JOURNAL OF MATERIALS SCIENCE 3 (1968) 524-533

# Grain-Boundary Slide-Hardening in Zinc Bicrystals

R. L. BELL
*Engineering Laboratories, The University, Southampton, UK*
N. B. W. THOMPSON
*Department of Education and Science, London, UK*
P. A. TURNER
*Bell Telephone Laboratories, Murray Hill, New Jersey, USA*

*Received 26 March 1968*

Zinc bicrystals containing high-angle tilt boundaries, and others containing twist boundaries were subjected to constant shear stresses parallel to the boundary at temperatures in the range 20 to 300° C. At stresses both above and below that necessary to cause macroscopic slip in the constituent crystals, the grain-boundary sliding rate decreased with time. This "slide-hardening" at the grain-boundary was identified with the formation of asperities in the grain-boundary which were generated first near the intersection of boundary and free surface. Removal of the layer containing these asperities restored the boundary behaviour to that of a virgin bicrystal in certain cases. This leads to the conclusion that when slide-hardening occurs, the rate-limiting process for grain-boundary sliding is that associated with the deformation of the crystal regions which have been introduced into the original boundary plane by grain-boundary migration.

## 1. Introduction

There have been many studies of grain-boundary sliding in what one would suppose to be the simplest kind of specimen – the bicrystal. However, even in this situation the behaviour proves to be anything but simple, and the recent reviews [1, 2] show that little real progress has been made in sorting out the various important factors. One point of general agreement is that under constant stress conditions the rate of sliding decreases with time, i.e. hardening occurs, although in some cases this "slide-hardening" is preceded by a stage where the velocity of sliding is constant [3, 4]. Even at temperatures within a few degrees of the melting point the sliding at grain-boundaries in bicrystals of tin became progressively slower [5]. Clearly, therefore, the pseudo-viscous nature of the sliding process inferred from internal friction studies is not an adequate picture for the larger sliding displacements observed in bicrystal tests, and the possibility of several different stages in the sliding-time relation, analogous to those in the creep curves of single or polycrystalline materials, has to be considered.

In this situation it is not surprising that the question still remains as to whether sliding is a primary process governed by the shear stress in the boundary plane, or whether it is a secondary one, depending in some way on slip processes in the grains on either side. Under suitable conditions of very low stress, insufficient to cause macroscopic slip, it has been found recently that the grain-boundary can slide in a pseudo-viscous manner over distances up to 2.5 $\mu$m [6]. However, this present paper reports experiments conducted over a range of stresses which illustrate the important modifying influence of slip in causing boundary-hardening. In the stress-range pertaining more generally in creep, the sliding at a boundary is shown to be governed by slip processes.

## 2. Experimental Procedure

### 2.1. The Material

Two grades of zinc were used. These were nominally of "four nines" and "five nines" purities. Analysis of final specimens showed the total impurity contents to be 20 and 4 ppm, respectively, for bicrystals grown from the two grades of starting material.

A few experiments were performed on specimens which had been doped with 0.1 at. % cadmium.

### 2.2. Preparation of Bicrystal Specimens

Bicrystals, approximately 20 cm long and 2.0 × 0.5 cm in cross-section, were solidified in graphite boats from two monocrystalline seeds by a horizontal travelling furnace technique, similar to that described by Chalmers [7]. The furnace atmosphere was dry argon and the traverse rate 2 cm/h. Under these conditions the constituent crystals were free of any gross substructure, and the grain-boundary was plane and free from irregularities over distances of many cm.

Two basic bicrystal types were investigated. These contained "high-angle tilt" and "twist" boundaries, respectively. Fig. 1 shows the orientation of the basal (0001) planes and $[11\bar{2}0]$ directions in the individual crystals of the two kinds of bicrystal, and defines angles $\phi$ and $\theta$ which describe the grain-boundary misorientation in the two cases. (It should be noted that the tilt boundary geometry did not have its rotation axis perpendicular to a primary slip direction, so that even when $\phi$ was very small the boundary structure could not be described in terms of a single array of pure edge dislocations.) Any desired misorientation could be produced, but seeding tolerances were $\pm$ 3° so that intended "pure twist" boundaries were invariably found to have a small tilt component.

Individual specimens 5 to 10 mm long were cut from the bicrystal ingots by careful sectioning perpendicular to the growth direction using either a fine jeweller's saw or, in the later experiments, an acid thread saw. With the former technique it was necessary to remove the deformed regions adjacent to the saw cut by repeated processes of fine grinding and chemical polishing. The acid saw removed the necessity for this and smooth strain-free plane surfaces were produced simply by rubbing the cut surfaces very lightly on a "terylene" pad soaked in 50% nitric acid. To make sure that there were no residual stresses in the saw-cut specimens they were vacuum-annealed for 16 h at 380° C before testing. This was shown to be unnecessary for those cut by the acid saw.

Fiducial marks perpendicular to the boundary plane were made on surfaces A and B (fig. 1a), and E and F (fig. 1b). In the early experiments these were made by gently touching them with a

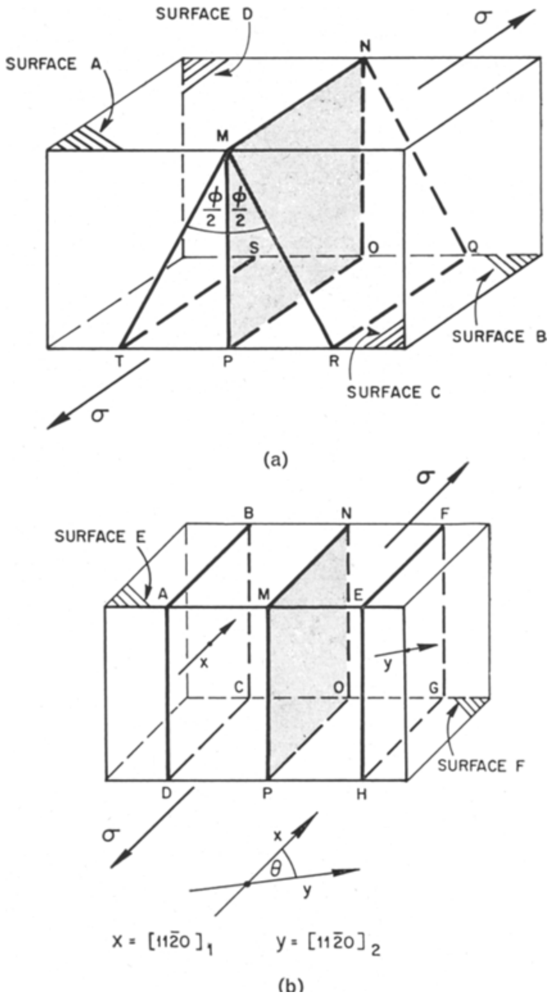



*Figure 1* The geometry of the bicrystals. (a) Specimen containing a high-angle tilt boundary MNOP; MNQR and MNST indicate the positions of the (0001) planes in the two crystals. Both have $[11\bar{2}0]$ parallel to MN. (b) Specimen containing a twist boundary MNOP. The positions of the (0001) planes in the constituent crystals are shown by ABCD and EFGH. The twist angle $\theta$ is given by the angle between the $[11\bar{2}0]$ directions in the respective crystals.

razor blade, but in the later ones by lightly wiping the surface with a "Kleenex" tissue soaked in alcohol. This second procedure gave marks only ~ 1 $\mu$m wide, without any detectable surrounding damage.

## 2.3. Testing Procedure

All of the tests were made under constant shear stress and the displacement of the fiducial marks was measured as a function of time. To ensure that the grips did not overlap the boundary the grip assembly (fig. 2) deliberately incorporated a small gap S. The separation P of the grips was carefully adjusted for each particular specimen so as to allow for differential expansion during heating to the test temperature.

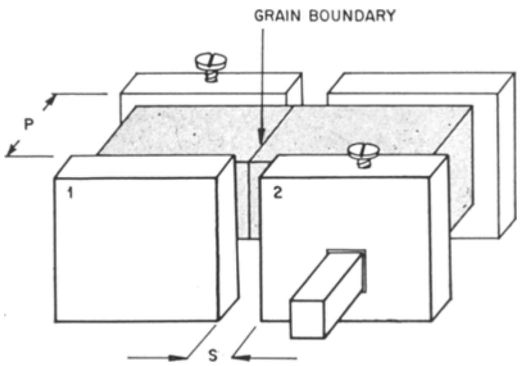



*Figure 2* Bicrystal grip arrangement.

For tests above room temperature specimens were heated by a recirculating stream of purified argon, and the specimen temperature, as measured by a thermocouple located in the grip assembly very close to the boundary, was maintained to within $\pm$ 2° C of a predetermined value.

Observations of the specimen surface condition and measurements of fiducial mark displacements were made through a microscope fitted with a long working distance reflecting objective, focused on to the specimen through a silica observation port. An automatic camera was used to obtain a sequential record of the fiducial mark displacements. This film record was calibrated by taking a photograph of a stage micrometer placed in the specimen plane.

# 3. Experimental Results

## 3.1. Boundary Sliding as a Function of Time

Tests were made to determine the effect on sliding behaviour of variations in (i) the applied shear stress, (ii) the temperature of test, (iii) the boundary misorientation, and (iv) impurity additions.

### *3.1.1. Effect of Stress*

When the applied shear stress was less than 250 g/mm² the curves of sliding displacement versus time were of smooth sigmoidal shape and there was no sign of an incubation period, of an extended initial constant velocity region, or of cyclic variations in the sliding rate, such as have been reported previously. Figs. 3 and 4 show typical curves for high-angle tilt, and for twist boundaries, respectively, at a number of different values of the stress; the test temperature was in all cases fixed at 200° C. Individual curves could be well described by an expression of the form $d = At^n$ where $d$ is the sliding displacement, $t$ the time and A and n are constants. However, the reproducibility of individual curves, as tested by duplicate experiments on specimens cut from the same bicrystal – e.g. W7 and W8 in fig. 4 – was generally poor. Some specimens slid unexpectedly fast (e.g. Specimen T8, fig. 3);

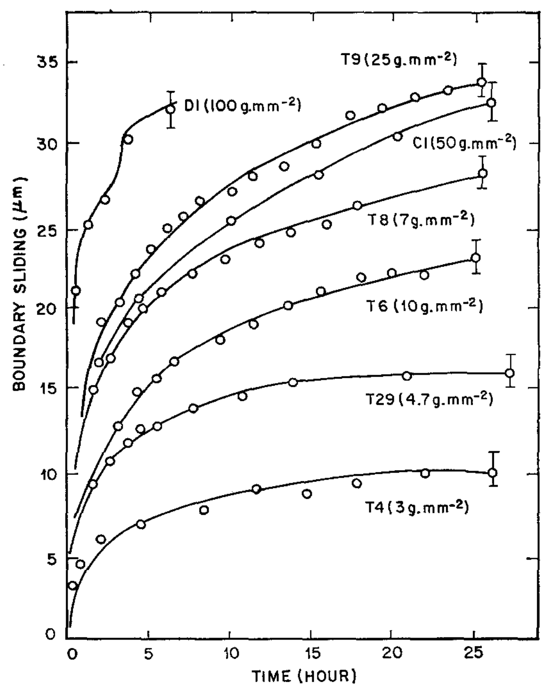



*Figure 3* Grain-boundary sliding versus time curves for specimens containing high-angle tilt boundaries. The different curves were obtained at the stresses marked on them. All tests were at 200° C.

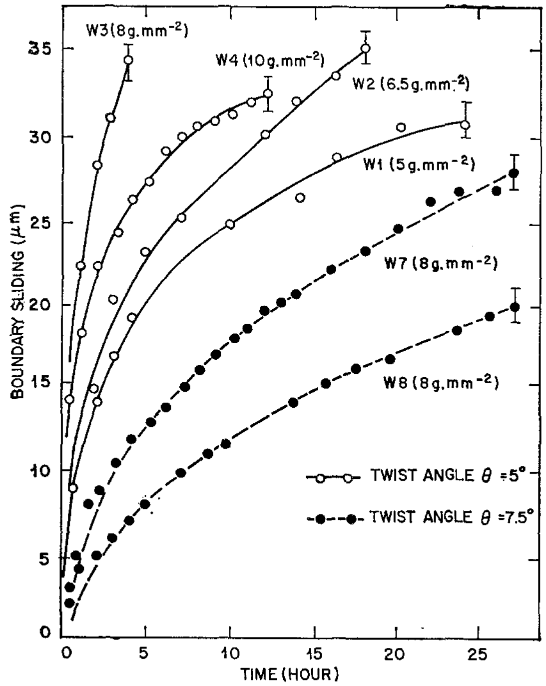



*Figure 4* Grain-boundary sliding versus time curves for specimens containing twist boundaries. All tests at 200 °C.

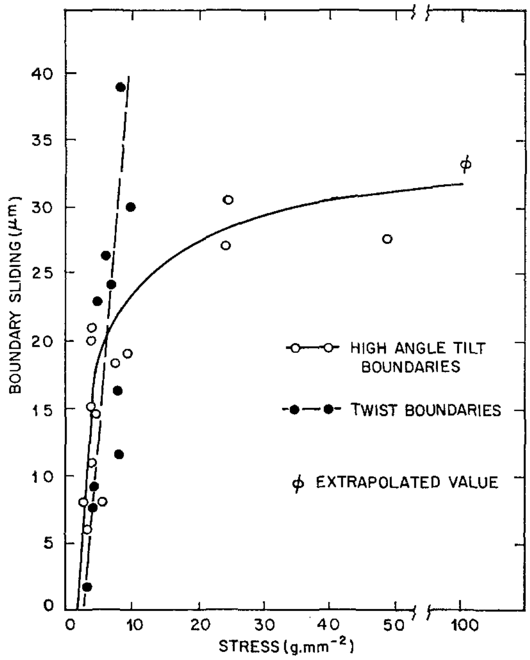



*Figure 5* Sliding displacement in 10 h as a function of stress. Data derived in part from figs. 3 and 4.

in others the rate was slower than expected from the trends. It is not surprising, therefore, that A and n values did not correlate in any simple way with the stress. This, it is suggested, is due to some uncontrolled variable in the microstructure, evidence for which is given by the fact that at any given time in a test the displacements recorded at different positions along the boundary varied by up to 10%. There is one general feature of the A and n values which is noteworthy, and which is manifest if figs. 3 and 4 are superposed. This is that both A and n values for twist boundaries were greater than for tilt boundaries. In other words sliding was more rapid, and the boundaries hardened less rapidly, in the former case.

Despite the difficulty of obtaining reproducibility, an important conclusion emerges from the results on the high-angle tilt boundaries when they are analysed in the manner illustrated in fig. 5. Here the sliding displacement attained after an arbitrary period (10 h) is plotted as a function of stress. This and curves for different arbitrary time values all show a marked change in slope at a stress of around 10 g/mm$^2$, which is the stress above which heavy basal slip markings were observed on the surface of the component crystals. Data for the twist boundaries are also included in fig. 5, but these stop short of 10 g/mm$^2$ since at stresses greater than this value rapid and extensive deformation occurred by crystal slip and it was not possible to determine what happened to the boundary sliding behaviour.

When high-angle tilt boundaries were subjected to stresses greater than 250 g/mm$^2$ the sliding versus time behaviour was broadly the same as that described above. However, repeat tests were even more irreproducible and wide variations in sliding occurred from position to position along a particular specimen boundary. Heavy basal slip lines appeared immediately the load was applied and later, in some areas, there would be non-basal slip, twinning, and even recrystallisation with little sliding at the position of the original grain-boundary; in other areas there would be sliding displacements of up to 200 $\mu$m with no sign of recrystallisation. Several tests at 25° C and at 100° C showed a long "incubation period" before sliding began. However, the length of this incubation period was erratic and, contrary to what might be expected, was sometimes greater at the larger stresses.

A few tests on high-angle tilt boundaries were conducted with the shear forces applied in the directions ON and MP (fig. 1a). With stresses in the range 800 to 2250 g/mm$^2$ at 25° C, and 250 to 800 g/mm$^2$ at 100° C there was very little sliding, and invariably less than in corresponding specimens stressed in the usual direction.

### *3.1.2. Effect of Test Temperature and of Intermediate Annealing Treatments*

If a test was interrupted when the boundary had already begun to harden, the stress removed but the specimen maintained at test temperature, there was no marked increase in the sliding rate on reloading. Similarly, intermediate annealing treatments at temperatures as high as 400° C produced no significant recovery. However, if during a test the temperature was suddenly changed with the load maintained, or if separate specimens under similar stress but differing test temperatures were compared, the temperature dependence of the boundary sliding rate was apparent in both the initial and later stages of sliding.

In an attempt to characterise this behaviour, values of the activation energy $Q$ were obtained by two different procedures, firstly from the change in sliding velocity produced by a sudden temperature change in the middle of a test, and secondly from a comparison of the sliding rates in separate specimens. The former procedure is generally preferred in creep studies because the sudden temperature change gives the possibility of maintaining all the structural variables constant. Values of $Q$ obtained in this way were in the range 25 $\pm$ 5 kcal/mole for temperature changes from 200 to 250° C. The calculation of $Q$ from tests on separate specimens is complicated not only by the possibility of fine structural differences, but also by the lack of a steady-state condition in the tests. The procedure adopted was to compare sliding distances in an arbitrarily chosen time. It was found that the choice of this interval had little influence on the $Q$ obtained, but for temperatures in the range 25 to 200° C values were consistently around 5 kcal/mole. A discussion of the wide disparity between the $Q$ values obtained by the two different procedures is left to section 4.

### *3.1.3. Effect of Boundary Angle*

High-angle tilt boundaries with $30° < \phi < 90°$ all behaved similarly, but with $\phi \leqslant 20°$ sliding displacements saturated at less than 5 $\mu$m with an applied shear stress of 4.6 g/mm$^2$ at a temperature of 200° C. A similar high resistance to sliding at low-angle boundaries has been reported for other materials, but it is interesting to note that the angular range (20 to 30°) over which the transition in sliding behaviour of boundaries in zinc occurs, coincides with that in which Weinberg [8] noted a change in the incipient melting at grain-boundaries in the same material.

Specimens which had complex high-angle boundaries behaved in a similar way to those having high-angle tilt boundaries. The only exception came when grains were close to a twin relationship and then the boundaries were very resistant to sliding.

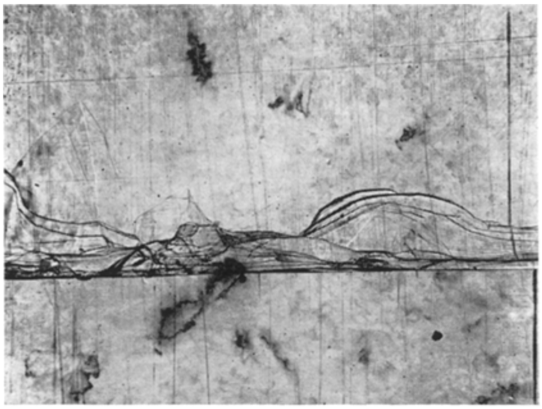
In the case of twist boundaries sliding was equally easy with values of $\theta$ from 23° down to 5°.

### *3.1.4. Impurity Effects*

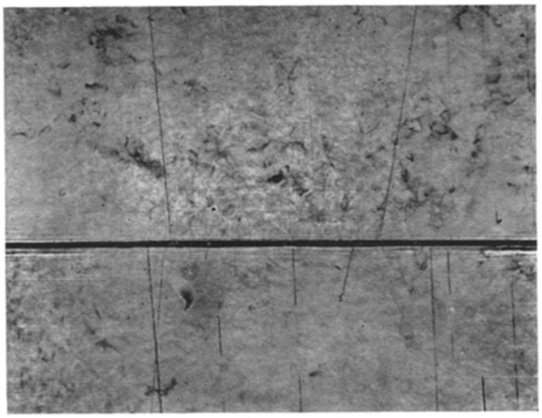
No significant differences were noted in the sliding behaviour of specimens prepared from the two different grades of starting material. However, the addition of 0.1 at. % cadmium gave rise to bicrystals with irregular boundary surfaces and the sliding rates at these were much lower than in corresponding tests on undoped specimens.

## 3.2. Metallographic Observations

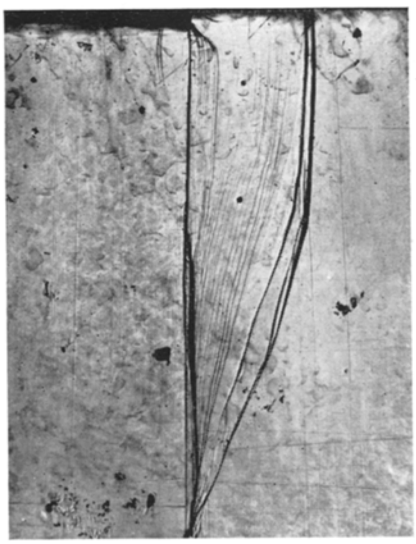
Except for the specimens prepared from Cd-doped material, the grain-boundary traces were always quite straight in the unstressed bicrystals. After applying the stress, however, there was evidence of grain-boundary migration within a few minutes. In the high-angle tilt boundary specimens there was a marked difference between the migration on the A surface and that on the B surface (fig. 1a). On the A surface, the boundary migrated in a highly irregular way, and the region between the original and final positions of the boundary showed evidence of subgraining and lattice rotation. Though the extent of these effects was reduced as the stress and temperature were reduced, even at stresses lower than those required for macroscopic crystal slip (10 g/mm$^2$) irregular migration occurred on the A surface. Fig. 6a shows this effect in a sample subjected to a stress of only 4.6 g/mm$^2$; in some places the boundary has migrated through more than 150 $\mu$m. The faint vertical lines are the scratch markers which show that the two grains have become displaced by a total distance of about



(6a)



(6b)



(6c)

*Figure 6* (a) Irregular boundary migration on the A surface of a high-angle tilt boundary specimen after 11 h under a stress of 4.6 g/mm². Test temperature 300° C. (b) Appearance of B surface at same point in test. (c) Appearance of C surface near corner with A surface at same point in test. All micrographs at magnification of 70×.

40 μm in a series of sliding movements at the successive positions of the boundary. At the same point in the test the appearance of the B surface, fig. 6b, was quite different. The boundary has migrated a small distance (10 μm) but has remained sensibly straight. Examination of the C and D faces of this specimen showed that the extensive migration noted on the A surface extended some 800 μm into the body of the specimen (fig. 6c). The depth to which this gross migration extended increased as the stress, temperature, and duration of test were increased.

In specimens carrying shear stresses greater than 25 g/mm², heavy basal slip bands, occasional prismatic slip traces, and boundary serrations developed on A surface.

On twist boundary specimens the grain-boundary migration was, for the most part, of an entirely different character from that on the A surface of the high-angle tilt boundary samples. Fig. 7 shows a typical example of the appearance of an E (or F) surface, where sliding and migration had occurred alternately, but in such a way that most of the boundary trace remained straight. However, there were always some regions on the surface where small misalignments of

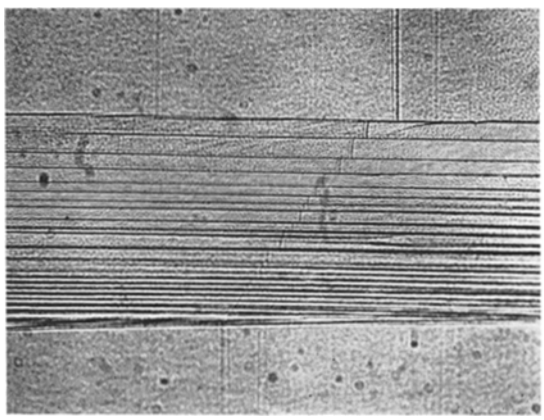


*Figure 7* Regular boundary migration on the surface of a twist boundary specimen after 65 h under a stress of 5.8 g/mm². Test temperature 205° C (× 224).

the basal planes in the two seed crystals resulted in grain-boundary-slip-plane configurations similar to those on surface A (fig. 1a) of tilt boundary specimens. Here irregular boundary migration occurred.

### 3.3. Etching Experiments

Bell and Thompson [9] first showed that a regeneration of the sliding rate was obtained in high-angle tilt bicrystals of zinc which had become slide-hardened if material from the A surface (fig. 1a) was removed by etching. A similar effect was subsequently observed in bicrystals of tin [10], but in neither case was the specimen restored to its virgin condition. Now the depth to which the structural damage at the grain-boundary extends beneath the A surface depends on the stress, temperature and duration of test. By limiting the stress to values less than 10 g/mm$^2$ the damage is restricted to a layer which can be removed by a light etch. The boundary is then restored to its original virgin condition both as regards appearance and its subsequent behaviour under stress. Thus in fig. 8 the sliding data from two successive tests on the same specimen stressed at 4.6 g/mm$^2$ are seen to lie, within experimental error, on a single curve. Between the two tests the specimen was removed from the rig, surface A given a light chemical polish and on re-insertion subjected to the same *stress* as in the original test. The same procedure could be repeated many times. Thus the specimen T17 in fig. 9 had been subject to ten periods of one minute under a stress of 4.6 g/mm$^2$ with intermediate etches, and in each cycle the sliding displacement was reproduced within experimental error. In this figure the ten cycles are plotted sequentially for comparison with the behaviour of the identical specimen T17 which was stressed continuously.

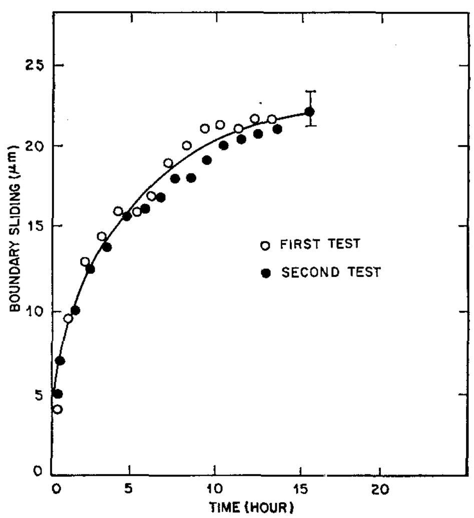



*Figure 8* The grain-boundary sliding in two successive tests at 200° C on the same specimen (containing a high-angle tilt boundary) under a stress of 4.6 g/mm$^2$. Between the tests a light etch was given to surface A. Points plotted from same zero to show reproducibility.

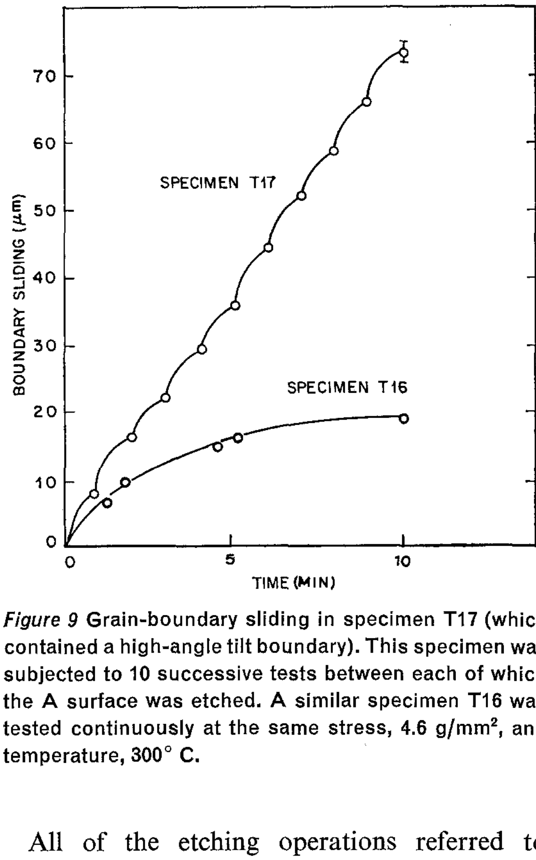



*Figure 9* Grain-boundary sliding in specimen T17 (which contained a high-angle tilt boundary). This specimen was subjected to 10 successive tests between each of which the A surface was etched. A similar specimen T16 was tested continuously at the same stress, 4.6 g/mm$^2$, and temperature, 300° C.

All of the etching operations referred to above involved the thermal cycling of the specimen from the test temperature down to room temperature and back up again, but blank tests, in which the etch was omitted, showed that this thermal cycle had no effect on the subsequent sliding behaviour. Similarly if B, C or D surfaces (fig. 1a) were etched instead of A there was no acceleration of sliding when the load was reapplied.

This specificity of the etch sensitivity of bicrystal faces was less marked in twist-boundary specimens. Here the inadvertent tilt component was not in general, parallel to an axis of the specimen and irregular migration was found on more than one face. However, if these regions of irregular migration were etched away, a hardened boundary could be restored to its original behaviour.

## 4. Discussion

Once it has been recognised that grain-boundary sliding comprises a series of complex phenomena, it is important to try to separate these and study them separately. In the present experiments one form of slide-hardening has been clearly identified with the structural rearrangements that occur preferentially at a particular boundary-surface intersection. That the observed progressive diminution of sliding rate was not due to the exhaustion of regions of easy sliding was demonstrated by the ability to restore the sliding rate of the whole specimen by the removal of the hardened surface layer. Thus the sliding behaviour was analogous to the transient stage in high-temperature creep, where hardening occurs at a greater rate than that of recovery.

At stresses less than that required for macroscopic slip this hardening was wholly confined to a thin region near a particular type of surface, but at increasing stresses the same kind of microstructural changes were found at progressively greater depths. There are two aspects of this hardening that need to be clarified. Firstly, what is it about the structural changes that occur near the A surface that causes hardening? In other words, what is the rate-limiting process in sliding after these changes have occurred? Secondly, why should these structural changes that are responsible for the hardening occur preferentially at an A surface?

### 4.1. The Mechanism of Slide-Hardening

The structural rearrangement which occurred near an A surface is shown in idealised form in fig. 10. Here a small section BCDE of the grain-boundary has migrated away from its original plane BDE, so as to leave grain 2 protruding into grain 1. Further shear in the original grain-boundary plane necessitates *crystal slip* on one or more systems in grain 2 so as to give a resultant in the plane BDE. Alternatively, if this grain were rigid, the promontory could plough through grain 1. The distinction between these alternatives disappears when the model is developed so as to include promontories advancing into each grain, but the essential point remains, that slip on planes other than

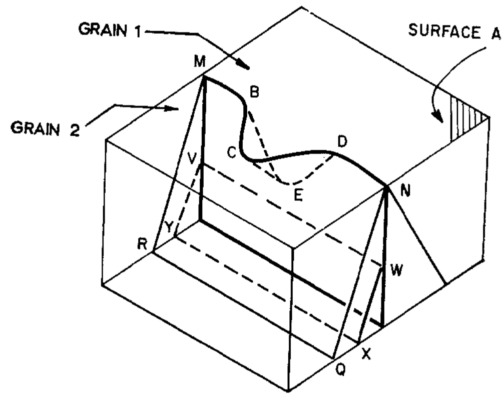



*Figure 10* Diagram to illustrate the mechanism of formation of the boundary asperities near surface A. The diagram shows one greatly exaggerated asperity BCDE, which causes the originally straight grain-boundary MN in surface A to become MBCDN.

(0001) is required in order to produce a shear with a resultant in the plane of the boundary. It is suggested that this is the process limiting further shear in the plane MNWV. The progressive hardening is attributed to the steadily increasing proportion of crystalline regions in the boundary plane, rather than to any progressive hardening within them, because it was observed that the hardening is resistant to annealing treatments.

Of the two widely different activation energies quoted in section 3.1.2, the one that best fits in with the above reasoning is that obtained by the more reliable temperature change technique. This gave a value of 25 $\pm$ 5 kcal/mole for temperatures in the range 200 to 250° C, which is in good agreement with the value of 28 to 30 kcal/mole found by Tegart and Sherby [11] for creep in polycrystalline zinc in the same temperature region. Here the process limiting polycrystalline creep is thought to be prismatic slip, whose dynamics have been determined by Gilman [12]. Assuming all the load to be carried on areas such as BDE, whose total can be estimated from the micrographs, it is found that the stress on such regions would give prismatic glide rates roughly the same as the observed grain-boundary sliding rates.

### 4.2. The Origin of the Asperities that Give Rise to Slide-Hardening

Bell and Thompson [9] attempted to explain the uniqueness of A-type surfaces in terms of the concentration of stress at the head of the blocked slip planes, which are longest just below the intersection of the grain-boundary and the A surface. Puttick and Tuck [10] put up several detailed objections to this and concluded that the local boundary migration is activated by the strain energy of dislocations generated by the sliding process. That macroscopic slip is unnecessary is shown by the present observations of slide-hardening below the critical stress for macroscopic slip; on the other hand the very pronounced change in slope of the sliding rate versus stress curve at 10 g/mm$^2$ suggests either that an alternative and more important hardening process is introduced once macroscopic slip occurs, or that the restricted motion of slip dislocations below this stress makes the same hardening process much less effective. It is clear from interferometric studies, and more particularly from etch-pit studies, that slip dislocations are mobile at stresses well below the critical resolved shear stress for slip, and so it is reasonable to suppose there to be just the one cause of asperity formation – boundary migration stimulated by an accumulation of slip dislocations. The detailed model proposed below differs from that suggested earlier in that the uniqueness of the A surface is attributed not to the length of the blocked slip planes (QN in fig. 10) but to the shortness of the extrapolation of the slip planes in the neighbouring grain.

Consider first slip dislocations on planes such as VWXY (fig. 10) which intersect the grain-boundary well below the free surface. Three forces act on a dislocation in such a plane as it approaches the boundary: the resolved component of the applied stress driving it towards the boundary, a long-range repulsive stress from the second crystal and a short-range attraction to the boundary itself. Near surface A the second term is reduced because the extrapolation of the slip planes beyond the boundary lies in free space; consequently, dislocations on such slip planes will approach the boundary more closely and more effectively promote boundary migration. This proposal accounts for the present observations satisfactorily, and a corollary of it copes with one remaining objection of Puttick and Tuck [10]. They found that slip introduced prior to an anneal did not give rise to boundary migration; the shortcoming of their experiment is that the dislocations blocked at the grain-boundary would retreat on removal of the stress. Their suggestion that the dislocations responsible for migration are generated by grain-boundary sliding is inadequate both for their own and for the present observations in that it incorporates no feature specific to the A surface.

### 4.3. Comments on Other Recent Investigations

There has been much controversy in the literature on grain-boundary sliding; in part this controversy is due to the tendency of authors to try to squeeze a whole series of related but possibly different phenomena into the one simple picture. From the experiments discussed above, it is clear that grain-boundary sliding is a complex phenomenon involving subtle interactions between grain and grain-boundary processes. The conclusion that, in the particular set of conditions of these present experiments, grain-boundary sliding was limited by a slip process with resultant in the plane of the boundary, does not rule out the possibility that in other situations different factors might be rate-controlling. However, it is interesting to note that in several recent investigations on both bicrystals and polycrystals, the activation energy for grain-boundary sliding has been identified with that for slip [13-15], whilst the relevant component of the stress has been shown to be that resolved in the plane of the boundary [16].

## 5. Conclusions

(i) Most observations of grain-boundary sliding are dominated by slide-hardening, which is so structure sensitive as to make it extremely difficult to perform reproducible experiments.
(ii) In the present experiments slide-hardening was caused by irregular boundary migration following the accumulation of slip dislocations near the boundary.
(iii) Sliding at the corrugated boundary was limited by the shear resistance of the crystalline regions in the original boundary plane.

## Acknowledgements

The experimental work described in this paper was carried out in the Department of Metallurgy, Imperial College, London, and the authors are indebted to Professor J. G. Ball for the provision of laboratory facilities. One of us (N.B.W.T.), and part of the work, was supported by a contract from the UKAEA, whilst another (P.A.T.) was in receipt of a Science Research Council studentship.

## References


1. R. C. GIFKINS, in "Fracture" (edited by B. L. Abervach *et al*) (Wiley, New York, 1959) p. 579.
2. R. N. STEVENS, *Met. Revs.* **11** (1966) 129.
3. K. E. PURTICK and R. KING, *J. Inst. Metals* **80** (1951-52) 537.
4. S. K. TUNG and R. MADDIN, *Trans. AIME* **209** (1957) 905.
5. N. B. W. THOMPSON, M.Sc. thesis, London (1959).
6. P. A. TURNER, Ph.D. thesis, London (1965).
7. B. CHALMERS, *Canad. J. Phys.* **31** (1953) 132.
8. F. WEINBERG, *Acta. Met.* **6** (1958) 535.
9. R. L. BELL and N. B. W. THOMPSON, *Nature* **193** (1962) 363.
10. K. E. PUTTICK and B. TUCK, *Acta. Met.* **13** (1965) 1043.
11. W. J. MCG. TEGART and O. D. SHERBY, *Phil. Mag.* **3** (1958) 1287.
12. J. J. GILMAN, *Trans. AIME* **206** (1956) 1326.
13. P. R. STRUTT, A.-M. LEWIS, and R. C. GIFKINS, *J. Inst. Metals* **93** (1964-65) 71.
14. R. L. BELL and T. G. LANGDON, *J. Materials Sci.* **2** (1967) 313.
15. C. A. P. HORTON, N. B. W. THOMPSON, and C. J. BEEVERS, *Metal Sci. J.* **2** (1968) 19.
16. R. C. GIFKINS, T. GITTINS, R. L. BELL, and T. G. LANGDON, *J. Materials Sci.* **3** (1968) 306.