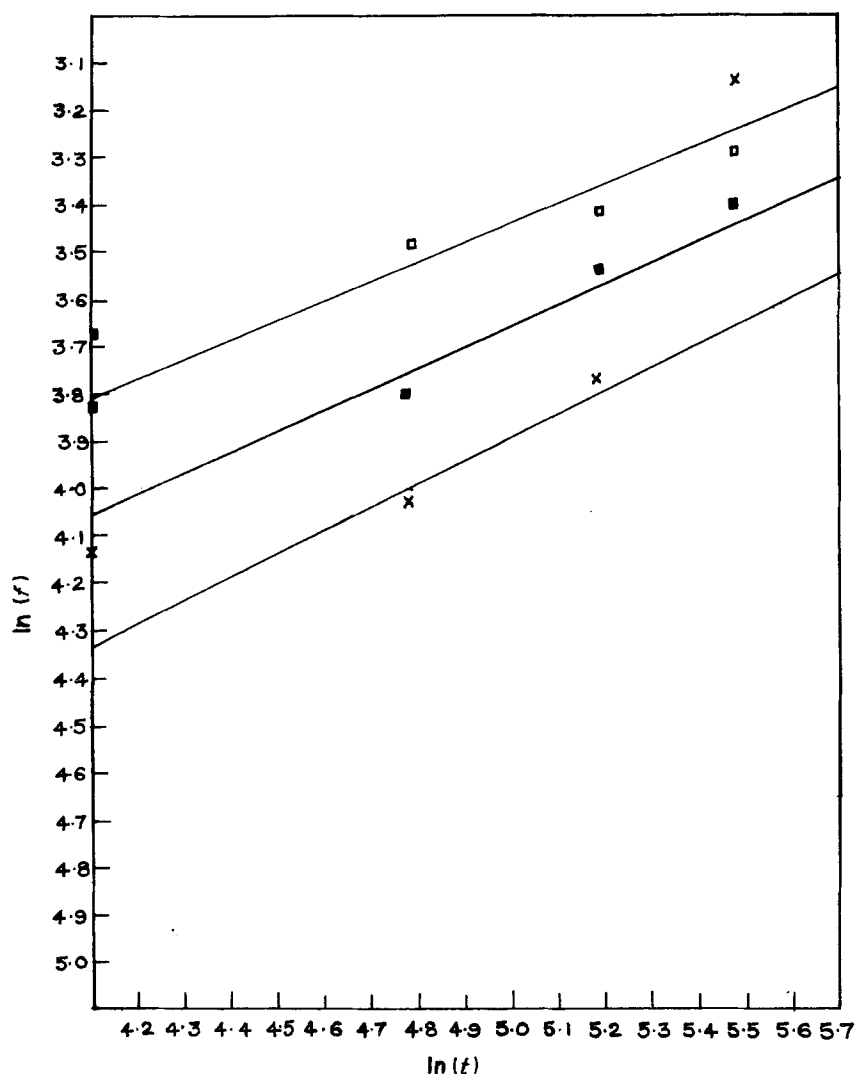


Figure 2 Plot of  $\ln f$  against  $\ln t$ . (■) 873 K, (×) 973 K, (□) 1273 K;  $m = 0.457$ .

TABLE I Data for size = 100  $\mu\text{m}$ , pressure = 600 Mpa,  $m = 0.46$  (value obtained from slope of curve in Fig. 2)

| Time (h) | Temperature, $T$ (K) | $f = \Delta L/L_0$ | $\left(\frac{\ln f}{m} + \ln T\right)$ | Range of temperature (K) | Activation energy (eV) | Effective operative mechanism* |
|----------|----------------------|--------------------|--|--------------------------|------------------------|--------------------------------|
| 1        | 873                  | 0.0221             | -1.5149                                | Below 1173               | 0.517                  | S.D.                           |
|          | 973                  | 0.0160             | -2.1091                                | Above 1173               | 3.619                  | G.B.D.                         |
|          | 1073                 | 0.0099             | -3.0546                                |                          |                        |                                |
|          | 1173                 | 0.0069             | -3.7602                                |                          |                        |                                |
|          | 1273                 | 0.0252             | -0.8529                                |                          |                        |                                |
| 2        | 873                  | 0.0221             | -1.5149                                | Below 1173               | 0.246                  | S.D.                           |
|          | 973                  | 0.0176             | -1.9020                                | Above 1173               | 2.068                  | V.D.                           |
|          | 1073                 | 0.0160             | -2.0110                                |                          |                        |                                |
|          | 1173                 | 0.0145             | -2.1350                                |                          |                        |                                |
|          | 1273                 | 0.0305             | -0.4379                                |                          |                        |                                |
| 3        | 873                  | 0.0290             | -0.9258                                | Below 1173               | 0.483                  | S.D.                           |
|          | 973                  | 0.0237             | -1.3200                                | Above 1173               | 3.106                  | G.B.D. and/or V.D.             |
|          | 1073                 | 0.0129             | -2.4785                                |                          |                        |                                |
|          | 1173                 | 0.0230             | -2.5113                                |                          |                        |                                |
|          | 1273                 | 0.0328             | -0.2790                                |                          |                        |                                |
| 4        | 873                  | 0.0330             | -0.6432                                |                          |                        |                                |
|          | 973                  | 0.0435             | -0.0648                                | Below 973                | 0.550                  | S.D.                           |
|          | 1073                 | 0.0115             | -2.7372                                | Below 1073               | 2.413                  | G.B.D. and/or V.D.             |
|          | 1173                 | 0.0496             | +0.0366                                | Below 1173               | 3.107                  | G.B.D. and/or V.D.             |
|          | 1273                 | 0.0374             | +0.0550                                | Above 1173               | 0.655                  | (R.C.)                         |
| 5        | 873                  | 0.0344             | -0.5519                                |                          |                        |                                |
|          | 973                  | 0.0290             | -0.8156                                | Below 973                | 0.280                  | S.D.                           |
|          | 1073                 | 0.0076             | -3.6285                                | Below 1073               | 2.413                  | G.B.D. and/or V.D.             |
|          | 1173                 | 0.0427             | +0.2105                                | Below 1173               | 4.136                  | G.B.D. and/or V.D.             |
|          | 1273                 | 0.0382             | +0.0512                                | Above 1173               | 0.256                  | (R.C.)                         |

\*S.D. = surface diffusion. V.D. = volume diffusion. G.B.D. = grain boundary diffusion, R.C. = recrystallization.

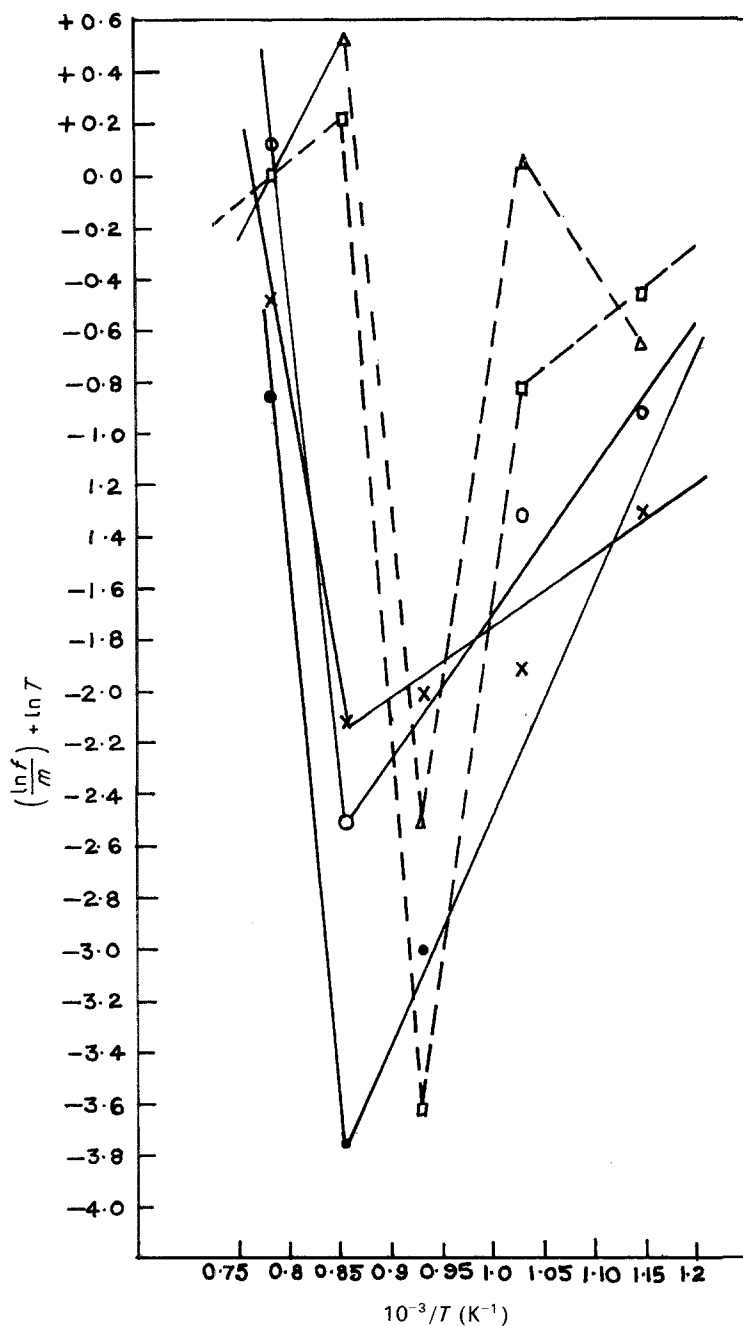


Figure 3 Plot of  $\{[(\ln f)/m] + \ln T\}$  against  $1/T$ .  
 (●) 1 h, (×) 2 h, (○) 3 h, (△) 4 h, (□) 5 h.

activation energies are found to be much less than the activation energy for volume diffusion  $Q_v (= 2.07 \text{ eV})$  for copper. So it is felt that the mechanism in this range may be surface diffusion only, as the surface atoms have fewer bonds than those inside. Beyond 1173 K, grain boundary diffusion plays a prominent role. As the sintering temperature and duration are increased, volume diffusion starts [4]. This can be observed between the 2 and 3 h curves beyond 1173 K. The deviation at lower temperatures for 1 to 3 h curves may initially be due to particle rearrangement and/or porosity. This deviation is more prominent for the other curves (4 and 5 h) at lower temperatures. A similar result of retardation in neck growth and densification at lower temperatures has been reported for copper by Eloff and Lenel [5].

For 4 and 5 h curves, as the slope extends up to 1073 K, the surface diffusion terminates there. Grain boundary and/or volume diffusion sets in at 1073 K, beyond which the abscissa increases up to 1173 K. In this range (1073 to 1173 K) grain boundary diffusion

and volume diffusion are responsible, as also confirmed by Masuda and Watanabe [4]. The calculated activation energy gives an average value of 2.764 eV, which agrees well with the reported values of Overhauser [6] and Kuper *et al.* [7]. From 1173 to 1273 K the anomalous decrease of  $\{[(\ln f)/m] + \ln T\}$  could be due to recrystallization. Recrystallization at higher temperatures and longer durations has also been suggested by Novikov *et al.* [8].

### Acknowledgements

The authors are thankful to Professor K. Rama Reddy, Head, Department of Physics, Osmania University, and one of the authors is also grateful to Fr Paul Sathyanarayana, Principal, Loyola Academy, Secunderabad for encouraging our work.

### References

1. K. M. R. ACHARI, M. B. REDDY and R. B. RAMACHANDER, to be published.
2. W. D. KINGERY and M. BERG, *J. Appl. Phys.* **20** (1955) 1205.

3. D. N. LEE, in "Materials Science Research", Vol. 6, Proceedings of International Conference on Sintering and Related Phenomena, edited by G. C. Kuczynski (Plenum, New York, 1972) p. 261.
4. Y. MASUDA and R. WATANABE, *Sci. Sintering* **13** (1981) 117.
5. P. C. ELOFF and F. V. LENEL, "Modern Developments in Powder Metallurgy", Vol. 4 (1971) p. 198.
6. A. W. OVERHAUSER, *Phys. Rev.* **90** (1953) 393.
7. A. KUPER, H. LATAW, L. SLIFKIN, E. SONDER and C. TOMIZUKA, *ibid.* **96** (1954) 1224.
8. V. I. NOVIKOV, L. I. TRUSOV, V. N. LAPOVOK and T. P. GELESHVILI, Translated from *Proshkovapa Metallurgiya*, **247** (7) (1983) 39.

*Received 10 May  
and accepted 18 August 1987*