

THE ROLE OF GRAIN BOUNDARY SLIDING IN CREEP.

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by

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ABSTRACT.

Creep tests were carried out in the temperature range 21°C - 300°C , using the solid-solution magnesium alloy "Magnox AL80". The incidence of grain boundary sliding was determined throughout the tests by measuring the average offset, perpendicular to the surface, between adjacent surface grains. The results showed that in the temperature range 125°C - 300°C the average offset initially increased linearly with the strain, but a deviation from linearity occurred at strains greater than about 1 - 6%. By sectioning, it was found that the average internal angle between the boundaries and the surface changed from an initial value of about 58° for a polished or "as-cut" surface to a value of about 75° at some small finite strain. The strain at which the angle saturated was shown to be similar to that at which the sliding-extension curve ceased to be linear.

The strain within individual grains was measured from a grid printed photographically on to the specimen surface, and these results were used to indirectly calculate the contribution made by sliding to the overall deformation. The dependence of sliding on stress and grain size was investigated at a temperature

of 200°C, and it was found that, under conditions of very slow rates of strain and small grain sizes, sliding could account for up to 70 - 80% of the total deformation. The sliding contribution was also calculated from measurements of the offsets occurring in the plane of the surface. The possibility of determining the internal contribution from grain shape measurements was investigated.

In the temperature range 21°C - 75°C, true sliding did not occur, but, owing to differences in the deformation behaviour of neighbouring grains, a narrow zone of accommodation was often formed immediately adjacent to the boundaries.

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CHAPTER 1. INTRODUCTION.

At the present time, the magnesium alloy "Magnox AL80" is in use as a fuel-element can in gas-cooled reactors such as Calder Hall and Chapelcross. The prime function of these cans is to act as an impermeable envelope, stopping the escape of fission products, and at the same time preventing an ingress of coolant gas which would result in oxidation of the uranium. During irradiation, the uranium fuel undergoes growth and distortion, and it is therefore necessary that the cans should be capable of deformation without fracture under very slow rates of strain. However, it has been found that small voids or cavities develop in the grain boundaries during this slow deformation, and these ultimately link to give inter-crystalline failure. Although the mechanism of nucleation and growth of such cavities is still not resolved, a number of workers have suggested that they are intimately associated with the process of grain boundary sliding - that is, the process by which two

adjacent grains may be displaced relative to each other, by movement along their common boundary in a direction parallel to the boundary plane.

Many previous workers have investigated grain boundary sliding in polycrystalline materials, and the majority of these have attempted to determine the percentage contribution made by the sliding process to the overall strain. Often, their results have shown that sliding accounts for only about 20% of the total strain, and there has been a tendency to relegate sliding to a secondary, and relatively unimportant, mode of deformation. However, a close analysis of this early work suggests reasons for thinking that such a view be untenable. There are, for example, many inconsistencies in the methods used by different workers to calculate the sliding contribution. In addition, the tests have usually been carried out at fairly rapid rates of strain, but in those cases in which very slow strain rates were used, the sliding contribution was often as high as 80 - 90%. The object of the present work was therefore two-fold. Firstly,

to develop an accurate method of assessing the contribution made by sliding to the total strain. Secondly, to investigate the incidence of sliding in magnox, particularly under slow creep conditions.

The majority of tests were undertaken at 200°C , equivalent to $0.51 T_m$, where T_m is the melting point in degrees Absolute, since grain boundary sliding only becomes important at temperatures greater than about $0.4 T_m$. Sliding at the surface was investigated under varying conditions of stress and grain size, and an attempt was made to link these results with those on internal sliding obtained by means of a grain shape technique. In addition, tests were also carried out to investigate the dependence of sliding on temperature in the range $21^{\circ}\text{C} - 300^{\circ}\text{C}$ ($0.32 - 0.62 T_m$).

It is convenient at this stage to outline briefly the method of presentation employed in this thesis. The literature survey is contained in Chapter 2, and this includes a brief review of the theories of creep and grain boundaries, together with a detailed analysis of the results of previous grain boundary sliding

experiments. Particular emphasis is placed in this section on the results obtained with polycrystalline specimens. Details are given in Chapter 3 of the material used in this work, and the experimental techniques employed. Chapter 4 contains a complete record of the experimental results, and, with the exception of the grain shape measurements, these are subdivided according to the temperature of testing. Finally, the more important observations are discussed in Chapter 5, and a detailed analysis is made of the various ways of estimating the sliding contribution to the overall strain.

CHAPTER 2: LITERATURE SURVEY.

2.1. The Phenomenon of Creep.

Creep is the thermally activated process by which slow deformation occurs in metals subjected to a constant load or stress. There have been many reviews of the subject, but, since the more important theoretical interpretations are new in origin, only the most recent are referred to here¹⁻⁵. In section 2.1.1 of this chapter, the various processes contributing to the creep strain will be considered separately. Specific theories of creep are outlined in detail in section 2.1.2.

2.1.1. Structural Processes of Creep at High Temperatures.

The predominant processes of deformation involved in the creep of metals at high temperatures are:

- (i) Dislocation glide, giving rise to crystalline slip.
- (ii) Dislocation cross-slip and climb, giving rise to recovery and sub-grain formation.
- (iii) Grain boundary sliding.
- (iv) Grain boundary migration.
- (v) Vacancy diffusion.

Of these processes, (i), (ii) and (v) are trans-granular, so that they contribute to the extension within the

individual grains, E_s . Process (iv) refers to the bodily movement of the boundary in a direction perpendicular to the boundary plane, and this makes no significant contribution to the total extension. Process (iii) is localised at, or immediately adjacent to, the grain boundaries, and therefore contributes an elongation, E_{gb} , to the overall strain but none to the individual grains. Thus the total extension E_{tot} is due to the sum of these two component parts, such that

$$E_{tot} = E_s + E_{gb} \quad 2.1.$$

McLean⁶ attempted to measure the inter- and trans-granular contributions to the total strain in an aluminium specimen, using interference fringes to obtain the average vertical step heights at grain boundaries, and at slip lines, respectively. By this method, it was only possible to account for about one-half of the total extension, and McLean suggested that the major mechanism of deformation was by fine slip that was microscopically undetectable. To check this suggestion, he calculated the creep extension due to fine slip by measuring the orientation tilts between adjacent sub-grains, and found it to be of the same order of magnitude as the "missing" creep.

In later work, McLean⁷ revealed the fine slip lines between the prominent slip bands, and showed that the latter were simply lamellar regions where slip had occurred to an unusually large extent.

The occurrence of fine slip almost certainly accounts for many of the observations of "slipless" flow, as in the experiments of Ivanova⁸ and Rauzin and Zhelezniakova⁹, where it was incorrectly suggested that the absence of visible slip lines before some "critical" strain indicated that sliding accounted for the whole of the initial deformation.

The results of McLean constitute an important contribution to our understanding of the processes of creep, although it should be noted that the Al specimens were of a large grain size, so that the extension due to grain boundary sliding was at all times very small.

2.1.2. Specific Theories of Creep.

Many theories have been developed to explain the constant rate of flow occurring in steady-state creep. The more recent of these are based on rate-process theory. The first, by Kauzmann¹⁰, assumed the rate-controlling process was the motion of "flow units" through the lattice, and creep was due to the thermal activation of these units over free energy barriers. Although the flow unit was unspecified,

it would probably be identified with the movement of a group of dislocations along their slip planes, so that under this theory the dislocations would be held up at barriers which must be surmounted if creep were to continue. If Q is the activation energy required by the dislocation in order to surmount the barrier, the energy that must come from the thermal fluctuation is $(Q - B\sigma)$, since the applied stress σ will also make a contribution by moving the dislocation to the top of the barrier. The creep rate $\dot{\epsilon}$ can therefore be represented in this theory by a hyperbolic sine law of the form

$$\dot{\epsilon} = A \exp(-Q/RT) \sinh B\sigma/RT \quad 2.2.$$

where $A, B = \text{constants}$

$Q = \text{activation energy of secondary creep}$

$R = \text{gas constant}$

$T = \text{temperature in } ^\circ\text{K.}$

For high stresses, such that $B\sigma \gg RT$, this approximates to

$$\dot{\epsilon} = C \exp[-(Q - B\sigma)/RT] \quad 2.3.$$

where $C = \text{constant.}$

A comprehensive tabulation was made by Dorn^{11,12} of the results of a number of experimental investigations, and it was concluded that at low stresses the Kauzmann equation breaks down and the creep rate is given by

$$\dot{\epsilon} = C \sigma^n \exp(-Q/RT) \quad 2.4.$$

where C = constant.

To account for this stress dependence, Weertman¹³ developed a theory of steady-state creep in pure metals or simple alloys, in which it was suggested that the rate-controlling process was dislocation climb in the manner originally proposed by Mott¹⁴. In this theory, it was assumed that dislocations on intersecting slip planes were able to form immobile Lomer-Cottrell¹⁵ dislocations, and that mobile dislocations were then held up at such barriers, and piled up in rows. Under certain conditions the leading dislocations in the pile-up were able to circumvent the barrier by climbing out of their slip planes, through the creation or destruction of vacancies or interstitials. By assuming that the concentration of vacancies in the neighbourhood of a dislocation remained constant at constant temperature, Weertman was able to estimate the rate of dislocation climb from the concentration gradient. For low

stresses, he showed that the creep rate was of the form

$$\dot{\epsilon} = A (\sigma^n/RT) \exp(-Q/RT) \quad 2.5.$$

where A and n were constants ($n \sim 3-4$), and the activation energy Q was that for self-diffusion. For high stresses, the creep rate increased more rapidly with the stress, and the equation became

$$\dot{\epsilon} = A' \sigma^m \exp(B \sigma^\beta/RT) \exp(-Q/RT) \quad 2.6.$$

where A', m, B and β were constants ($m \sim 1-2$; $\beta \sim 2$).

Weertman considered the original theory to be inapplicable to the creep of hexagonal metals, because at that time it was not thought possible to form immobile dislocations in such a system. Since a power law dependence had already been observed in a hexagonal material (ice¹⁶), Weertman¹⁷ later developed a theory which did not require the formation of immobile dislocations. In this model, it was suggested that pile-ups occurred between dislocations on neighbouring slip planes, and that the leading dislocations of each group were able to climb out of their planes and annihilate each other. This theory led to a stress exponent of $n = 4.5$ which was in good agreement with the value of 4.2

obtained for ice¹⁶. Furthermore, it gave a better correlation with the existing results for Al^{18,19} and Ni²⁰. However, McLean³ has pointed out that the exponent of 4.5 arises directly from the use of an incomplete model of strain-hardening.

In later work, Weertman²¹ considered the case of steady-state creep controlled by dislocation glide, and derived a stress exponent of $n = 3$. Since experimental results showed the stress exponent to decrease upon alloying from about 4.5 to 3.0 for increasing alloy content, Weertman concluded that the rate-controlling process changed from a dislocation climb process in the pure metals to a dislocation glide controlled mechanism, such as the movement of Cottrell-Jaswon atmospheres, in the alloys.

To account for creep at very low stresses or temperatures near the melting point, Nabarro²² and Herring²³ developed a diffusion model in which the operative mechanism was the stress-directed diffusion of vacancies. In this model, the boundary was assumed to act as a free source or sink for vacancies, and creep to occur by the migration of vacancies under the action of the applied stress from boundaries perpendicular to boundaries parallel to the stress axis. For these specialised conditions, it was shown that the rate of diffusion creep should be linearly proportional to the applied stress, in contrast to creep

controlled by slip or climb processes where the creep rate was found to vary as a non-linear power of the stress.

A summary of the behaviour of pure metals was made by McLean and Hale²⁴, who plotted the steady-state creep data for a number of materials to test the equation

$$\dot{\epsilon} = A (\sigma/G)^n \exp(-Q/RT) \quad 2.7.$$

in which the stress was normalised by dividing by the shear modulus G . This yielded straight lines for conditions of high temperature and low stress, with a stress exponent n between 5 and 6. Since the results lay in a narrow band, it was concluded that the mechanism of creep was similar in all the materials studied. However, as theory indicates that the temperature T should appear in the denominator, and the power indices of the stress and modulus should be different, McLean³ has suggested a more correct form of the equation to be

$$\dot{\epsilon} = \frac{A \sigma^n}{T G^m} \exp(-Q/RT) \quad 2.8.$$

where n and m differ by about an integer.

McLean and Hale²⁴ also found that at high stresses and low temperatures, outside of the range of full recovery creep, the data fitted an equation of the form

$$\dot{\epsilon} = A \exp\left[-(Q - B\sigma/G)/RT\right] \quad 2.9.$$

which is similar to equation 2.3, with the exception that the stress has again been normalised by dividing by G . Zhurkov and Sanfirova²⁵ have also demonstrated the applicability of equation 2.3, by undertaking experiments on Al covering a very wide range of creep rates.

A useful method was developed by Dorn and co-workers²⁶ to measure Q by rapidly changing the testing temperature by a few degrees under conditions of constant stress, and measuring the strain rates immediately before ($\dot{\epsilon}_1$) and after ($\dot{\epsilon}_2$) the temperature change. The structure was presumed to be the same immediately before and after the change, and thus the activation energy could be determined from the equation

$$\dot{\epsilon}_{1,\text{exp}} (Q/RT_1) = \dot{\epsilon}_2 \exp(Q/RT_2) \quad 2.10.$$

where T_1 and T_2 were the initial and final temperatures. This technique enabled Q to be measured at any temperature, and, using high purity Al²⁷, it was found that the

activation energy of high temperature creep was constant and equal to that of self-diffusion. This indicated control by dislocation climb at high temperatures, but the value of Q was less than that of self-diffusion for temperatures below about $0.4 T_m$ (T_m = melting point in $^{\circ}K$). Extensive work^{28,29} yielded similar results for a wide range of materials, and the value of Q at high temperatures was found to be independent of stress, strain and grain size. An anomaly exists here, however, since Q was also found³⁰ to be independent of stress in a region in which cross-slip was thought to be the rate-controlling process, although the theory of creep under such conditions suggests that Q should be stress-dependent.

An analysis of much experimental data by Sherby³¹ similarly revealed the applicability of Weertman's theory of control by dislocation climb in pure metals tested at high stresses. At low stresses or very high temperatures, the Nabarro-Herring^{22,23} model of vacancy diffusion was established, and it was suggested that the stress at which the Weertman model took over was dependent upon the elastic modulus and grain size of the material. Sherby³² also investigated the apparent increase in activation energy for the creep of pure metals with increasing temperature in the range $0.5 - 1.0 T_m$. By accounting for temperature variations in the elastic modulus, the true activation energies for

creep (Q_{creep}) of pure Cd and Al were shown to be equal to those of self-diffusion ($Q_{\text{s.d.}}$) for all temperatures above $0.5 T_m$, and it was therefore concluded that the steady-state creep rate was of the form shown in equation 2.7. It was further pointed out that the results of Dorn et al^{27,28,29}, showing an equivalence between Q_{creep} and $Q_{\text{s.d.}}$, were explicable since the effect of elastic moduli would be negligible in the range $0.5 - 0.6 T_m$.

Tegart and Sherby³³ carried out compression creep tests on polycrystalline Zn, and concluded that high-temperature creep was controlled by two thermally activated processes operating additively. In the temperature range $0.5 - 0.6 T_m$, the activation energy of creep was equal to that of self-diffusion, thereby suggesting control by dislocation climb. However, in the temperature range $0.8 - 1.0 T_m$, the activation energy was constant, and greater than that of self-diffusion. It was suggested that creep was then controlled by prismatic slip. A high activation energy for creep has also been reported for Mg³⁴ at temperatures greater than $0.75 T_m$.

Recent work by Garofalo³⁵ has shown that the dependence of secondary creep rate on stress at constant temperature can be defined over a very wide stress range by the relation

$$\dot{\epsilon} = A (\sinh \alpha \sigma)^n \quad 2.11.$$

where A , α and n are constants at a particular temperature.

This expression reduces to a power dependence at low stress and an exponential dependence at high stress, and also satisfies a linear relation of the form $\dot{\epsilon} = B\sigma^n$ at low stresses and temperatures near the melting point. The equation was found to hold for a number of metals and alloys tested within the range $0.5 - 0.99 T_m$, and the value of the exponent n was in good agreement with that obtained from the Weertman equation ($n \sim 2 - 4$ for alloys; $n \sim 4 - 6$ for pure metals). An attempt was made by Li³⁶ to explain this relationship, by considering the rate-controlling process to be the cooperative motion of a short dislocation segment.

2.1.3. Conclusions.

Providing the temperature is sufficiently high, usually greater than about $0.2 T_m$, mechanical recovery may occur to oppose the work-hardening, in a manner similar to that first put forward by Bailey³⁷. The present theory of recovery creep considers that, in the temperature range $0.2 - 0.5 T_m$, cross-slip occurs to eliminate screw dislocations, but this does not lead to a complete recovery. The creep rate is then exponentially dependent on the stress. At temperatures greater than this, however, climb may also occur to eliminate edge dislocations, and complete recovery is possible, thereby giving rise to the observed steady-state creep. If climb is slower than cross-slip, then climb will

be the rate-controlling process, and, under these conditions, the creep rate will be dependent on stress through a power law.

Much of the current experimental evidence is in agreement with this theoretical approach, although there are some conflicting results. In this context, the recent tensile and compressive tests of Davies et al.³⁸ should be cited. Working on Ni, they found that the creep rate in compression was about three times as rapid as in tension under the same stress, and, since the vacancy concentration was probably lower in compression, they concluded that a vacancy-producing mechanism was the rate-controlling process. In later work³⁹, it was suggested that the emission of vacancies at jogs in moving screw dislocations was rate-controlling.

The theories of creep outlined in the previous section were developed to account for the experimental results obtained from short term laboratory tests, usually up to a maximum of about 2000 hours. However, these conditions contrast strongly with those pertaining to engineering applications. In reactors, for example, the design criterion is that the magnox cans must not deform more than 1% in 40,000 hours, and it is therefore necessary to be able to make long term predictions from short term data. This is not generally possible at the present time, since

long exposure at elevated temperatures may lead to structural changes within the material and so alter the creep behaviour, or the creep mechanism may be a different one at these low strain rates.

It is clear that a full understanding of creep will only be obtained when a better knowledge has been gained of the contributions made by different processes to the overall deformation, and when an identification is possible of the critical mechanism under different conditions of temperature and strain rate. In the present work, an investigation was carried out to determine the contribution made by grain boundary sliding, and the nature of grain boundaries will now be considered.

2.2. The Structure of Grain Boundaries.

A grain boundary in a metal may be defined as the surface separating two crystals or grains of differing crystallographic orientations. At low temperatures, the boundary acts as a source of strength in the material, since it obstructs the movement of dislocations. As the temperature is raised, however, the strength of the boundary region decreases rapidly, until at a temperature T_e , known as the "equi-cohesive temperature"⁴⁰, it is equal to the strength of the grains. At temperatures greater than T_e , the boundaries are a source of weakness in the material,

and grain boundary sliding becomes an important mode of deformation. The temperature T_g represents the point at which the fracture changes from predominantly trans-granular to predominantly inter-granular, and, in practice, this is of the order of $0.4 - 0.5 T_m$ for specimens tested under slow rates of strain.

In this section, the theories put forward to explain the behaviour of grain boundaries will be briefly examined. The subject has been reviewed a number of times, and the more recent papers are listed in the bibliography⁴¹⁻⁴⁵.

2.2.1. Early Theories of Grain Boundaries.

The first attempt to explain the grain boundary in detail was the amorphous cement theory put forward by Rosenhain⁴⁶, in which the boundary was considered to consist of an amorphous material about 10 - 100 atoms thick. One disadvantage of this theory, however, was the inability to account for the existence of a thick amorphous layer in equilibrium with the crystalline material. The later transition lattice theory⁴⁷ did not involve this difficulty. Here, the atoms were assumed to occupy their correct lattice positions up to the grain boundary, with the exception of one or two atomic layers immediately adjacent to the boundary wherein the atoms existed in compromise positions. Thus, unlike the amorphous cement theory, this model implied

the boundary properties to be dependent on the relative orientation between the two adjacent crystals. Evidence for this was provided by the classic work of Chalmers⁴⁸, who used Sn bi-crystals to show that the obstruction offered by grain boundaries to slip along the crystal glide planes depended on the angle between the two component crystals. This orientation dependence, together with the rapid development of dislocation theory, led to the general acceptance of a form of transition lattice theory as the best representation of the boundary structure, although it was not easy to understand how grain boundary sliding could occur in such a system.

2.2.2. Modern Theories of Grain Boundaries.

An important step was taken by Burgers⁴⁹ when he applied dislocation theory to the transition between mosaic blocks in a single crystal, and suggested the transition between two symmetrically rotated blocks could be represented by a row of equally spaced edge dislocations. A similar model was possible to describe the junction between two adjacent grains, but physical limitations then existed since the distance between the dislocations decreased with increasing disorientation. Thus the individuality of a dislocation structure was lost when the disturbed regions surrounding them, known as "dislocation

cores", were sufficiently close for interaction to occur, and it was therefore necessary to distinguish between low angle boundaries, clearly resolvable into discrete dislocations, and high angle boundaries in which such resolution was no longer possible.

2.2.2.(a) Low Angle Boundaries.

The original work of Burgers suggested a symmetrical pure tilt boundary consisted of one type of edge dislocation. This theory was later extended by Shockley and Read⁵⁰, who considered an unsymmetrical pure tilt boundary, in which the boundary was parallel to the planes of one of the grains, and suggested this to consist of two kinds of edge dislocations having mutually perpendicular Burgers vectors. Other workers⁵¹ considered a pure twist boundary, in which the rotation axis was perpendicular to the contact plane, and showed this could be represented by a grid of pure screw dislocations. Since, in general, the plane of a grain boundary is in an arbitrary orientation with respect to the rotation vector, the boundary needs to contain dislocations of both types.

The dislocation content of very low angle tilt boundaries has been clearly revealed by the direct observation of dislocations with etch-pits⁵², and the subsequent correlation of etch-pit density with the angle

of mis-orientation⁵³. Investigations of the variation of relative boundary energy with angle of mis-orientation have been carried out on a number of materials⁵⁴, and the results for small angles show remarkably good agreement with the theoretical predictions of Shockley and Read.

2.2.2.(b) High Angle Boundaries.

No one theory of high angle boundaries has been entirely satisfactory, since each was usually put forward to explain some particular property. For example, two theories have been advanced specifically to explain the process of grain boundary sliding. The first, by Mott⁵⁵, considered the boundary to consist of "islands of good fit" in which the atomic fit between atoms of the two adjacent crystals was good, surrounded by regions where the atomic fit was poor, and the second, due to Kê⁵⁶, considered the boundary to consist of an assembly of disordered groups of atoms. The sliding velocity was originally considered by Mott to be governed by the rate of shearing of the islands of good fit, but, since this did not agree with existing experimental evidence, a second model was proposed in which the velocity was dependent on the rate of disordering of atoms around the islands. In the Kê model, sliding was considered to occur by atomic rearrangement within the disordered groups.

Kronberg and Wilson⁵⁷ developed a "coincidence site" model, in which it was suggested that special orientation relationships existed, such as 22° and 38° about a common $\langle 111 \rangle$ axis and 28° about a common $\langle 100 \rangle$ axis in f.c.c. structures, where the lattice matching across the boundary was unusually good. Later work by Aust and Rutter⁵⁸ produced qualitative agreement with this model, when they showed that these "special" boundaries migrated at a faster rate than more random ones. However, it has been pointed out⁵⁹ that their results show experimental deviations of up to 10° from the ideal orientation, whereas the coincidence site theory permits a deviation from the ideal of not more than 1° . It appears therefore that density of coincidence sites is not the correct criterion to distinguish special from random boundaries.

Smoluchowski⁶⁰ proposed a tilt boundary dislocation model specifically to explain grain boundary diffusion, in which it was considered that at tilt angles greater than about 15° the groups of dislocations condensed to form misfit regions, and the length of these regions increased with increasing tilt up to about 35° . At angles greater than this, the boundary was considered to be a continuous misfit region.

Holländer⁶¹ attempted an extension of the Shockley and Read⁵⁰ model to high angle boundaries, by assuming that the size of the region around a dislocation within which Hooke's law failed was dependent on the angle of misfit of the boundary. Using this relationship, he derived an expression for the energy of a large angle boundary consisting of n two-dimensional parallel arrays of dislocations.

A recent model for a high angle tilt boundary by Li⁶² attempted to interpret all boundary properties over a complete angular range, by considering the interaction between the stress fields of the dislocation cores. In this model the boundary reduced to an array of edge dislocations at very low angles, and, as the tilt angle was increased, a critical angle was reached ($\sim 37^\circ$) at which the cores of the individual dislocations came into contact. At larger angles, the cores combined to form a slab, of a width proportional to the sine of the half-angle of misfit. This model is therefore similar in many ways to that of Smoluchowski⁶⁰, with the exception that the cores come together at a higher angle. To explain the observed mechanical properties of high angle boundaries, Li suggested the boundary contained an equilibrium number of jogs or ledges, distributed randomly, and increasing in number with increasing angle of tilt. This model is fairly satisfactory in many respects, but it has the disadvantage that a

calculation of the grain boundary energy yields sharp cusps at the "cut-off" angle at which the slabs begin forming. Experiments have not revealed the existence of such cusps, and Li has suggested they are smoothed out by thermal agitation. It further predicts the energy to remain essentially constant over a wide range of high angles, which is in agreement with some, but not all, experimental evidence.

In the last three or four years, some workers have attempted to examine the boundary structure directly using the field ion microscope. Brandon and Wald⁶³ were the first to produce direct evidence that the boundary thickness was of the order of 1 - 3 atomic spacings, and recent work⁶⁴ has indicated the boundary to consist of a stepped structure. A model of high angle boundaries was put forward, based on the Kronberg-Wilson coincidence theory⁵⁷, in which it was suggested that a random boundary in general followed the most densely packed coincidence site boundary (good fit) but contained a superimposed dislocation sub-boundary giving rise to ledges (bad fit). However, recent experimental work by Ryan and Suiter⁶⁵ has cast doubt on certain of the predictions arising from this model.

2.2.3. Conclusions.

The interpretation of low-angle boundaries in terms of a dislocation structure has been substantiated by much experimental evidence. At high angles, however, no one theory is entirely satisfactory. A model such as that due to Kronberg and Wilson⁵⁷ is inadequate in that it deals only with special orientation relationships, and therefore is inapplicable for the majority of boundaries. On the other hand, it is difficult to experimentally verify many of the more important predictions in the rigorous treatment by Li⁶². In general, a high angle boundary appears to have a random misfit structure with a width of 2 or 3 atomic diameters, and there is probably a smooth transition from a dislocation structure at low angles to some disordered form at high angles, in the manner suggested by the theories of Mott⁵⁵, Smoluchowski⁶⁰ or Li⁶².

2.3. Grain Boundary Sliding.

The process of grain boundary sliding was originally inferred from the qualitative observation by Rosenhain and co-workers⁴⁶ that steps were formed at the grain boundaries of deformed specimens. At a later date, Moore, Betty and Dollins⁶⁶ were the first to report that surface marker lines, scribed on a Pb-2% Sn alloy, remained straight and continuous within the grains during creep testing, whereas

offsets occurred at the grain boundaries. Since these early observations, a number of workers have undertaken quantitative investigations into the occurrence of sliding, and it is now clear that, under conditions favourable to sliding, the process can no longer be relegated, as suggested by some workers⁶⁷, to a minor or unimportant role in creep deformation.

A number of critical reviews⁶⁸⁻⁷⁰ have been published in recent years, covering the major types of grain boundary sliding experiments. These can be categorised into three sections:

(i) Torsion pendulums have been used to measure the anelastic effects due to grain boundaries.

(ii) Tests have been carried out on bi-crystals of a number of metals. These have often attempted to clarify the mechanism of sliding, by measuring fundamental properties such as the activation energy for sliding or the effect of differing boundary orientations.

(iii) Tests have been carried out on polycrystalline specimens. These have usually attempted to measure the contribution made by sliding to the overall deformation, and to investigate the effect of such variables as stress, temperature or grain size.

It is convenient to consider the results of these experiments separately.

2.3.1. Anelastic Measurements of Sliding.

The first anelastic measurements of sliding were made by Kê⁷¹, using aluminium wire specimens as the suspension of a torsion pendulum with a natural frequency of oscillation of the order of 1 cycle/sec. Measurements were taken of

(i) the variation of internal friction and dynamic rigidity with temperature.

(ii) creep under constant stress.

(iii) stress relaxation at constant strain.

The internal friction was calculated from the logarithmic decrement of the freely swinging pendulum, and when this was plotted against temperature it was found that a peak was obtained for polycrystalline Al but not for single crystals. Kê⁷² later found that the internal friction peak occurred at a higher temperature with an increase in either grain size or frequency of vibration.

The internal friction peak was explained in terms of the Zener⁷³ mechanism of grain boundary sliding, by which two grains are considered to slide over each other viscously. If the boundaries behave in a viscous manner, it therefore seemed likely that the viscosity values obtained from these experiments would extrapolate to those of the liquid metal at the melting temperature. A calculation was made by McLean⁴¹, using a boundary thickness of 3 atomic diameters, and the results obtained showed significant agreement at the

melting point, thereby supporting the postulate that high angle boundaries resemble a layer of liquid a few atoms thick.

However, Kê's results have been criticised by Betteridge⁷⁴ and Bleakney⁷⁵, who pointed out that

(a) the longitudinal load applied to the wire was sufficient to cause plastic flow in some of the grains. This is substantiated by the creep curve obtained by Kê under constant stress, which appears to show a small permanent set at a considerable time after removal of the load.

(b) Kê used 99.2% aluminium for his single crystal experiments, and 99.99% aluminium for the polycrystalline experiments. Thus the experiments are not strictly comparable.

2.3.2. Experiments with Bi-crystals.

The first demonstration of grain boundary sliding in a bi-crystal was made by King, Cahn and Chalmers⁷⁶, by subjecting a bi-crystal of tin to a shearing stress at a temperature of a few degrees below the melting point. Fine marks on the specimen surface perpendicular to the boundary revealed the displacement of the two crystals, and it was observed that the rate of movement diminished with time.

A number of metals have subsequently been used to investigate sliding in bi-crystals, and these are summarised below:

Al and Al alloys⁷⁷⁻⁸³, Cu⁸⁴⁻⁸⁶, Pb^{87,88}, Sn⁸⁹⁻⁹¹, Zn⁹²⁻⁹⁵.

2.3.2.(a) Variation of Displacement with Time.

Sliding displacements have usually been measured by means of marker lines placed across the boundary, although two workers^{86,95} have also used interferometric methods to measure very small displacements. A number of workers have plotted displacement-time curves, and these often show the displacement rate to decrease steadily with increasing time. Interesting deviations from this have also been noted, such as reports by some workers^{78,89,90,91} that the rate of displacement was initially linear and then decreased after some finite time.

Rhines, Bond and Kissel⁷⁷ used Al specimens having the boundary inclined at an angle of 45° to the stress axis, and found that sliding measured transversely occurred after an "induction" period, and subsequently showed cyclic variations, whereas sliding measured longitudinally was continuous with no induction period. An explanation for this was put forward in terms of the displacement occurring in a layer of finite thickness at the boundary. However,

if the measurements were taken at the trace of the boundary, it is difficult to understand how such variations could occur. Gifkins et al⁸⁸, using Pb bi-crystals of a similar configuration, have recently reported that there was no systematic difference between the longitudinal and transverse sliding components. Induction periods have also been reported for Al⁷⁸ and Sn⁹⁰ bi-crystals with the boundary parallel to the stress axis, and it has been found that the length of the induction period is dependent on stress⁷⁷, temperature⁷⁷, and the relative orientation between the crystals^{77,78}. Some other workers^{78,85,92} have also reported cyclic sliding variations, but others^{81,88,95} have specifically recorded the absence of cycles.

Using interferometry, Harper⁸⁶ measured the step height at the same points of a sliding boundary in a Cu bi-crystal at different times during the test, and found that the sliding rate occurred in a cyclic manner with the positions of maximum and minimum displacement varying continuously. Similar variations have also been reported for Zn⁹².

2.3.2.(b) Boundary Migration and Zone Shear.

Puttick and King⁸⁹, working on Sn, found that in some tests sliding occurred without lateral boundary movement, but at other times sliding and migration alternated

cyclically so that the boundary gradually progressed into one of the grains. After migration had occurred, a reference line across the boundary was sometimes found to be curved in the migrated zone, as if sliding and migration had occurred concurrently, and at other times the line would remain straight within the zone but show discontinuities at the positions of the old and new boundaries. Curved reference lines within the migrated zone have also been reported for Al⁷⁸.

Weinberg⁸¹ observed alternate sliding and migration in Al bi-crystals, and in this case the marker line was broken into a number of straight segments within the migrated zone. It was found that boundary migration, and local deformation in the form of fine slip adjacent to the boundary, always occurred if the test was continued for a sufficient length of time, although the extent would vary from specimen to specimen and from place to place along a single boundary. It was also observed that once a boundary had swept through a particular region of specimen, that region no longer took part in the shearing process.

Adsit and Brittain⁹², working on Zn, found no explicit relation between sliding and migration, but they did observe that the migration only took place after sliding had ceased, and this was followed by a delay time before sliding recommenced. In contrast, Tung and Maddin⁷⁸ found cyclic

variations in the displacement-time curve for Al when there was no evidence of boundary migration.

No migration was observed in Cu⁸⁶, using specimens with the boundary inclined at 45° to a compressive stress, or in Al^{77,79} or Pb⁸⁷, using similarly shaped specimens under a tensile stress. However, Rhines et al⁷⁷ found that, with increasing temperature or stress, the grain boundary deformation in Al became distributed through a zone of increasing thickness, with the formation of sub-grains immediately adjacent to the grain boundary. It was therefore suggested that sliding was not localised entirely at the boundary, as would be the case if one crystal were simply sliding over the other, but that sliding occurred over a zone of shear at the boundary. It has been pointed out⁹⁶ that the lack of migration in these specimens may have been due to the presence of a thick aluminium oxide film.

Intrater and Machlin⁸⁵ considered that two different physical processes occurred which acted together to produce a tangential grain displacement along the grain boundary - namely "pure" grain boundary sliding, and zone shear due to slip within the grains - and they minimised the latter by using a specially shaped bi-crystal, with the orientations chosen to inhibit slip as much as possible. Their results showed that the relative absence of crystal slip enhanced the operation of pure boundary sliding at the expense of deformation in a boundary zone, and they concluded that pure sliding was of a viscous nature.

Using Pb bi-crystals with the boundary inclined at 45° to the tensile axis, Gifkins et al⁸⁸ found that surface marker lines remained straight after sliding, even at high magnification (x4000), and there existed a sharply defined zone on either side of the boundary in which two or three non-primary slip systems operated. This gave rise to fine and closely spaced slip lines adjacent to the boundary, in contrast to the coarse primary slip lines in the body of the two crystals. Later work by Gifkins⁸⁷, using gauge lengths straddling the grain boundary, showed the percentage contribution of sliding to total extension was $100 \pm 10\%$ in a zone of width 0.3 mm. across the boundary, but fell rapidly to a value of about 20% at a distance of a few mms. from the boundary. From these results, it was concluded that sliding occurred at, or very close to, the boundary itself, and was accompanied by fine accommodating slip in a narrow zone on either side of the boundary.

2.3.2.(c) Slide Hardening of the Boundary.

The continuously decreasing sliding rate reported by a number of workers indicates that some form of "slide hardening" is taking place at the boundary, and this was investigated by Bell and Thompson⁹⁴. Using Zn bi-crystals with the basal planes symmetrically inclined to the boundary plane, they found that, after the sliding velocity had

decreased to a very low value, the boundary trace on the upper face, where it was intersected by the basal slip planes, was always most irregular, showing non-basal slip lines and small angle boundaries. On the lower face, however, where the boundary was not so intersected, the trace always remained perfectly straight. By removal of about 0.3 mm. from the top face they again revealed a straight boundary, and re-testing gave rapid initial sliding which subsequently decreased again. It was suggested that, since the boundary on the top face was at the head of the longest blocked slip plane, the stress concentration would be greatest at this face, and this would lead to the formation of irregularities in the boundary, and a progressive diminution of the sliding velocity.

Similar observations have also been reported by Puttick and Tuck⁹¹ using Sn bi-crystals, although they were not in agreement with the Bell-Thompson explanation since a compression test, giving comparable resolved shear stresses on the operative slip systems, produced no migration in the absence of sliding. They therefore concluded that the dislocations required for boundary migration were generated by the sliding process rather than coming from stress-activated sources within the crystals. However, the difficulty of obtaining a comparable resolved shear stress in compression makes this conclusion questionable.

Turner⁹⁵ attempted to overcome slip interaction with the boundary in Zn bi-crystals by using (a) prismatic tilt boundaries, and (b) basal twist boundaries, with the basal planes perpendicular or parallel to the boundary respectively, and by using basal tilt boundaries and applying a stress that was lower than the critical shear stress necessary for basal slip to occur. In each case slide hardening was observed, so that the sliding velocity decreased with time. It was suggested that this was a result of the introduction of segments of single crystal into the boundary plane by migration, and that the sliding rate was then controlled by the rate at which the shear resistance of these segments could be overcome. A plot of sliding displacement against stress was found to yield an abrupt change in slope in the stress range where the critical shear stress for basal slip was exceeded. Experiments showed that for very short term tests on high-angle tilt boundaries, of less than about 0.5 seconds duration, the sliding increased linearly with time. It was suggested that this referred to a "pure" sliding process, and measurements were taken of the "pure" sliding velocity. The results were found consistent with the first theory of Mott⁵⁵, in which sliding was due to the block shearing of the islands of good fit, and it was concluded that pure sliding was a viscous process.

2.3.2.(d) The Effect of Angle of Mis-Orientation.

Working under conditions of constant temperature and stress, Weinberg⁸¹ found that in Al the amount of shear per unit time increased as the angle of mis-orientation rose from 5° to 17° , but there was little change between 17° and 30° . This indicated that the shearing process was closely related to boundary structure, in agreement with some boundary models already outlined. However, Weinberg also found a small but significant increase in the amount of shear for boundaries of higher angles, up to 85° , which is difficult to interpret in terms of dislocation theory. In contrast, Turner⁹⁵, experimenting with Zn bi-crystals, found there was no observable difference in the amount of sliding for high-angle boundaries having angles between 30° and 90° .

Rhines and co-workers⁷⁷ reported that, with the exception of tests in which more than one slip system was operative in a crystal, the rate of sliding varied linearly with $(\Theta + \varpi)$, where Θ was the angle between the two slip directions, and ϖ the angle between the intersections made by the two slip planes in the grain boundary. This is an interesting result since it affords a direct comparison with the suggestion of Mullendore and Grant⁸², obtained from a study of a polycrystalline specimen, that sliding at the boundary represented the unresolved component of the shear when slip from one crystal crossed the boundary to cause

slip in the adjacent grain. The validity of this latter notion is discussed in more detail in a later section, but it should be noted that Mullendore and Grant disagreed with the observation of Rhines et al, and suggested that, as a first approximation, the amount of sliding was a function of $\sin \Theta \cos \omega$, so that sliding increased for decreasing values of ω at constant Θ . This lack of correlation between an Al bi-crystal and an Al-2% Mg coarse-grained polycrystalline specimen throws some doubt on the results obtained by Rhines et al. In particular, the presence of extensive boundary polygonisation in their specimens makes the use of the term "bi-crystal" somewhat questionable.

2.3.3. Experiments with Polycrystalline Specimens.

When two surface grains X and Y slide over each other in a polycrystalline specimen, offsets are produced at the boundary in the manner shown schematically in fig. 2.1. In the diagram, $\vec{AC}$ is the sliding vector, u represents the component of sliding resolved along the stress axis, w represents the component measured in the plane of the surface perpendicular to the stress axis, and v represents the component measured perpendicular both to the stress axis and to the specimen surface. Two angles are also defined here, since these will be required at a later stage: Θ represents the angle between the stress axis and the trace

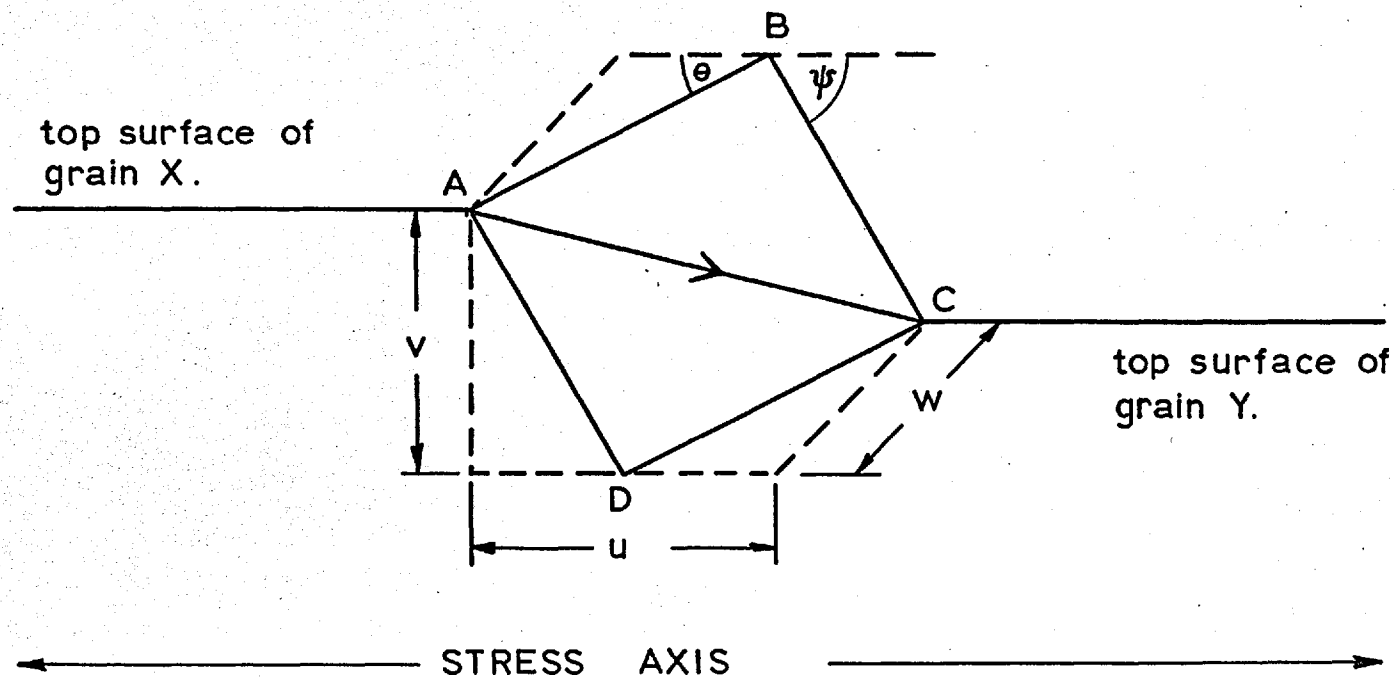


FIG.2.1. Schematic representation of grain boundary sliding.

of the grain boundary in the plane of the surface, and ψ represents the internal angle between the boundary and the surface measured on a longitudinal section.

Three methods have been used to investigate grain boundary sliding, and these are summarised below:

(i) The "vertical" component (v) has been measured. This may be done either interferometrically, by focussing on either side of the boundary, or by using a profile-measuring device.

(ii) Scribed lines on the specimen surface have been used to measure the longitudinal (u) or transverse (w) offsets.

(iii) Measurements have been made of the grain shape before and after deformation, and any change in length attributed to slip processes within the grains. The sliding contribution is then obtained from the difference between the total extension and the increase in length of the grains.

Only the latter method is capable of giving the sliding contribution in the interior of specimens, and the majority of results have been obtained using methods (i) and (ii) which relate solely to the surface conditions. It is convenient to consider the surface results separately in sections 2.3.3.(a) - 2.3.3.(d), and to relate them to the internal measurements in section 2.3.3.(e).

2.3.3.(a) Variation of Sliding with Extension.

Curves of "sliding" versus extension have been plotted for a number of materials, where the sliding is represented by the average vertical offset ($\bar{v}$), and these have always yielded an initial linearity, at least through the period of primary creep. In some metals (β -brass⁹⁷, Mg⁹⁸, Pb-2.2% Tl^{87,99}) the plots were found to deviate from linearity at some finite strain, such that the sliding thereafter increased at a slower rate than the strain, but in other materials (Al alloy¹⁰⁰, Cu-0.37% Be¹⁰⁰, Fe¹⁰⁰) a linear plot was found to exist up to the point of fracture. In some experiments (Al¹⁰⁰⁻¹⁰², Al alloys¹⁰³, Cd¹⁰⁰, Cu¹⁰⁴, Fe-30% Ni¹⁰⁵, Ni¹⁰⁶⁻¹⁰⁹, Pb⁸⁷, Sn¹⁰⁰, Zn¹⁰⁰) a linear relationship was plotted up to and within secondary creep, but the tests were discontinued before fracture occurred. All of these results therefore give a linearity, at least initially, and it will be shown later that the apparent discrepancy between continuous linearity and deviations therefrom may be explicable in terms of specimen preparation.

One possible exception to this was obtained with β -brass¹¹⁰, where the standard deviation of the "vertical" displacement was found to be proportional to $(\text{extension})^{\frac{1}{2}}$. However, since the standard deviation was utilised in this case rather than $\bar{v}$, it is not possible to compare this result directly with the others.

2.3.3.(b) The Contribution of Sliding to the Overall Extension.

The contribution of sliding to extension is generally expressed as a percentage by the ratio E_{gb}/E_{tot} , where E_{gb} represents the elongation along the stress axis due to grain boundary sliding, and E_{tot} represents the overall extension. A number of complications arise in a calculation of this ratio, since it is necessary to convert measurements of the offsets either perpendicular to the surface (v) or in the plane of the surface (u or w) to the resultant longitudinal elongation of the specimen. Gifkins⁶⁹ has pointed out that a general equation to cover this conversion is given by

$$E_{gb} = k n \bar{x} \quad 2.12.$$

where n = number of grains/cm.

$\bar{x}$ = average displacement at the boundary ($\bar{u}$, $\bar{v}$ or $\bar{w}$)

k = a geometrical averaging factor. For $\bar{v}$, this is dependent on the angle between the sliding vector and the normal to the specimen surface.

A number of workers have calculated E_{gb}/E_{tot} for a wide range of materials, or, in some cases, have obtained sufficient readings that a calculation can be made from their results. A comprehensive review is given in Table 2.1, in which a classification has been made according to the

Table 2.1.

Previous Determinations of E_{gb}/E_{tot} :

Material.	E_{gb}/E_{tot} from "vertical" (v) offsets.	E_{gb}/E_{tot} from "horizontal" (u, w) offsets.	E_{gb}/E_{tot} from grain shape.		
			(i)*	(ii)	(iii)
Al	6,100,101,104, 111,112,113	6,113,115,116,117	97,113, 117,118		
Al alloy	100,103,104	82,116,119			
Au	120				
β -brass	97,110	97	97		
Cd	100				
Cu	100				
Cu-0.37% Be	100				
Fe	100		121,122		123
Fe-30% Ni	105				
Mg	98	124			
Ni	108,109,125,126				
Pb	87				
Pb-2.2% Tl	87,99				
Pt	127				
Sn	100				
Zn	100				
Steel				128	129

* (i) = Surface and interior.

(ii) = Surface only.

(iii) = Interior only.

method of measurement. The numbers in the Table refer to references given in the bibliography. However, although there exists this large volume of work devoted to measuring E_{gb}/E_{tot} , it is usually not possible to compare results directly, since different workers have not always used the same method of calculation.

The value of k in equation 2.12 is dependent both on the parameter used for $\bar{x}$, and on the method of measurement. For example, if $\bar{u}$ is the chosen parameter, the value obtained will depend on whether measurements are taken randomly, or along a longitudinal or transverse traverse of the specimen. This fact has been overlooked by the majority of previous workers, and the values utilised for k have often been based on incorrect geometrical assumptions. This is discussed in more detail in Chapter 5. A comparison between the results of different workers is therefore only possible if allowance is made for these discrepancies.

2.3.3.(c) The Effect of Stress and Temperature.

It has been established for a number of materials (Al^{101,104,130}, Al alloys^{103,104}, Ni^{107,108}) that a decrease in stress for a given grain size gives an increase in E_{gb}/E_{tot} . A tentative attempt was made by McLean¹⁰¹ to extrapolate to zero stress, and this yielded a value of $E_{gb}/E_{tot} = 40\%$. However, two independent groups of

workers^{115,116} have found that, whilst E_{gb}/E_{tot} increases with decreasing stress, there is a reversal at stresses less than about 30 p.s.i.

The effect of temperature is more difficult to determine, since it is not possible, owing to the large variations in creep rate, to test at constant stress over a wide range of temperature. Some investigators^{124,131,132} have reported E_{gb}/E_{tot} to increase with an increase in temperature, but their results can be discounted as the tests at the higher temperatures were conducted at a reduced stress, and it seems probable that this was the reason for the apparent increase. Fazan, Sherby and Dorn¹¹⁴ carried out tests at the same stress on pure Al in the temperature range 337°C-474°C, and reported an invariance in E_{gb}/E_{tot} with temperature. Martin, Herman and Brown¹¹⁰ found a similar independent relationship for β -brass by undertaking tests at identical stresses in the range 450°C-501°C. An invariance of E_{gb}/E_{tot} with temperature has also been reported by Rozenberg¹⁰⁸ for Ni, using constant stress in the range 600°C-750°C, and by Dorn et al¹¹⁵ for Al under the specialised conditions of a very low stress (13.5 p.s.i.) in the range 597°C-647°C. Brunner and Grant¹¹⁶ found E_{gb}/E_{tot} to rise to a maximum at about 300°C for high purity Al and two Al alloys, and then to decrease at higher temperatures under a "constant" creep rate. It should be noted in the

last named work, however, that (a) in two of the three materials the creep rate was substantially faster at the highest temperature, and (b) the work has been criticised¹³³ for using specimens containing only two or three grains in the cross-section.

The conclusion is therefore reached from these results that E_{gb}/E_{tot} is invariant with temperature under conditions of constant stress. In contrast to this, however, McLean and Farmer¹⁰⁰ investigated the effect of temperature on Al under conditions of constant rate of strain, and found E_{gb}/E_{tot} to increase for temperatures up to 350°C, and thence to remain constant up to 500°C. Since a constant rate of strain can only be obtained by a reduced stress at the higher temperature, and E_{gb}/E_{tot} has been found to increase in Al for a decrease in stress¹⁰¹, these results suggest that, under certain conditions, E_{gb}/E_{tot} may decrease with increasing temperature for tests under constant stress.

In a recent paper devoted to sliding in Pt, Lozinsky and Ferenets¹²⁷ reported that E_{gb}/E_{tot} increased with increasing temperature in the range 400°C-1000°C under conditions of constant strain rate, and they contrasted this with the result obtained by McLean and Farmer¹⁰⁰ on Al. However, they overlooked the fact that they were working in the range 0.42-0.62 T_m , whilst the invariance reported for Al only occurred at temperatures greater than 0.67 T_m .

2.3.3.(d) The Effect of Grain Size.

Working on Al, McLean^{101,104} found that E_{gb}/E_{tot} was reduced with an increase in grain size, and a similar result was also reported by Gifkins^{87,99} for a Pb-2.2% Tl alloy. On the other hand, Brunner and Grant¹¹⁶ tested an Al-1.9% Mg alloy under constant temperature and stress, and found E_{gb}/E_{tot} invariant, within experimental error, over a wide range of grain size (0.04 - 1.5 mm.).

One difficulty in determining the effect of grain size is that of obtaining a range of grain sizes with the same dislocation structure in the grain interior. In the results just quoted, for example, the grain size was varied by two different techniques:

- (i) By variation of the temperature of anneal¹⁰¹.
- (ii) By variation of the time of anneal at constant temperature⁸⁷.

A further difficulty arises, as pointed out by Parker and Washburn⁶⁷, since a large grained specimen will consist of an array of low energy boundaries, because the high energy boundaries, having the greater mobility, will be annihilated during the annealing treatment. Thus an intrinsic difference may exist between the structure of the boundaries in coarse and fine grained material.

Insufficient results are available at the present time for any quantitative statement to be made. In general, it appears that a fine grain size gives a faster minimum creep rate under conditions of constant temperature and stress, and this is probably due in part to the greater contribution made by sliding to the overall deformation. It seems insufficient, however, to account for the very large increases in creep rate which are sometimes observed, and there is almost certainly an increase in the grain strain rate due to the various heat treatments changing the internal structure of the grains.

2.3.3.(e) Internal Measurements of Sliding.

The results so far reviewed have all referred to surface measurements, but it is important to know if these measurements are representative of the internal sliding, or whether they are merely applicable to a narrow surface layer. Rachinger¹¹³ attempted to resolve this problem by measuring the grain elongation after deformation, as outlined in method (iii) of section 2.3.3, and, since the results of this investigation are of considerable importance, they will be considered in detail.

Rachinger carried out the test on 99.95% purity aluminium, and extended specimens approximately 50% by tensile testing at various temperatures in the range

20°C-350°C, and at either high (10% elongation/minute) or low (0.1% elongation/hour) rates of strain. After deformation, the specimens were sectioned and grain counts made in directions both parallel and perpendicular to the axis of tensile stressing. An average value of the grain dimensions was obtained by measuring the length of traverse containing a given number of grains, and thus N_L and N_T , the mean number of grains per mm. in the longitudinal and transverse directions, was determined. Rachinger related these values to E_s , the longitudinal strain within the grains due to slip, by calculating that, for grains initially equi-axed,

$$E_s = (N_T/N_L)^{\frac{2}{3}} - 1 \quad 2.13.$$

Since the total overall strain of the specimen is the sum of the contributions due to slip within the grains and sliding at the boundaries, such that $E_{tot} = E_s + E_{gb}$ (2.1), values of E_{gb}/E_{tot} can be obtained from Rachinger's results. These show that, for specimens slowly strained to an extension of 50%, E_{gb}/E_{tot} for the interior grains rose from zero at 20°C to a value of about 12% at 200°C, and $87 \pm 13\%$ in the temperature range 250°C - 350°C. The corresponding ratios for specimens subjected to rapid straining were very much less than this.

Rachinger also obtained E_{gb}/E_{tot} at the surface, by measuring the offsets u , v and w , and it was found that, at a total strain of 50%, specimens strained at the slow rate in the range $250^{\circ}\text{C} - 300^{\circ}\text{C}$ yielded values for E_{gb}/E_{tot} of about 20%. A measurement of E_{gb}/E_{tot} by grain shape at a depth of 0.001 in. below the surface gave a value of $38 \pm 12\%$, and it was therefore concluded that the surface deformation was predominantly due to slip, and not typical of the specimen as a whole. It was further shown that there was a depth effect of about 0.01 in., equivalent to two grain diameters, over which the value of E_{gb}/E_{tot} changed from about 38% near the surface to about 90% at two grains depth.

These results have cast serious doubts on the validity of surface measurements, since Rachinger's surface values are consistent with those obtained by other workers¹⁰⁴. To overcome objections by McLean⁴¹, who suggested that the action of surface tension forces may retain the grains in an equi-axed configuration by boundary migration, Rachinger¹¹⁸ later carried out two additional experiments:

(i) An equi-axed specimen was subjected to alternate slow and rapid straining, and it was shown that the grain elongation produced was approximately equal to the extension resulting from the periods of rapid strain.

(ii) A specimen was tested with an initially elongated grain structure, and was said to show no spheroidization of the grains after creep. However, this test was inconclusive, for an analysis of the results shows that there was a significant "rounding-off" of the grains. The length to breadth ratio was reduced from 3.1 ± 0.3 initially to 2.75 ± 0.25 at a strain of 16%.

Shabalin¹²² has also reported similar results using armco iron. In this case, E_s/E_{tot} was determined at the surface by photographing the same area before and after deformation, and in the interior by sectioning and directly measuring the grain shape. It was found that at low strain the grain elongation in the interior was less than one third of that at the surface, but there are two reasons which make these results unacceptable:

(i) the experiment was undertaken at room temperature, and thus no grain boundary sliding would be expected,

(ii) other workers^{121,134} have carried out identical tests and found no such variation between surface and internal grains.

Some attempts have been made to explain the Rachinger results. McLean and Gifkins¹³⁵ pointed out that the high values of E_{gb}/E_{tot} obtained from the interior measurements may be merely a consequence of the very fine grain size used in this work. Gifkins⁹⁹ further showed that the value of

E_{gb}/E_{tot} (82%) obtained at the surface of a Pb-Tl alloy at a strain of 5% was equal to the value obtained internally by grain shape measurements ($86 \pm 8\%$) at a strain of 50%. At this latter strain the surface value had fallen to $61 \pm 3\%$, and it was therefore suggested that surface measurements were typical of the interior at low strains, but not typical after the deviation from linearity in the sliding-extension curve.

Conflicting evidence has recently been presented by Gittins⁹⁷, who repeated the Rachinger experiments under very similar, although not identical, conditions, but with considerably different results. In the original work, Rachinger measured the number of grains per unit length in both the transverse and longitudinal directions. An improvement can be made on this method by measuring the maximum length and breadth of every grain individually¹³⁶. In this way scatter due to irregularity in grain size is eliminated, and thus a smaller number of total grains need be counted. Gittins originally applied this technique to beta and beta-gamma brass and found no measurable difference between E_{gb}/E_{tot} at the surface and in the interior, and then, to correlate the work with that of Rachinger, he repeated the experiments using pure Al. The results for Al, together with those of Rachinger, are summarised in Table 2.2. It will be seen that, with only a factor of two difference

Table 2.2.

Comparison of Surface and Interior Values of E_{gb}/E_{tot} :
(Pure Al tested at 300°C).

Worker and Reference.	Grain Size in mm.	Strain rate %/hr.	Total Strain.	E_{gb}/E_{tot} at		Method.
				Surface	Interior	
Rachinger ¹¹³	0.1	0.1	50.0%	20%		(i)
	"	"	"	20%		(ii)
	"	"	"	$38 \pm 12\%^*$	$87 \pm 13\%^{**}$	(iii)
Gittins ⁹⁷	0.2	5.0	46.0%	$57 \pm 10\%^{***}$	$42 \pm 13\%$	(iii)
	0.2	0.15	47.0%	$45 \pm 9\%^{***}$	$39 \pm 8\%$	(iii)

Note:

* = at a depth of 0.001" below the surface.

** = at a depth of two grain diameters or more.

*** = after electro-polishing and etching.

(i) By longitudinal and transverse displacement of grid lines (u and w).

(ii) By measurement of surface contour (v) along a longitudinal traverse.

(iii) By grain dimensions.

in the grain size, Gittins obtained a slightly lower value of E_{gb}/E_{tot} in the interior. A similar result for Al, also obtained by grain shape measurements, has recently been reported by Grant and co-workers¹¹⁷. However, the validity of Gittins' results is questionable, since, as shown in the Table, he obtained a larger value of E_{gb}/E_{tot} for a specimen tested at a fast rate of strain (5.0 %/hour) than for one tested at a slow rate (0.15 %/hour), although a number of workers have established that E_{gb}/E_{tot} decreases with an increase in strain rate.

The reason for the apparent anomaly between the results of Rachinger¹¹³ and those of Gittins⁹⁷ and Grant¹¹⁷ has not been satisfactorily explained, although it will be shown in section 5.2.2.(c) that some explanation is possible in terms of specimen preparation. In the meantime, however, until the results are available of an investigation at present in progress¹³⁷, in which surface and internal boundary offsets are compared using an internal marker technique, it will be necessary to accept all surface measurements of sliding with some reserve.

2.3.4. The Dependence of Sliding on Slip.

The linear relationship between sliding and total strain, and thus between sliding and slip, indicates that some common controlling mechanism is present throughout at

least the initial stages of creep. However, it is not at first obvious whether the controlling mechanism is provided by deformation within the grains, or by the sliding process itself.

McLean and Farmer¹⁰⁰ studied the creep of a Cu-Be alloy, and found that a sudden deceleration in the creep rate, due to strain-ageing in the grain interior, resulted in an identical reduction in the rate of grain boundary sliding. It was therefore concluded that the controlling mechanism was slip within the grains. However, it has been pointed out¹⁰⁵ that strain-ageing may also result in a change in the boundary conditions, so that these results are not entirely conclusive. Further evidence was provided by Martin, Herman and Brown¹¹⁰, who investigated the creep of β -brass and found that the rate of strain and rate of sliding decreased proportionately when the test temperature was reduced below the ordering temperature. It was suggested that, since the ordering process changed the grain interior and left the boundary unaffected, deformation within the grain was the controlling factor. This same conclusion was also reached by Rozenberg¹⁰⁵, who tested a Fe-30% Ni alloy as a solid solution alloy with a face-centred cubic lattice (γ), and after the alloy had undergone a $\gamma \rightarrow \alpha \rightarrow \gamma$ transformation which brought about a fragmentation of each austenitic grain into many small

sub-grains. Experiments showed that the creep rate and sliding rate increased in almost the same proportion in the transformed material. Thus the general conclusion from all three experiments is that sliding is controlled by slip within the grains.

Mullendore and Grant⁸² carried this concept a stage further, by suggesting that sliding was slip-induced and merely represented the unresolved component of shear at the boundary. Some recent results by Adsit and Brittain⁹³ on Zn bi-crystals appear to support this suggestion, since they found that the amount of sliding after a given time was proportional to the resolved shear stress on the slip plane. On the other hand, the results of Turner⁹⁵, also on Zn bi-crystals, suggest that sliding is initially an independent process, but, as a result of boundary migration, it is limited by the rate of shearing of segments of single crystal.

2.3.5. The Role of Sliding in Cavitation.

When a metal is subjected to a low rate of strain at an elevated temperature, small voids or cavities are formed in the grain boundaries, and the linking of these may ultimately lead to inter-granular failure. It is currently thought that grain boundary sliding plays an important role in the nucleation of such cavities, and it is therefore

appropriate at this stage to indicate briefly how this may occur.

The first attempt to explain the development of inter-crystalline cracks during creep at elevated temperatures was made by Greenwood¹³⁸, who suggested that cavities may be formed in the boundaries due to an agglomeration of vacancies. In subsequent work¹³⁹, the presence of such cavities in Cu, Mg and α -brass was established.

At a later date, Machlin¹⁴⁰ showed that the mechanism proposed by Greenwood was unsatisfactory, since the supersaturation of vacancies required to form a stable cavity by homogeneous nucleation was much too large. A number of alternative mechanisms have therefore been put forward, all of which incorporate a dependence on grain boundary sliding. One suggested mechanism postulates the existence of ledges in the boundary, which are then opened up by sliding to form small cavities. In particular, Gifkins¹⁴¹ has suggested that ledges are formed by the intersection of slip lines with the boundary, whilst Chen and Machlin¹⁴² have assumed the ledges to be in-grown. More recently, Harris¹⁴³ has shown that the opening up of a void at even a very small ledge would require unrealistically high rates of sliding, and has suggested instead that cavities are formed by the sliding of a

boundary containing second phase particles. He further showed that in magnox, the material used in the present work, such particles exist in sufficient numbers to account for the observed cavitation.

Although the method of cavity nucleation is still not clear, the importance of grain boundary sliding seems well established, and the sliding measurements presented later could well form the basis for some future investigation of a link between the degree of sliding and the incidence of cavitation.

2.3.6. Models of Grain Boundary Sliding.

A satisfactory model for sliding must account for the observed experimental results, and should therefore consider:

- (i) the dependence(if any) on stress, temperature, grain size and angle of mis-orientation.
- (ii) the interaction of migration and sliding.
- (iii) the linear relationship between sliding and crystal slip.
- (iv) the formation of a zone of fine complex slip, or of polygonisation, adjacent to the boundary.
- (v) the activation energy, which may be that of volume^{78,97,114} or grain boundary⁸⁸ self-diffusion.
- (vi) the effect (if any) of atmosphere of testing⁸⁵.

One of the first models of grain boundary sliding, already outlined briefly in section 2.2.2.(b), was developed by Mott⁵⁵ to explain the anelastic results of Kê^{71,72}. However, this model predicted very high rates of sliding, and other workers were therefore led to develop alternative theories of the sliding process. These theories will now be examined.

Dorn et al¹¹⁴ considered the stress to be concentrated at interlocking projections in the grain boundary, which would ultimately shear by slip to produce a polygonised zone adjacent to the boundary. This is similar to an earlier model by King and Chalmers¹⁴⁴, and satisfactorily accounts for requirements (ii) and (iii) in the previous list. Crussard and Friedel¹⁴⁵ developed the idea of sliding taking place over a narrow zone on either side of the boundary, and proposed a sliding mechanism whereby dislocations were split into partials when they had reached a point near to the boundary, and sliding took place by the movement of these partials with their Burgers vectors nearly parallel to the boundary. This movement would involve the diffusion of vacancies in the process of climb, and thus the activation energy would be equal to that of self-diffusion (requirement v).

From experimental evidence, Rhines and co-workers⁷⁷ also considered sliding to occur in a boundary zone, and a mechanism was proposed whereby dislocations piled up against the boundary during the incubation period,

polygonised to form a zone of softer material, and then yielded by slip directed along the boundary. This would restore the condition requisite for polygonisation, and the process was thus repeated in a series of slip-recovery operations. This mechanism has been criticised by Gifkins⁶⁸, since it seems probable that the greater amount of tilting adjacent to the boundary might be expected to make the zone harder rather than softer, by limiting dislocation movement.

Couling and Roberts¹²⁴ considered sliding to be made up of many small anelastic shears, of the type observed by Ké, and they suggested that elastic recovery of such shears was prevented by the action of migration. Boundary sliding was therefore considered to consist of cyclic sliding and migration, but this theory does not support an interaction between slip and sliding (requirement iii), and further cannot be applicable to the results of Rhines et al⁷⁷ where no migration was observed.

A model was put forward by Gifkins⁶⁹ in which dislocations were considered to pile up against the boundary, either from sub-grain sources or from an adjacent zone of complex slip, and then climb towards the boundary, thereby creating a local deficiency of vacancies. This deficiency was replenished by a vacancy flow along the boundary, analogous to the "melting" of Mott's islands of

good fit, giving rise to grain boundary sliding. After climb, the dislocations were evenly spaced along the boundary, and it was suggested that they might exert sufficient pressure to cause migration. This model therefore satisfies requirements (ii) and (v).

Tung and Maddin⁷⁸ developed a model of sliding involving a combination of slip and grain boundary self-diffusion, in which grain boundary shear occurred by the migration of vacancies along the boundary. They considered that when atoms exist in a strained configuration at the boundary, such as after non-uniform shear, this would constitute a barrier to further sliding, and the atoms would realign themselves giving rise to boundary migration (requirement ii).

McLean and Farmer¹⁰⁰ developed a detailed model in which sliding first occurred at the boundary interface, possibly by a viscous shearing, until it was arrested by ledges in the boundary. Stress was then concentrated upon the ledges by the shear introduced by screw dislocations arriving at the boundary, and ultimately the ledge would yield and set up a new avalanche of sliding, so that the process was cyclic in nature. Yielding of a ledge would send dislocation loops into the two crystals, which may subsequently contract and create new ledges. Gifkins⁶⁹ has pointed out that this mechanism may depend on

self-diffusion, in agreement with requirement (v), due to the climb necessary either to bring the dislocations to the boundary or to allow expansion and contraction of the dislocation loops. Some experimental results have been presented^{87,88} which appear to support this model.

2.3.7. Conclusions.

More systematic investigations are required to give a comprehensive picture of the sliding process. In particular, many of the bi-crystal results show significant trends, but there are still some fundamental properties which have not been resolved, such as the possible equivalence between the activation energy of sliding and that of self-diffusion. Many of these differences are probably attributable to specimen preparation or purity, and the presence of a thick oxide film on the Al specimens of Rhines et al⁷⁷ and Weinberg⁸¹ would tend to cast some doubts on the validity of their results.

The much larger volume of results on poly-crystalline specimens does little to systematize the role of sliding, since many workers have concentrated solely on the measurement of sliding components without relating these realistically to the overall deformation. The dependence of sliding on slip appears well established, but there is still conflicting evidence concerning the effect of changing

temperature or grain size. The wide variations in experimental results do not make it possible for any one model of sliding to cope adequately, although convincing evidence exists that sliding initially behaves in a viscous manner. In addition, there are many variations in the method of calculating E_{gb}/E_{tot} , and the results of Rachinger¹¹³ have cast doubts on any attempts to obtain this ratio directly from surface measurements.

CHAPTER 3: EXPERIMENTAL TECHNIQUES.

3.1. The Material.

Some preliminary experiments were carried out using high-purity magnesium, and these specimens are given the prefix "M". The impurities in this material, in parts per million, were as follows:

Al 3; Ca 1; Cu <1; Fe 20; Mn 8; Si 5; Na 1.

A problem soon encountered in the use of this material was that it was not easy to obtain a uniform grain size, since specimens were often found to contain two or three isolated grains which were much larger than the average size. Other workers¹⁴⁶ have also reported the same effect in high-purity Mg. At the time when this work was started, much interest was centred on the cavitation failure of reactor fuel-element cans manufactured from Magnox AL80, and, since preliminary tests revealed that it was often possible to obtain a regular grain size in magnox, it was decided to use this material in the present work. These specimens, which were used for almost all of the experiments, are given the prefix "MX".

Magnox AL80 (formerly "Al 2") is a single-phase magnesium alloy containing 0.78% Al in solid solution. A spectrographic analysis revealed the following impurities,

in parts per million:

Be 40; Ca <50; Fe 40; Si <80; Zn 70; Cu <50;
Mn <50; Sn <50; Ni <20.

As with magnesium, magnox AL80 has a close-packed hexagonal structure, with a c/a ratio, at room temperature, of 1.623. The melting temperature is 650°C. The mechanical properties of magnox, including an account of the extensive occurrence of cavitation during creep, have been reviewed in detail by Heal¹⁴⁷.

The material, in the form of $\frac{1}{2}$ in. diameter hot-extruded rod, was obtained in two separate batches from Magnesium Elektron Ltd., Manchester. The manufacturing conditions, which were the same for each batch, were as under:

- (i) A 12" diameter billet was extruded at 410°C at 60 f.p.m. into 3" diameter bar.
- (ii) The 3" diameter bar was re-extruded at 410°C at 30 f.p.m. into $\frac{1}{2}$ " diameter bar.

Under these conditions, the dominant texture was for the basal planes to lie preferentially in the extrusion direction¹⁴⁸. Heat treatment and subsequent creep testing revealed no apparent differences between material obtained in these two separate batches, and in both cases the grain size in the unannealed condition was of the order 0.006 - 0.008 cm.

3.2. Specimen Preparation.

Tensile specimens were produced in the form shown in fig. 3.1, with two parallel test faces approximately 1.5" in length, and a 0.5" Whitworth screw thread at either end. The specimens were prepared by grinding one, or in some cases both, test faces on successively finer grades of silicon carbide paper. They were then annealed for a constant time (two hours), at various temperatures in the range 430-540°C, the temperature being chosen to give the required grain size. All specimens were annealed inside a magnesium tube containing a few granules of titanium metal to absorb any oxygen, and after this treatment they were removed from the furnace, allowed to cool, and any slight tarnishing removed by repolishing on the finer SiC papers. Each specimen was polished for not less than 15 minutes on 7 μ diamond paste on a Selvyt cloth, and a further 5-10 minutes on 1 μ diamond paste. If shorter times than these were used, it was found that scratches remained which were difficult to remove in the subsequent stage. To prevent contamination of the diamond pads, the specimens were thoroughly washed in propylene glycol between each stage.

The second face, sides and ends of the specimen were then stopped off with Lacomit, and the test surface electropolished for 60 minutes in a mixture of 350 ml. of ortho-phosphoric acid and 625 ml. of ethyl alcohol¹⁴⁹.

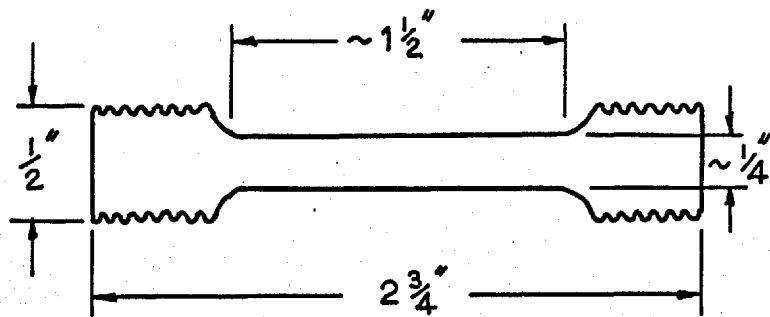


FIG. 3.1. Specimen dimensions.

Good results were obtained using a voltage of 3-5 volts and a current of 100 mA. The solution was stirred continuously throughout the electro-polishing, the stirring rate being kept to a minimum (about 100 r.p.m.) to prevent the formation of flow lines on the specimen surface. After this treatment, the specimen was quickly washed in methyl alcohol, since the free acid formed on hydrolysis immediately attacked the surface when the specimen was removed from the solution.

Finally, any slight pitting due to acid attack was removed using the "Ellopol" method developed by Jacquet¹⁵⁰. In this technique, a fibreglass sheath, impregnated with the electrolyte, was moved across the specimen surface such that contact was made only through the meniscus of electrolyte. Extreme care was necessary to ensure that the sheath did not touch, and thereby scratch, the surface, and, contrary to the given instructions, it was found easier to achieve the desired result by using an excess of electrolyte. Extremely good polished surfaces were obtained in this way.

In order to measure the grain size, the specimens were etched in either:

(a) a solution of 10 wt. per cent oxalic crystals in water; etching time = 10 seconds,

or (b) a 10% aqueous solution of acetic acid; etching time = 30 seconds.

Both solutions were found to show up the grain boundaries equally well. The grain size was determined by the linear intercept method, using a Zeiss integrating eye-piece. For each specimen, forty fields of view, totalling over one thousand intercepts, were taken in both the longitudinal and transverse directions. In general it was found that the grains were not equi-axed, but were 2-5% longer in the longitudinal direction. After the grain size had been measured, the etched surface was removed by repolishing on 1 μ diamond paste, and the polishing procedure repeated without a final etch.

Some difficulty was experienced in the production of a regular grain size. After the annealing treatment approximately one third of the specimens were

found to contain some very large grains in addition to grains of the required size. These irregular specimens were discarded and only those of the requisite grain size were used in the creep tests. When this problem became apparent, the specimens were etched immediately prior to polishing on 7μ diamond, so that the irregular specimens could be discarded before being taken through the complete polishing programme. Sectioning of regular specimens revealed that the surface grain configuration was typical of the interior, and there was no measurable difference in grain diameter between surface and interior grains.

3.3. Creep Testing of Specimens.

Creep tests were carried out in Denison Model T47E Creep Testing Machines. In these machines, the specimen was held centrally inside a furnace, and the load applied through a 10:1 ratio lever arm. The temperature within the furnace was continuously recorded by a calibrated chromel-alumel thermocouple held adjacent to the specimen surface near the mid-point of the gauge length, and preliminary tests were carried out to ensure that the

temperature variation over the gauge length of the specimen was not greater than $\pm 1^{\circ}\text{C}$. The temperature was held constant, to within $\pm 1^{\circ}\text{C}$, using a high-low circuit operated by a controller, such that the high current was just sufficient to raise the temperature higher than that required, and the low current was just insufficient to maintain it.

A strict testing procedure was adopted to ensure that all specimens were deformed under identical conditions. Before creep testing, a gauge length of the order of 2.5 cm. was carefully scribed on the test surface with a fine needle, and this length was measured using a travelling microscope. The width of the specimen was also measured at three different points using a micrometer. Oxidation of the specimen surface was prevented by coating the surface in silicone oil. The load on the creep machine was then adjusted to give the required initial stress, the furnace brought up to the test temperature, and the specimen introduced into the furnace. When the test temperature had been regained, the furnace was held at this temperature for one hour to allow temperature equilibrium throughout the specimen, and then the load was applied.

After a chosen interval of time, the load was removed, the specimen withdrawn from the furnace, and the silicone oil washed away with methyl alcohol. The gauge length was

re-measured, and readings were taken, in a manner described later, to determine the amount of grain boundary sliding that had taken place.

The majority of tests were conducted at temperatures up to and including 200°C, and at these temperatures the coating of silicone oil was sufficient to prevent surface oxidation. At temperatures greater than 200°C, however, this procedure was inadequate, and it was necessary to deform the specimens in an inert atmosphere. Specimens were not tested in vacuum because of the high vapour pressure of magnesium at temperatures greater than 200°C. One of the creep testing machines was modified so that the specimen under test was enclosed in a sealed stainless steel tube fitted within the furnace. The elongation was accommodated at one end of the tube through a sliding O-ring seal. To prevent excessive heating of the components of the machine, with consequent handling difficulties, water cooling was provided at either end of the tube. The specimen was introduced into the vacuum enclosure at room temperature, and the tube was successively evacuated and flushed with argon for three or four times to remove all traces of oxygen. Finally, the tube was filled with argon, and this was maintained at a slight positive pressure so that any leaks occurred outwards. After this procedure, the specimen was brought up to the test temperature,

held at this temperature for one hour, and the load applied as before. Using this method, it was possible to maintain a good stain-free surface at testing temperatures up to 300°C.

All tests were carried out by applying a fixed load. Thus, owing to the reduction in cross-sectional area during a test, there was a resultant increase in the applied stress. However, this increase was small during the initial stages of creep which were of primary interest in this investigation, and there was also the additional advantage that the results could be directly compared with those of other workers testing under the same conditions.

3.4. Measurements of Sliding.

Measurements were taken of the step height v between adjacent surface grains, representing the component of sliding perpendicular to the surface (fig. 2.1), at regular strain increments throughout the test. One of two methods was used, dependent on the mean value of the step height.

At low strains, where the mean step height was less than about 1μ , measurements were made using the Zeiss "Linnik" interference microscope. The principle of this microscope is that a beam of light from a white or monochromatic source is divided by a beam-splitting prism, so that half of it passes to the specimen whose surface contour is required, and the other half is reflected from

a plane mirror to provide a reference wavefront. The two reflected beams are then recombined to form interference fringes, which are observed in the microscope eye-piece. By means of a system of optical wedges, the fringes can be adjusted to lie perpendicular to the grain boundary under examination. Any step at the boundary perpendicular to the surface resulted in a sharp displacement of the fringes at the boundary, as shown by fig. 3.2, and it was possible to estimate the step height to an accuracy of 0.2 of a fringe. In cases where migration had also occurred, the step height was measured by extrapolating the fringes from one side of the boundary to the other, and again the same degree of accuracy was attained.

The usual method of measuring a step height by this means is to use a monochromatic light source having a known wavelength ($\lambda/2 = 0.27\mu$), but this becomes difficult if the step height is greater than one fringe displacement, since it is not possible to identify the same fringe on either side of the step. This problem is overcome by using a white light source, which gives an interference pattern having a dark central fringe and fringes of decreasing intensity on either side. This is clearly shown in fig. 3.2. In the present work, the large number of readings made it a tedious process to continually change from one light source to the other, and it was therefore deemed advantageous to be able

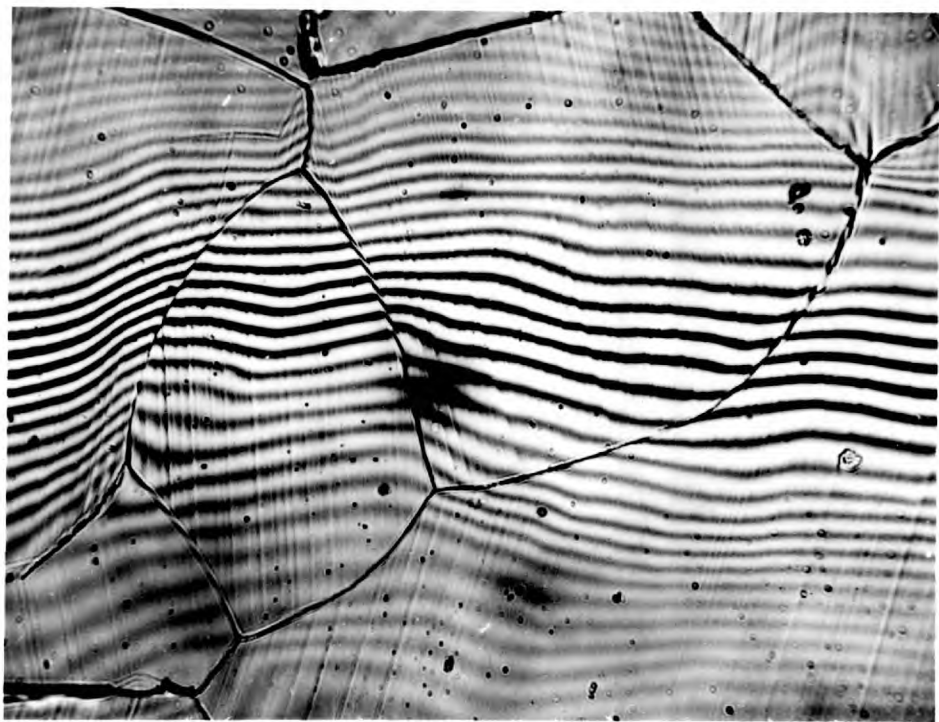


FIG. 3.2. Grain boundary offsets revealed by interference fringes. (X 460).

to measure small steps using only the white light fringes. To enable this to be done, a calibration test was carried out by which a large step was measured using both types of fringes, and it was then possible to estimate the predominant wavelength of the white light source to be 0.6μ . White light fringes were used for all step heights up to a maximum of about 1μ . For steps in the range $1-2\mu$, the white light fringes were not sufficiently visible away from the central fringe, and monochromatic light was utilised in the normal way.

It sometimes happened that one or two large steps, of a magnitude greater than about 2μ , occurred on specimens where the mean step height was still sufficiently small to use the interference technique. In these cases it was often difficult, if not impossible, to measure the step height, since, on checking the fringe displacement with the white light source, it would be found that the central dark fringe on one side of the boundary was displaced into the neighbouring grain. The focussing screw of the microscope was therefore calibrated in microns, by noting the depth of focus between the top and bottom of an impression of known depth. The large steps could then be measured accurately by focussing on one side of the boundary and noting the position of the central fringe, and then re-focussing on the other side so that the central fringe was in the same

position, and recording the distance rotated by the focussing screw.

At higher strains, where the mean step height was greater than about 1μ , the offsets were measured using a Vickers microscope, by focussing in turn on to small oxidation pits on either side of the boundary, and recording the step height directly from the calibrated focussing screw. Owing to the inherent difficulties of this technique, it was only possible to measure heights to an accuracy of $\pm 0.5\mu$.

With either method, the procedure adopted to obtain a value of $\bar{v}$, the mean step height, was to carry out a longitudinal traverse of the specimen, using a magnification such that the average grain diameter was about half the field of view, and to record the step height at any randomly selected position on every grain boundary passing through the field of view. When one traverse was completed, the field was changed to a new position and the process repeated. Thus the mean value obtained referred to boundaries disposed randomly with respect to the stress axis, rather than to boundaries intersected by a longitudinal traverse. This mean value was denoted by $\bar{v}_{av}$, to distinguish it from the values $\bar{v}_{long}$ or $\bar{v}_{trans}$ obtained by taking measurements along longitudinal or transverse

traverses respectively. It will be shown in a later section that the value of the mean step height is dependent on whether the readings are taken randomly or along a particular traverse. 300 readings were taken to determine $\bar{V}_{av}$, since a statistical analysis of similar results by Gittins⁹⁸ had already shown that this number was required to give an accuracy of $\pm 10\%$ at 95% confidence limits. This result was confirmed in the present work.

The measurements obtained by the two techniques of interferometry and direct focussing appeared entirely consistent, and there was no discontinuity in the resultant curves when the readings changed from one method to the other. As a further check, one specimen was chosen in which the mean step height was of the order of 1μ , and 300 readings were taken by each method. Within experimental error, the same value was obtained in each case.

3.5. Measurements of Grain Strain.

3.5.1. Grain Shape Measurements.

An important objective of this work was to obtain an accurate measure of E_{gb}/E_{tot} , the contribution made by grain boundary sliding to the overall extension, and to investigate the dependence of this ratio on stress, temperature and grain size. Rachinger¹¹³ developed a method

of doing this indirectly, by measuring the number of grains per unit length in directions parallel and perpendicular to the stress axis, and relating this to E_s , the strain due to slip within the grains, through equation 2.13. This method had the additional advantage that it could be used to determine E_{gb}/E_{tot} internally. It has recently been pointed out¹³⁶ that a more accurate measure is obtained by taking the length to breadth ratio of each grain individually, since this avoids the inaccuracies encountered by a large variation in grain size. Further, this improved technique enables measurements to be made at strains of the order of 10%, whereas the Rachinger method requires strains in excess of about 30%.

In the present work, measurements were taken to determine the length to breadth ratio of individual grains, both internally and at the original surface, using a fine grid in the eye-piece of a microscope.

3.5.2. Printed Grid Technique.

It has already been shown in section 2.3.3.(b) that E_{gb} can be calculated from the equation $E_{gb} = k n \bar{x}$ (2.12), but it was pointed out that previous workers have used different values of k with the same parameter $\bar{x}$, so that their results are not directly comparable. Wide discrepancies therefore

exist, such that, whilst Parker and Washburn⁶⁷ have suggested that E_{gb}/E_{tot} is small, and usually less than 10%, other workers^{100,124} have produced experimental evidence of values in the range 70-90%.

Since $\bar{v}_{av}$ is the most accurately measured sliding parameter, E_{gb}/E_{tot} is best calculated from the equation

$$\frac{E_{gb}}{E_{tot}} \% = \frac{100 \text{ k n } \bar{v}_{av}}{E_{tot}} \quad 3.1.$$

It was therefore necessary to develop a technique to determine experimentally the value of k for use with $\bar{v}_{av}$. This can be done by measuring E_s and subtracting it from E_{tot} to give E_{gb} by difference. Substitution of this value into equation 3.1, together with the measured value of $\bar{v}_{av}$, then yields a value for k.

In section 3.5.1, it was suggested that E_s could be determined directly from grain shape measurements. However, this method has been criticised by McLean⁴¹, who pointed out that the grains may retain their equi-axed structure under the action of surface tension forces. To overcome this difficulty, a technique was required to determine E_s from measurements taken entirely within the grains, and this was possible by putting a series of closely spaced parallel lines on to the specimen surface, perpendicular to the

stress axis, and of a spacing slightly less than the average grain diameter. If the spacing of the lines is known accurately before testing, the specimens can be creep tested to some known total strain, and E_s determined by measuring the line separation in those grains which are intersected by two lines. In fig. 3.3, for example, the extension due to slip could be measured at A, B, C, D, E, etc.

3.5.2.(a) Preparation of the Grid.

The first attempts to carry out this technique were unsuccessful, since it was not possible, with the facilities available, to put scribed lines on the surface with an accurately known separation. A high degree of accuracy was an important feature of this work. For example, at total strains of the order of 2%, and with a grain size of about 50 grains/cm., it was necessary, in order to resolve any increase in line separation, to be able to measure to a minimum accuracy of $\pm 1 \times 10^{-4}$ cm.

The method finally chosen for this work was to print a grid on the surface by a photographic means. A graticule was used for this purpose, consisting of a hardened photographic plate, with a negative image of a fine grid having 200 lines per inch in each direction. A negative of the grid was required to give a positive contact print on

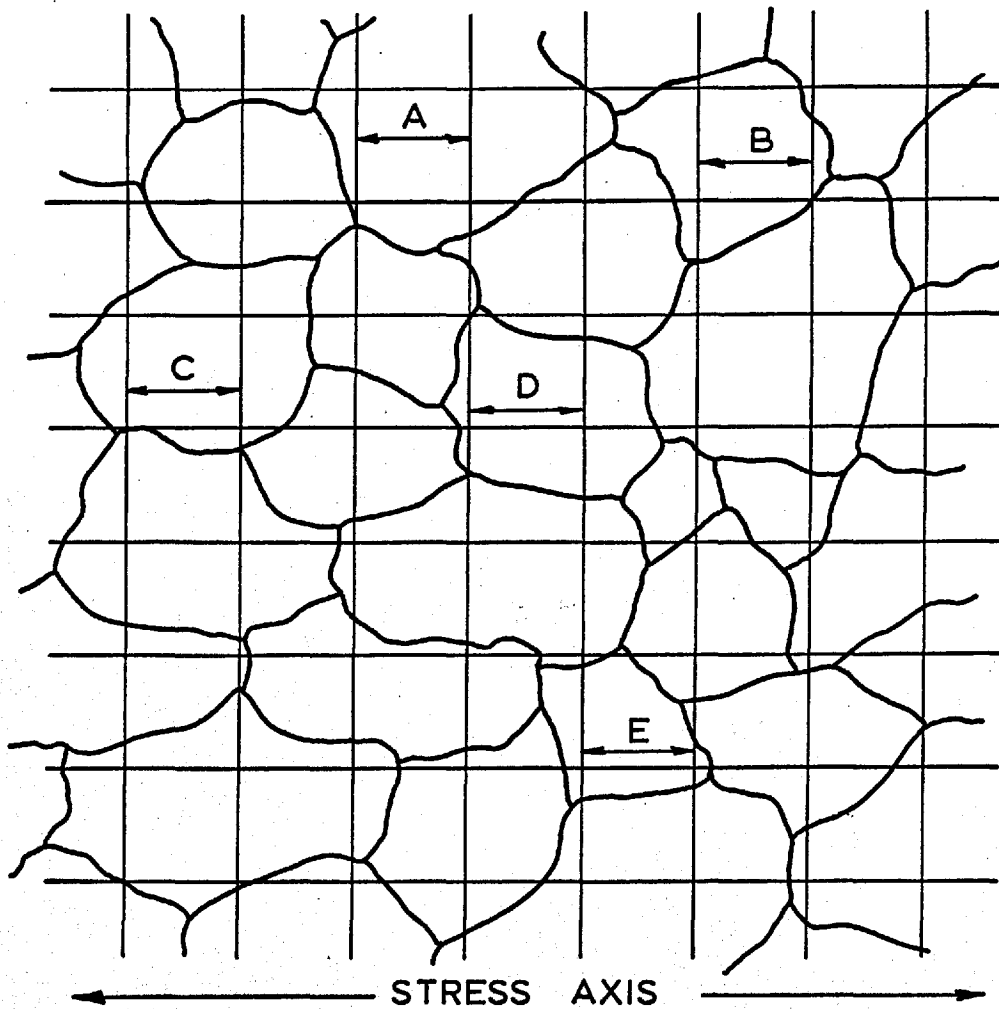


FIG. 3.3. Use of printed grid to determine E_s .

the specimen surface, and the plate was manufactured to a convenient size so that it fitted on to the test face of the specimens. The line separation, equivalent to 0.127 mm., was chosen to permit the use of specimens having a grain size of the order of 50 grains/cm. or larger. Although grain sizes smaller than this were used for many of the routine tests, it would not have been possible to measure the small grain extensions occurring in these specimens at very low strains.

The first attempts to reproduce a grid were made using an adaptation of the offset-litho printing process. This proved unsuccessful for the following reasons:

(a) It was necessary to agitate the surface during development, and this resulted in many fine scratches on the surface. If agitation were omitted, the undeveloped solution was not completely removed.

(b) The image obtained was of poor resolution, such that the edges of the grid were not sharply defined.

The method ultimately chosen for this work was direct contact printing, in a manner similar to that used for the production of printed circuit boards. The photographic materials used for this work were kindly supplied by Kodak Ltd., London.

A primary requirement of the photographic plate was cleanliness, since any dust or dirt would be reproduced in the image. The plate was therefore thoroughly cleaned in a vapour degreaser before each use. A photographic emulsion, Kodak Photo Resist (KPR), was then flowed onto the test surface, so that the whole surface was wetted, and the specimen was clamped horizontally, test surface uppermost, at the centre of a whirler, and rotated for 10 minutes at room temperature. This was necessary to provide a thin and even coating of KPR. A speed of approximately 100 r.p.m. was used for the first nine minutes, when the emulsion was delicate, but the speed was increased for the final minute to minimise the tendency for the coating to form a bead at the edges of the specimen. Drying was accomplished by whirling for a further 10 minutes in forced warm air at 60°C.

The photographic plate was then positioned on the test surface, held in place with rubber bands at either end, and the surface was exposed for a fixed time to a source of ultra-violet light. A preliminary test was carried out to determine the optimum exposure time. With an ultra-violet source of 400 watts at a distance of 3 ft., an exposure time of 10 minutes was required. After exposure, the specimen was immersed in KPR Developer at room temperature for two minutes, using intermittent agitation to remove any

unexposed emulsion. Finally, in order to accentuate the grid, the specimen was immersed for 30 seconds in KPR Dye, washed thoroughly with methyl alcohol, and dried. To ensure adhesion of the film, the specimen was baked for 30 minutes at 200°C , and the final image consisted of a sharply defined grid of dark blue lines.

3.5.2.(b) Measurements Using the Grid.

Measurements of the separation between grid lines were made on the screen of a Vickers projection microscope, by aligning the edge of a line with a vertical ruling on one side of the screen, and measuring the distance to the edge of the next line. Using this technique, at a magnification of about $\times 1000$, it was possible to measure each separation to an accuracy of $\pm 5 \times 10^{-5}$ cm. The method of measurement employed was to carry out a longitudinal traverse of the specimen along one of the grid lines, and measure the separation between lines perpendicular to the stress axis at every instance where two adjacent lines were contained within the same grain. Initially, 100 measurements were taken of the line separation in an undeformed specimen. This was a necessary preliminary, in order to check the variations in the master grid. The spread of readings was found to be extremely small, as indicated in fig. 3.4, and well within the accuracy required for this work.

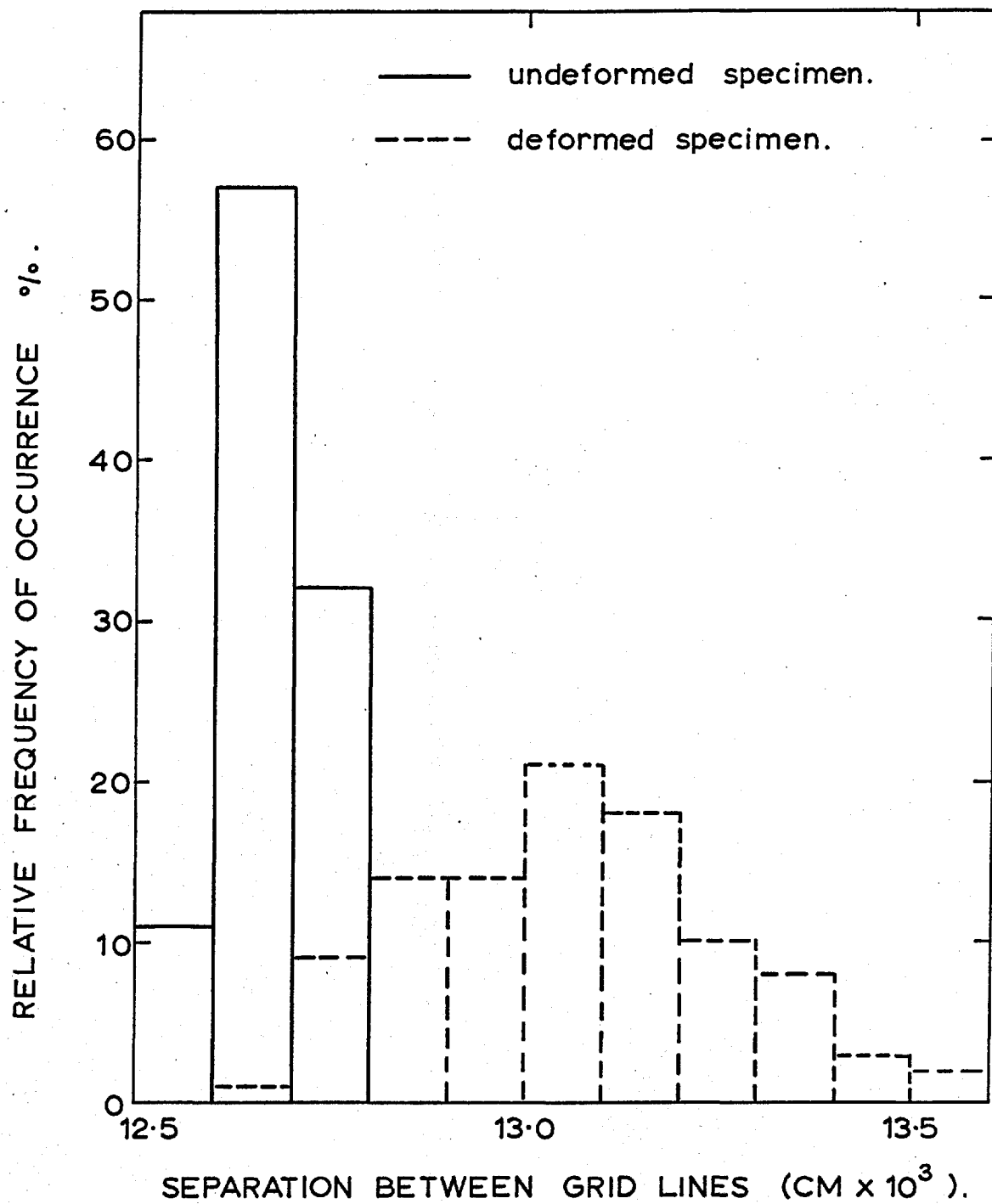


FIG. 3.4. Measurements with printed grid.

A preliminary test was made to check whether the grids would remain adhered to the specimens after straining, and also whether it was possible to measure the small extensions involved. A specimen was strained for 11 hours to about 5% extension, under an initial stress of 12,000 p.s.i. at 100°C. This temperature was chosen since it offered more ductility than at room temperature, but was sufficiently low that, at this high rate of strain, the grain boundary sliding contribution would be negligible*. Thus the total extension should be entirely due to strain within the grains, and should correlate directly with a measure of the mean grid separation.

300 measurements were taken of the grid separation in the deformed specimen. A wide variation in readings was observed, as indicated in fig. 3.4, and often the larger readings occurred in grains where there was much evidence of basal slip. Other workers¹⁵¹⁻¹⁵³, investigating the deformation of coarse-grained Al specimens, have also reported inhomogeneous elongation from grain to grain, and from point to point within individual grains. By calculating the average grain extension and relating this to the overall extension, it was found that $100 \pm 7\%$ of the deformation was due to extension within the grains, thereby confirming the reliability of this method.

* This is confirmed by experiments described in section 4.2.

CHAPTER 4: EXPERIMENTAL RESULTS.

Sections 4.1 - 4.4 of this chapter give details of the results obtained from tests carried out in the temperature range 21°C - 300°C ($0.32 - 0.62 T_m$). In general, these four sections are divided according to the temperature of testing. For convenience, the first section refers to those tests carried out at 200°C ($0.51 T_m$), since the majority of tests were undertaken at this temperature, and thus yield the most comprehensive results. It is therefore convenient to subsequently analyse the results obtained at other temperatures in terms of those obtained at 200°C . In fact, some overlapping between sections is necessary, since section 4.3 ($0.43 - 0.51 T_m$) deals especially with the effect of re-polishing specimens during the test, and includes details of a specimen tested at 200°C . The remaining sections, 4.5 - 4.9, are divided according to the particular topic under examination.

4.1. Tests at 200°C .

Several tests were carried out at a temperature of 200°C ($0.51 T_m$), covering a wide range of stresses and four different grain sizes. Details of the

experimental results are given in Table 4.1*. In this Table, and in the other Tables also, the number of grains/cm. refers to a measurement on the specimen surface in the longitudinal direction. The number of grains/cm. in the transverse direction was usually 2-5% greater than this. The value of the mean vertical step height, $\bar{v}_{av}$, is given at a total strain of 1%, and this value was used to calculate E_{gb}/E_{tot} in the manner indicated in section 4.1.3.

The creep curves for the six specimens of similar grain size are shown in fig. 4.1. These curves clearly show the strong stress dependence, and are representative of those obtained for all specimens. In general, there was a small instantaneous extension, followed by a short period of primary creep which gave way to secondary creep at a strain of about 1-2%. This gradually changed to tertiary creep, and, if the test was continued for a sufficient length of time, fracture occurred at a total strain in the region 10-35%.

4.1.1. Sliding Measurements.

Measurements were taken to give the mean step height $\bar{v}_{av}$, perpendicular to the surface, at different strains

* For ease of reference, Tables 4.1 - 4.7 are contained at the end of Chapter 4.

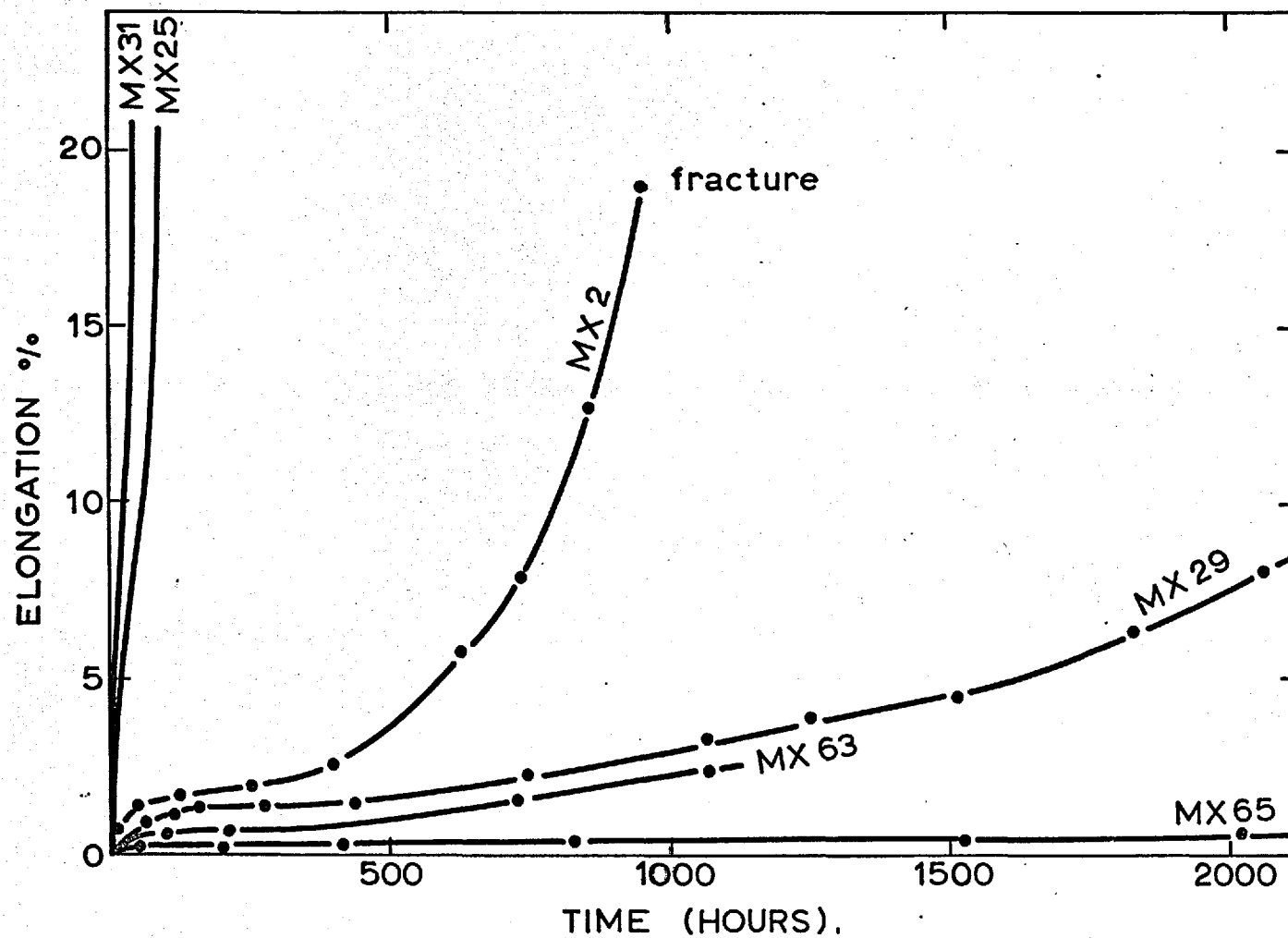


FIG. 4.1. Creep curves at 200°C.

throughout the tests, and these points are plotted against the overall extension for a number of specimens in fig. 4.2. For clarity, the individual points are only shown for two specimens.

The error bars represent the 95% confidence limits for $\bar{v}_{av}$. The Standard Error, σ , of v_{av} was calculated from

$$\sigma^2 = \frac{\sum v_{av}^2 - (\sum v_{av})^2 / N}{N - 1} \quad 4.1.$$

where N = number of readings taken.

The Standard Error of $\bar{v}_{av}$ was calculated from

$$\text{S.E.}(\bar{v}_{av}) = \frac{\sigma}{\sqrt{N}} \quad 4.2.$$

To calculate 95% confidence limits, the Standard Error of $\bar{v}_{av}$ was multiplied by 1.96. As a rough guide, it was found that, after a total of 300 readings, the error bars were approximately $\pm 10\%$, although they were often larger than this at high values of $\bar{v}_{av}$.

For all specimens, the sliding-extension curve was clearly resolvable into two distinct parts:

- (i) an initial linear portion, during which sliding increased linearly with strain,
- and (ii) a subsequent stage during which sliding increased at a slower rate than the creep strain.

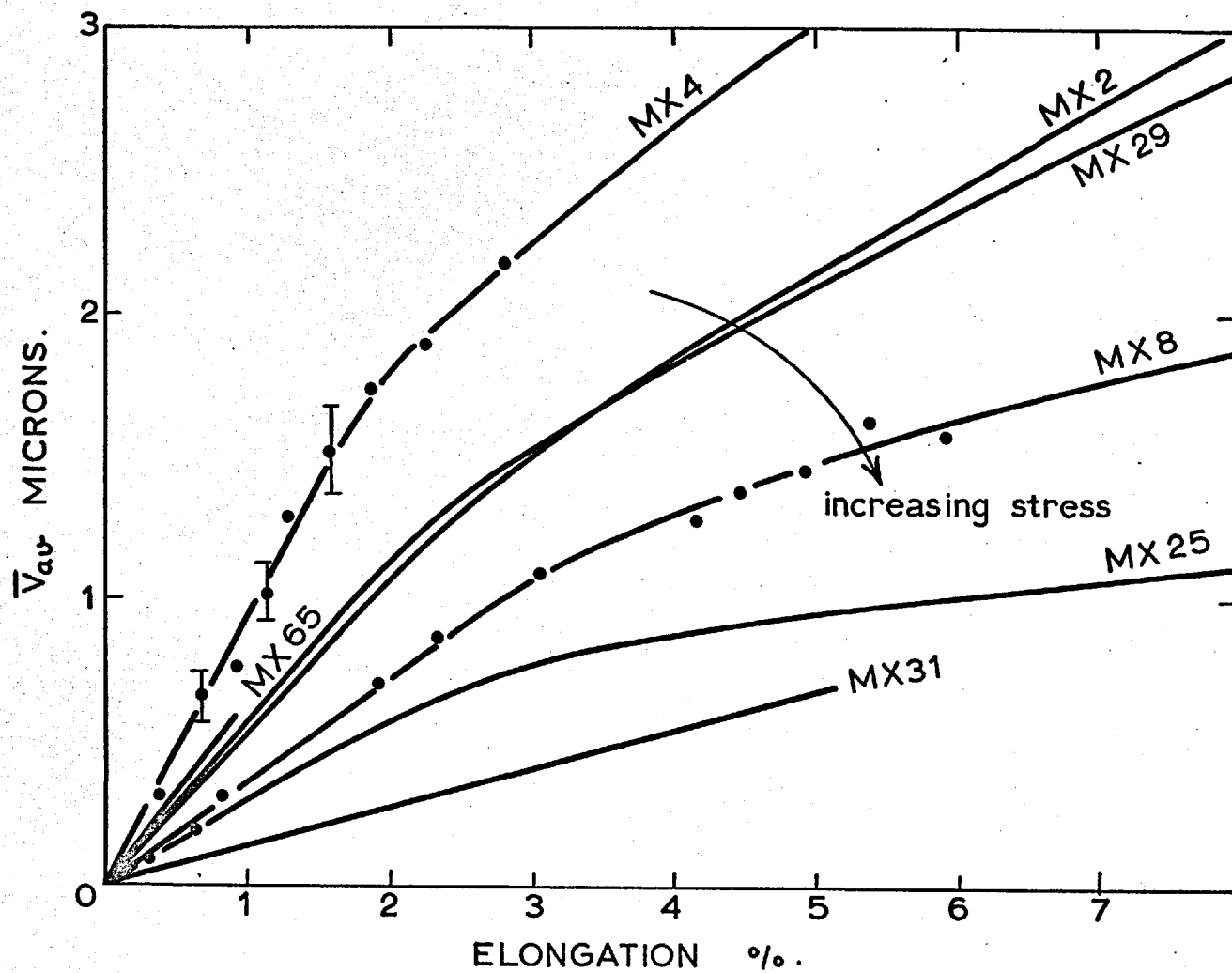


FIG. 4.2. Sliding -extension curves at 200°C.

The error bars were often too large to decide whether this second stage was also linear, since many of the curves could be drawn with almost equal validity as two linear stages, or a linear stage and subsequent curvature. It appeared, however, that the second stage was of a curved form provided the specimen was extended to a sufficiently high strain. Previous workers have been divided on this issue, with reports of two linear stages for β -brass⁹⁷ and Mg⁹⁸, and a linear stage and curved portion for a Pb-2.2% Tl alloy⁹⁹.

The point at which the deviation from linearity occurred at any given temperature appeared to be independent of the total amount of sliding and of the creep strain, and was instead dependent on the position reached on the creep curve. In general, the present results indicated that the deviation occurred during the latter stages of secondary creep, and this was substantiated by the observation that the point of deviation was stress dependent, such that it occurred at a lower total strain for a lower stress. An explanation of this effect is given later.

Typical sliding-time curves are shown in fig. 4.3, and a comparison with the creep curves of fig. 4.1 will show the similarity between these two sets of figures. The primary and secondary stages evident in these curves correspond closely to the similar stages in creep, due to the initial

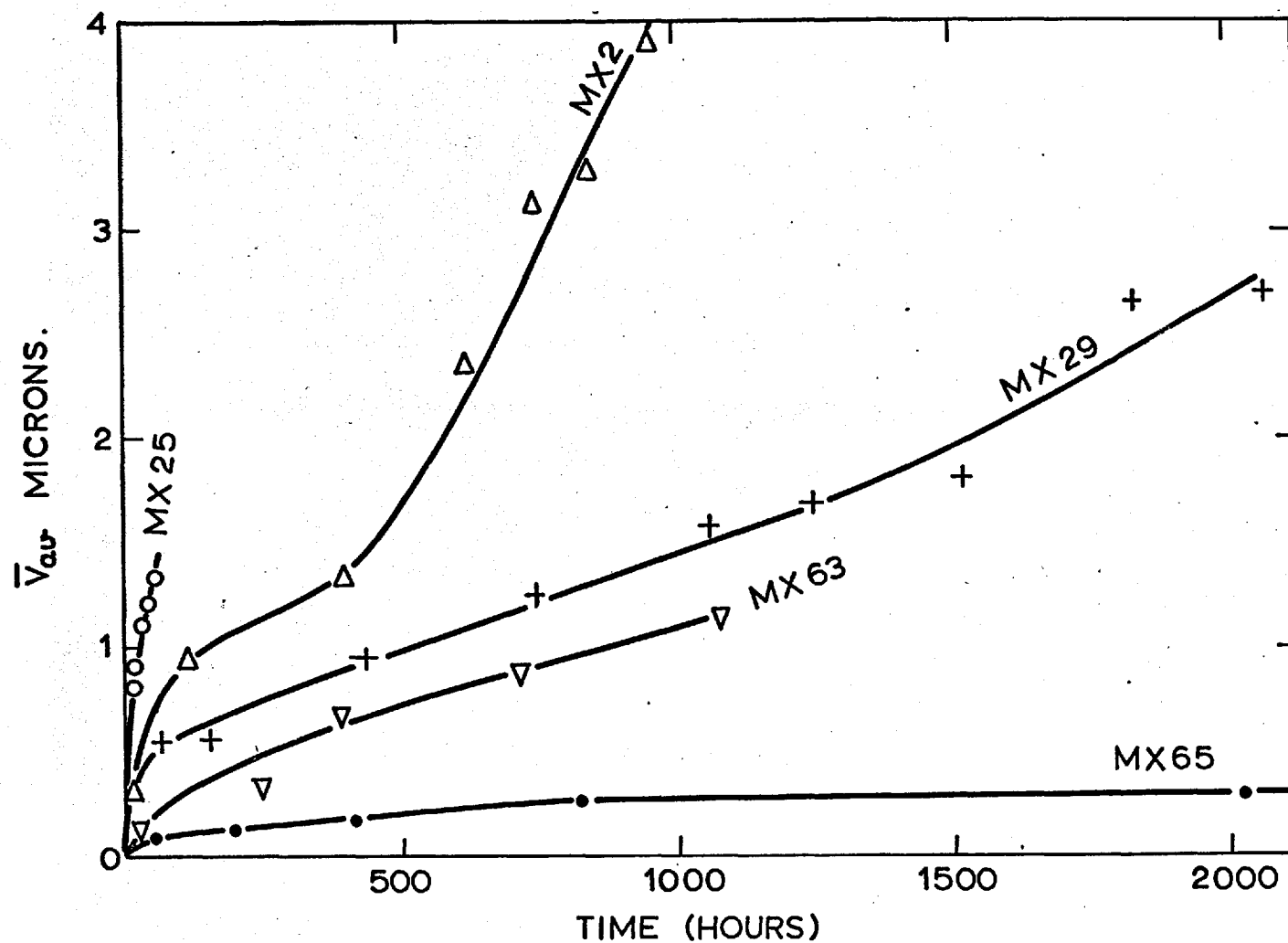


FIG. 4.3. Sliding - time curves at 200°C.

linear relationship between sliding and extension. However, owing to the deviation from linearity towards the end of secondary creep, the tertiary stage is not so marked.

4.1.2. Metallographic Observations.

Examination of the specimens by interferometry showed that the step height often varied from point to point along a single boundary, and this was especially the case for the common boundary between two very large grains. Variations along individual boundaries have also been reported by Harper⁸⁶ for Cu bi-crystals. It was further observed that the step height was often finite at a triple point. In order to obtain a true statistical average, a selection of position was necessary, and this was obtained by randomly choosing any position on the boundary, prior to aligning the fringes and without regard to the location of the triple points, and then recording the vertical offset at that particular point. High readings of v were often associated with particular patches of grains, and similarly other patches of grains would show little or no sliding.

During the initial stages of deformation at 200°C, the grain boundaries became visible on the surface and slip lines appeared within some of the grains. An example of the appearance of a specimen at a low strain is shown in fig. 4.4. In this case the strain rate was high so that the

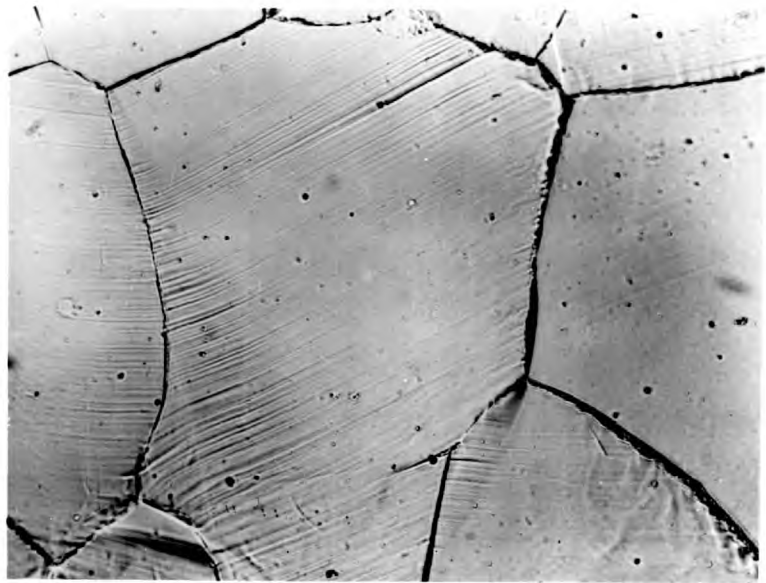


FIG. 4.4. Slip lines formed at low strain.
Specimen MX 3 at 1.26 %
strain. (X 300).

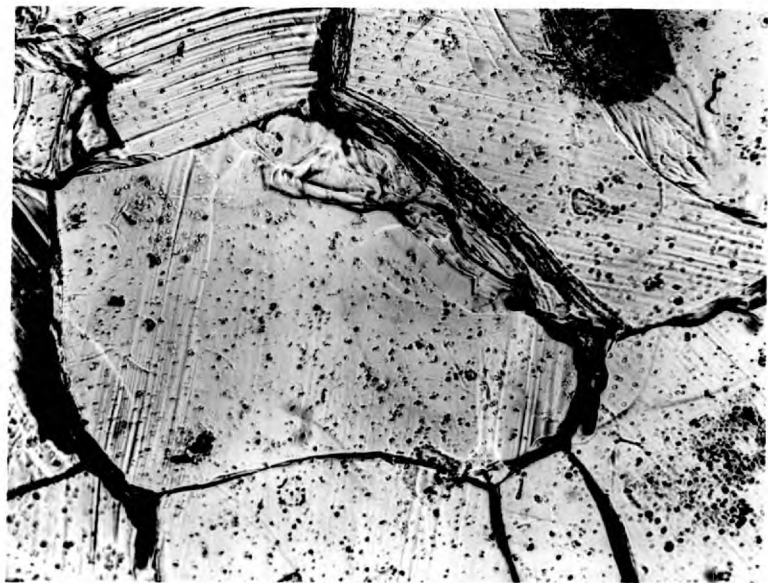


FIG. 4.5. Extensive migration at 200°C.
Specimen MX 29 at 6.38 %
strain. (X 270).

slip lines were very prominent. At higher strains, there was often much evidence of deformation within the boundary region, and this was especially manifest in specimens subjected to small stresses. This is illustrated in fig. 4.5, showing the occurrence of extensive migration after a long period of slow deformation. Migration of this type was often observed at low strains, of the order of 0.4%, and it increased in extent as the elongation progressed. In some cases it appeared that the boundaries were migrating to straighten their length between two triple points, so as to obtain a lower energy configuration, but in other cases the boundaries were found to migrate away from their centre of curvature. Similar observations have also been made on Pb¹⁵⁴ and Mg¹²⁴. Triple point folds were often observed, similar to those reported by other workers^{155,156}, and were particularly evident in specimens in which there was a large amount of sliding. These folds often extended up to half way across a grain, and occasionally curved into the slip direction. A typical fold is shown in fig. 4.6.

Straight basal slip lines were usually observed from the early stages of creep, especially in tests carried out at a high rate of strain, and these became more pronounced at higher extensions, when finer slip was often resolvable between the bands of coarse slip. Occasionally, a wide band of enhanced slip would occur in a particular region of a

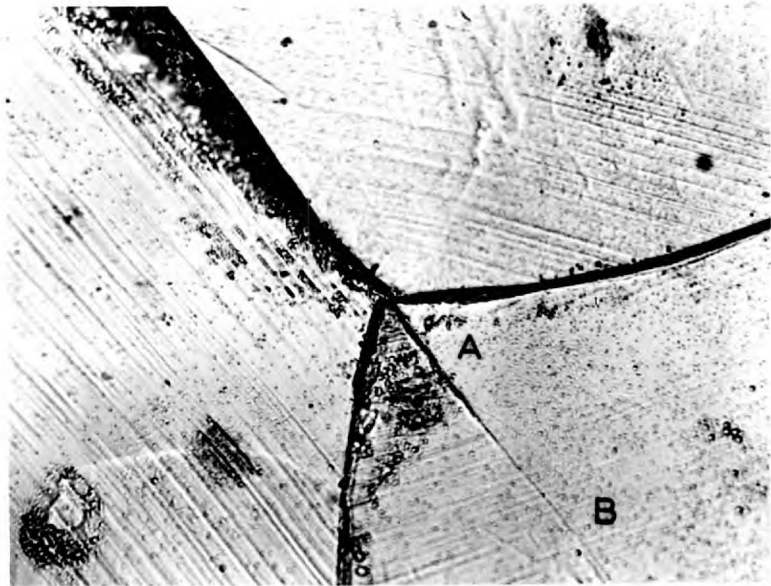


FIG. 4.6. Formation of triple point fold AB.
Specimen MX31 at 5.18%
strain. (X 570).

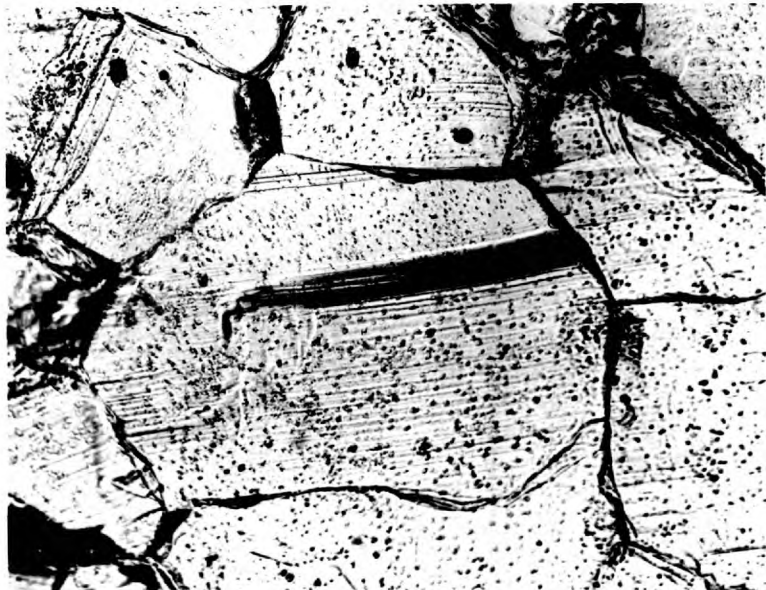


FIG. 4.7. Enhanced slip at 200°C.
Specimen MX29 at 6.38%
strain. (X 270).

grain, as shown in fig. 4.7. Non-basal slip lines were evident in some grains during secondary creep, in the form of coarse, fairly parallel but irregular, traces, and these became more extensive as creep continued. Deformation twins were also observed in some grains, although twinning was not a common feature of the deformation mechanism at $200^{\circ}\text{C}^{157}$.

The formation of sub-grains was usually noted during the early stages of secondary creep, in the form of a narrow band of very elongated sub-grains around the edge of the parent grain. During the later stages of secondary creep, sub-grain boundaries would often divide a small percentage (5-10%) of the grains into three or four large sub-grains surrounded by smaller sub-grains adjacent to the boundary. An examination with the interference microscope showed that the fringes were often bent, but not displaced, at the sub-boundaries, in a manner similar to that of the slip lines shown in fig. 4.8.

Some of the tests were terminated after the commencement of the tertiary stage, since the major interest of this work was the contribution made by grain boundary sliding during the initial stages of creep. However, many of the specimens were tested to fracture, and this usually occurred at a total strain of about 20-30%. Sufficient specimens were tested in this way for it to be generally observed that the ductility substantially decreased with a

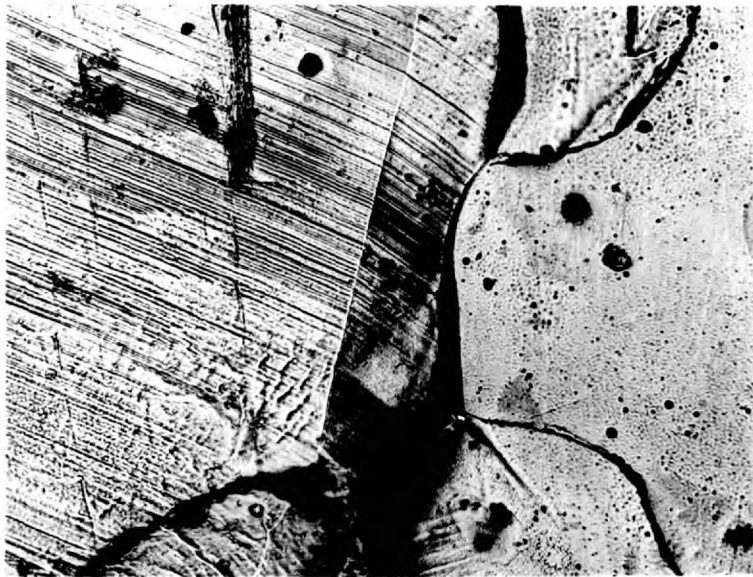


FIG. 4.8. Sub-grain formation.
Specimen MX8 at 8.76%
strain. (X175).



FIG. 4.9. Cracking at grain boundary.
Specimen MX8 at 8.76 %
strain. (X 200).

reduction in creep rate, in a manner similar to that reported for Mg¹³⁹. In the limiting cases, for example, specimen MX29, tested at 3000 p.s.i., fractured at about 9% strain after a period of over 2200 hours, whereas specimen MX31, tested at 8000 p.s.i., fractured at a strain in excess of 40% after 34 hours. Very little necking occurred in specimens tested at a slow rate of strain, and an examination of the fracture surface revealed it to be predominantly intercrystalline. Occasionally there was evidence of cracking along the grain boundaries during tertiary creep, as shown in fig. 4.9. From surface observations alone, it was not possible to tell if the crack was originally nucleated by the linking of many small cavities, since, owing to the highly deformed nature of the surface, any small voids occurring in the boundary region would not be clearly resolved.

Several specimens were sectioned at, or immediately prior to, fracture, and examined for cavitation. These specimens were mounted in cold-setting resin and polished to 1 μ diamond paste in the normal manner. Between each stage they were cleaned thoroughly in an ultra-sonic bath to remove any polishing material from the cavities. Electro-polishing was not carried out, since it has been shown¹⁵⁸ that this may considerably enlarge the cavities and round them off. The specimens were therefore examined

either after the 1 μ diamond stage, or, in some cases, after a better finish had been obtained by polishing on magnesia using the Samuels "skidding" technique¹⁵⁹. After this treatment, rows of small cavities were observed in the boundaries of many of the specimens, especially those in which sliding was an important mode of deformation. In general, the cavities appeared to be more numerous near the point of fracture.

An interesting feature, observed after sectioning, was that the boundaries were no longer of a smooth appearance, as on the original surface, but were instead wavy or corrugated, with many local irregularities. Similar boundaries have also been reported in other materials, and for specimens of magnox tensile tested at 2%/hour at 230°C¹⁶⁰. A detailed study of the occurrence of such boundaries in Mg was made by Suiter and Wood¹⁶¹, and they suggested that the irregularities were due to the formation of sub-grains in the boundary region. Mullendore and Grant¹⁶² investigated similar irregularities occurring in Al-Mg solid-solution alloys, and concluded they were formed, under the combined action of sliding and migration, at the points of intersection between sub-grains and the boundary. The occurrence of wavy boundaries in the present work is examined in more detail in sections 4.3.2 and 5.2.1.

4.1.3. Determination of E_{gb}/E_{tot} :

Before it was possible to calculate E_{gb}/E_{tot} , the sliding contribution to the overall extension, it was necessary to derive an experimental value of k for use in equation 3.1. This was done using the printed grid technique to determine E_s , as outlined in section 3.5.2. All tests using this technique were carried out at a temperature of 200°C , with the exception of the initial test at 100°C already described. A direct correlation was therefore possible with the many routine tests undertaken at this temperature. From an additional experiment it was also established that the printed grid remained in adherence with the surface at temperatures up to and including 300°C .

A number of specimens was tested with printed grids, and in each case they were creep tested to total strains of slightly greater than 2% . During this period, readings were taken to determine $\bar{v}_{av}$ at four different strains. There were two reasons for choosing a strain of about 2% for the grid measurements. Firstly, it would not have been possible to measure the extremely small grain extensions at strains smaller than this. Secondly, earlier results on specimens without printed grids had revealed an initial linear relationship between sliding and extension up to about 3% strain (fig. 4.2), and these readings were therefore taken so as to be still on the linear portion of the curve.

For each specimen, 300 readings were taken of the grid line separation within individual grains, and these were used to calculate E_s , and hence to obtain k in the manner already indicated.

An examination of the specimen surfaces after testing showed the grids to be firmly affixed, and to be apparently reproducing without restriction the deformation of the surface grains. This was indicated by the sharp offsets which were visible at a number of boundaries (fig. 4.10), and there was also evidence of alternate sliding and migration (fig. 4.11).

Full details of the results obtained with these specimens are given in Table 4.2. The error bars on k represent the 95% confidence limits. Two of the specimens used for this work (MX67 and MX69) were tested under the same conditions as two specimens without printed grids (MX4 and MX8 - see Table 4.1); similar creep curves and similar sliding-time curves were obtained for both pairs of specimens. There was therefore no evidence that the presence of a grid had any effect on the surface behaviour.

There was some scatter in the calculated values of k , although they were all within the range 1.00-1.20, which is lower than the value used by many previous workers. This is discussed in more detail in section 5.2.2.(a). The mean value of k was 1.07, and this was used to calculate E_{gb}/E_{tot}

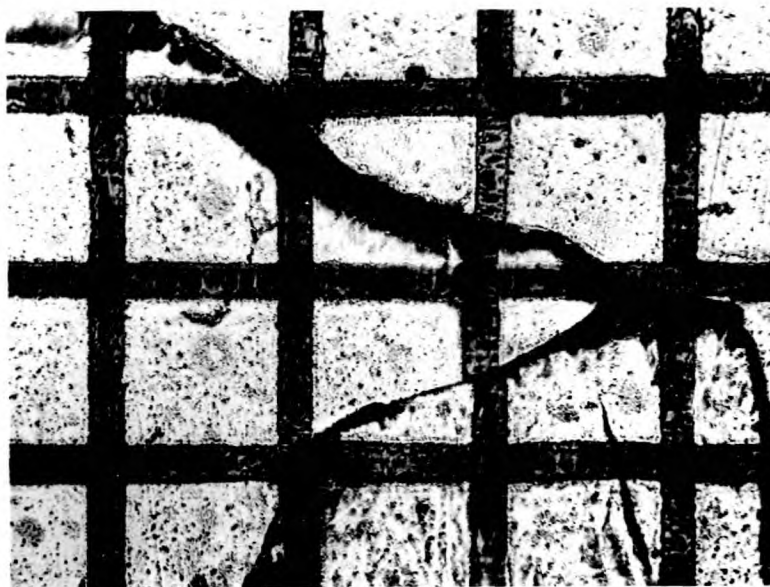


FIG. 4.10. Offsets revealed by printed grid; stress axis horizontal. Specimen MX67 at 1.11 % strain. (X 180).

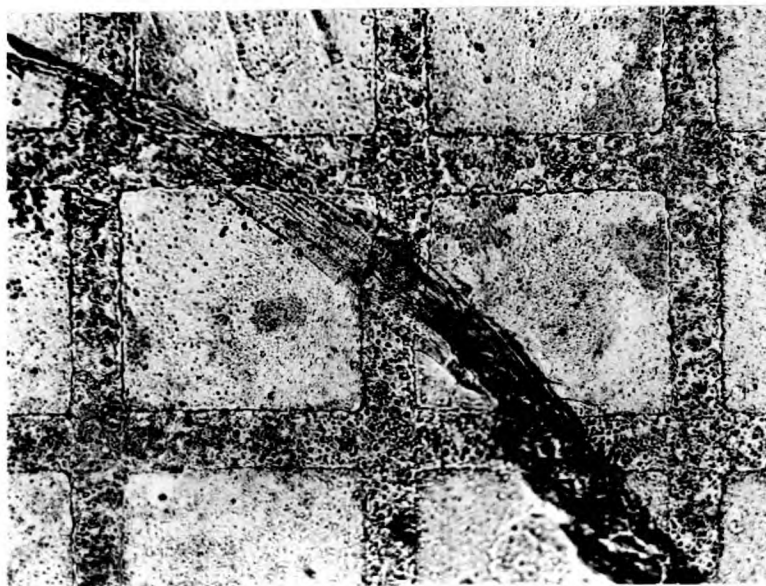


FIG. 4.11. Alternate sliding and migration. Specimen MX 73 at 2.08 % strain. (X 275).

for the specimens tested without printed grids, by taking the value of $\bar{v}_{av}$ for a chosen value of E_{tot} (1%) on the linear portion of the sliding-extension curve. Because of the linearity, the value obtained for E_{gb}/E_{tot} was independent of the chosen total strain. It should be noted that in the theoretical discussion presented later it is suggested that the value of k is dependent on the position reached on the linear portion of the sliding-extension curve. Thus, it is not strictly correct to use the same value of k for all specimens. No allowance was made for this, however, since the experimental variations in k were only very small.

The results obtained for E_{gb}/E_{tot} , as given in Table 4.1, showed that the ratio was very dependent on stress and grain size. In general, it was found that E_{gb}/E_{tot} increased with decreasing stress, or, for a given stress, E_{gb}/E_{tot} decreased with increasing grain size. A similar trend was also observed with the specimens used to obtain k (Table 4.2), and this trend was of a sufficiently large magnitude that it could not be accounted for merely by the small scatter in the value of k . It seems probable that the experimental scatter was sufficient to mask this effect for the four specimens tested in the range 3500-4500 p.s.i., although the high value of E_{gb}/E_{tot} obtained for specimen MX23 is almost certainly attributable in part to the smaller grain size of this specimen.

A plot of E_{gb}/E_{tot} against stress for all of the specimens in the two Tables, fig. 4.12, showed linearity for each grain size, in a manner similar to that reported by McLean¹⁰¹ for Al specimens, and an extrapolation to zero stress yielded a value of about 100%. The decrease in E_{gb}/E_{tot} with increasing grain size showed that, although the amount of sliding on a single boundary per grain extension was greater for the larger grain size (fig. 4.13), it was not sufficient to compensate for the smaller number of boundaries present.

4.1.4. Conclusions.

By photographically printing a grid on the surface of a number of specimens before deformation, it was possible to obtain an indirect measure of E_{gb} , and hence an experimentally derived value of k for use in equation 3.1. Using a mean value of k of 1.07, the values of E_{gb}/E_{tot} at low strain were calculated for all specimens tested at 200°C. The value of k thus obtained was lower than that used by the majority of other workers, and, if it also holds for other materials, would indicate that many previous calculations have substantially overestimated the contribution made by grain boundary sliding.

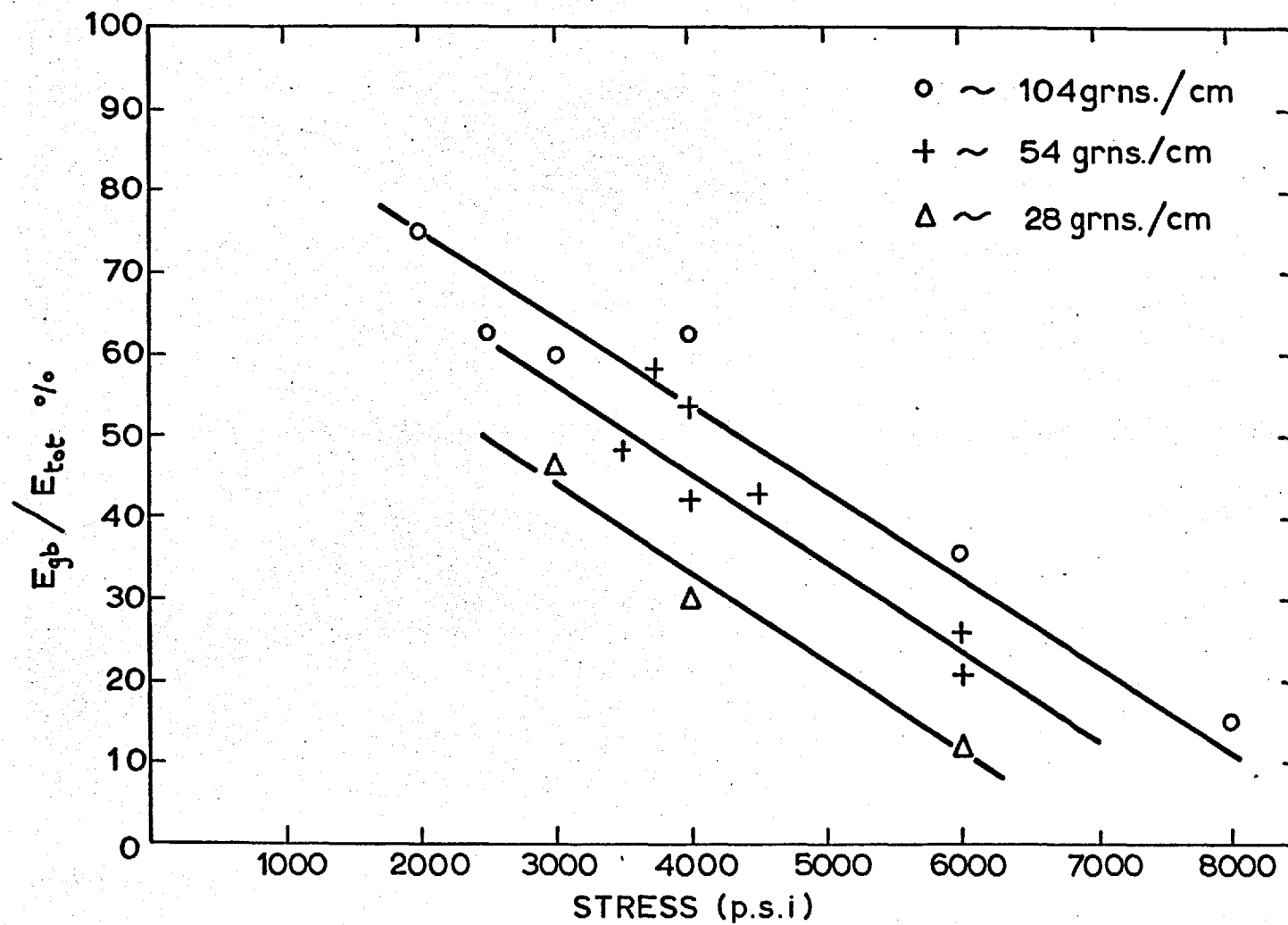


FIG. 4.12. Stress dependence of E_{gb}/E_{tot} at 200°C.

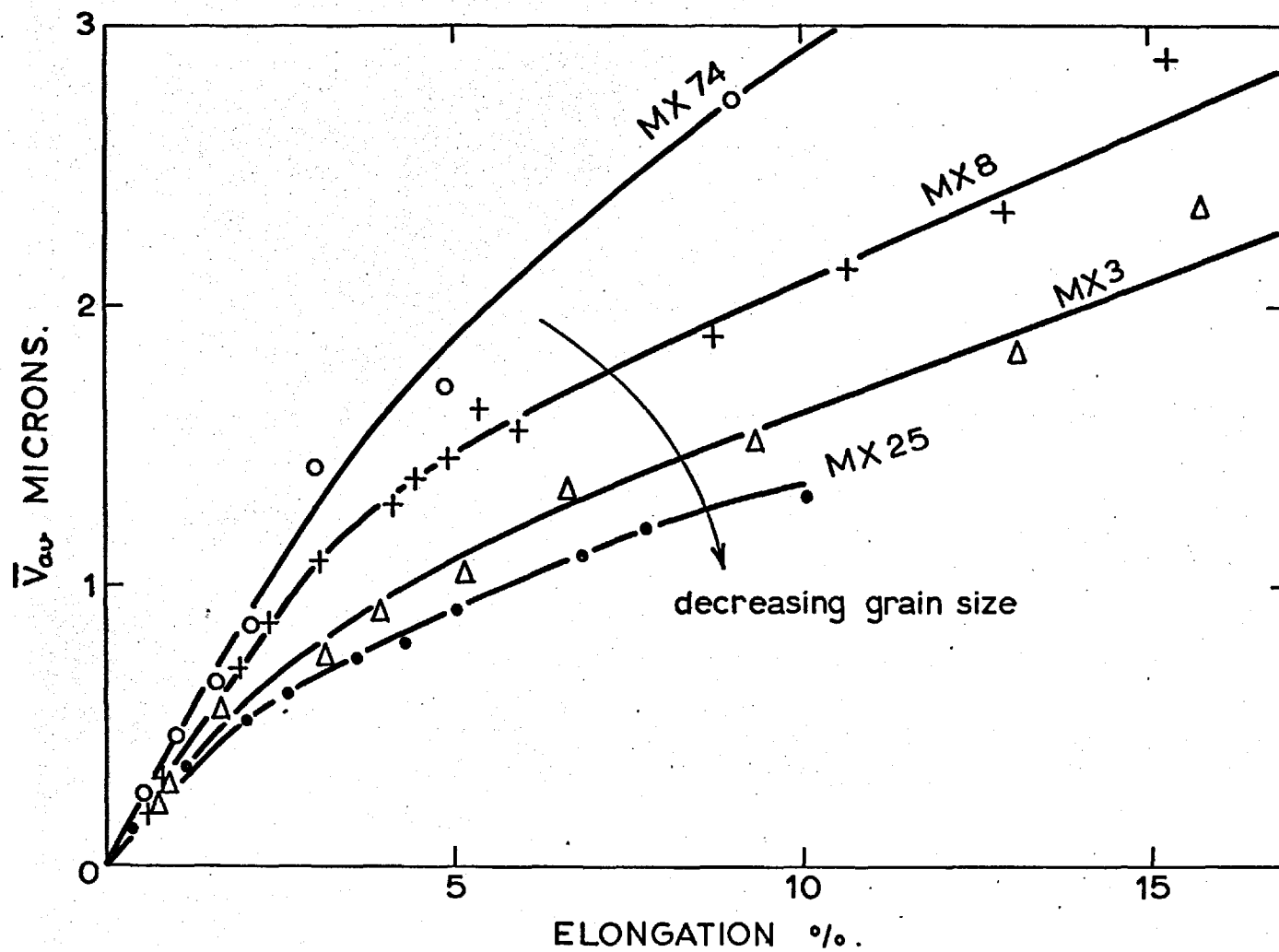


FIG. 4.13. Variation of sliding with grain size.

One possible inaccuracy in the present work may have been due to the method of measurement, since the grid technique resulted in the grain extensions being recorded predominantly in the centre of the grains. Thus the figure obtained for E_s assumed homogeneity of strain up to the boundary itself, whereas some workers^{87,163} have found that grain deformation is restricted in the boundary region. However, for a number of reasons, outlined below, it was felt that this was unimportant:

(i) Hargreaves and Boas¹⁵² measured the extension of individual grains in a coarse-grained Al specimen, and found that the deformation near a boundary was greater or smaller than in the grain interior, depending on whether the neighbouring grain was more or less deformed. It is therefore reasonable to assume that, on average, the deformation adjacent to the boundary is the same as that in the interior.

(ii) Urie and Wain¹⁵¹ reported a restriction in deformation at the boundaries of a polycrystalline Al specimen, but an examination of their results indicated that, under the conditions used in the present tests, the percentage error involved in measuring the grain extensions entirely in the grain interiors would be very small.

It was therefore concluded that the mean value of 1.07 obtained for k was an accurate value for magnox tested under these conditions.

4.2. Tests in the Temperature Range 21°C - 125°C.

There is much qualitative evidence⁶⁹ to indicate that grain boundary sliding only becomes an important mode of deformation at temperatures greater than about $0.5 T_m$. Recently, however, some workers have reported the occurrence of sliding at much lower temperatures, and it was decided to investigate this phenomenon in the present work.

4.2.1. Review of Low Temperature Sliding.

Dorn and co-workers¹⁶⁴ were the first to report low-temperature sliding, observing that marker lines on a high purity magnesium specimen were displaced at the grain boundaries during creep at room temperature ($0.3 T_m$). They found that displacements were visible even at very low strains, less than about 0.2%, and it was estimated that, at a total strain of 2.4%, the sliding contributed about 0.1% to the overall extension. A similar report was also made by Grant et al¹⁶⁵, using an Al-10% Zn alloy. They found that machining grooves on the specimen surface were in some cases displaced at the boundaries during deformation at room temperature ($0.3 T_m$), and suggested that the viscosity of the grain boundaries in Al was sufficiently low at room temperature for sliding to occur. This result was criticised by Perryman¹⁶⁶, who suggested that the observed sliding was due to the use of a two-phase structure rather

than a single-phase solid solution alloy. However, Grant¹⁶⁷ has pointed out that the presence of a precipitate would probably tend to lock the boundary, and so make shearing more difficult.

Additional support for low temperature sliding in Al was provided by Cuff and Grant¹⁶⁸, who used the electron microscope to examine surface replicas of a specimen strained approximately 8% at room temperature. They found that surface markers, resulting from chemical polishing prior to deformation, showed sharp lateral offsets at high magnification, the distance of sliding being of the order of a few tenths of a micron. They also noticed the existence of a band of deformation at one boundary, where sections of the marker lines were slanted in the direction of the applied stress, and postulated a mechanism of alternate sliding and migration to explain this, thereby introducing the additional phenomenon of migration at unexpectedly low temperatures.

Dorn and co-workers¹⁶⁹ also carried out tests on Mg at 78°K, and found that displacements were a rare, but occasionally observable, occurrence even at this temperature. Furthermore, two recent papers have reported sliding at a temperature of 4.2°K. The first, by Gindin and Starodubov¹⁷⁰, resulted from a study of the plastic deformation of high purity coarse-grained iron, in which it

was found that specimens examined under the interference microscope showed some fringe discontinuities at the grain boundaries. The postulate that this was due to a genuine sliding process seems untenable, however, since, in addition to the very low temperature, the specimens were deformed under a high rate of strain. The second, by Chin et al¹⁷¹, reported sliding in Al specimens deformed at 4.2°K as revealed by the displacement of tool markings at the boundary and the presence of boundary cracks. They developed a theory of a second, very low, equi-cohesive temperature, due to the intersection of curves for the temperature dependence of the strength of the crystals and the inherent strength of the boundaries, below which sliding was again an operative process. As with the previous paper, however, sliding of the form observed at high temperatures would not be expected in this work, since, in addition to the low temperature, these workers were also using a high rate of strain ($3 \times 10^{-4} \text{ sec}^{-1}$).

Results of this nature have led to the inclusion of low temperature sliding as an established phenomenon in some reviews^{4,70} of grain boundary sliding, and it has been incorporated as a prerequisite in any sliding model. However, since a number of workers have shown high temperature sliding to be a thermally activated process, sliding would **not** be expected at low temperatures under fast

rates of strain, and it was therefore decided to investigate this alleged sliding in the temperature range from 21°C to 125°C (0.32 - 0.43 T_m).

4.2.2. Sliding Measurements.

An initial exploratory experiment was carried out using a coarse-grained magnesium specimen. The surface of this specimen was lightly scribed with marker lines, both parallel and transverse to the stress axis, using a fine diamond stylus fixed to a micrometer stage, and the specimen was extended, under constant load, to a strain of 0.9% at room temperature. A microscopic examination of the specimen surface after deformation revealed no sharp discontinuities at the grain boundaries, but some marker lines were found to be bent in a small zone close to the boundary, and these appeared as sharp offsets under low magnification. This is clearly shown in figs. 4.14a and 4.14b, at low and high magnification respectively. The second figure shows that the bend in the marker line is associated with a zone, on one side of the boundary only, in which there is much slip and twinning. Light etching revealed that the boundary had not moved laterally during the test, thus proving that the bending of the marker line was not due to a process of alternate sliding and migration. A close examination of the published photographs of supposedly low temperature sliding



FIG. 4.14a. Apparent offsets in scribed markers. $T = 21^{\circ}\text{C}$
Specimen M4 at 0.9% strain. (X 290).



FIG. 4.14b. Part of same area as in fig. 4.14a showing curvature of marker at boundary. (X 1390).

then revealed that some of the offsets were similarly bent. For example, in fig. 16b of the first paper by Dorn et al¹⁶⁴, and in fig. 10 of their second paper¹⁶⁹, the marker lines are curved adjacent to the grain boundary, rather than showing a sharp offset, whilst the photograph of Grant et al¹⁶⁵ is too diffuse in the boundary region for any conclusions to be drawn.

A second magnesium specimen (M4 - see Table 4.3) was then creep tested at room temperature, and measurements taken of the vertical steps between grains at regular strain increments of approximately 0.1%, in a manner similar to that used in the tests at high temperatures. On using the interference microscope to examine the specimen after deformation, three types of fringe pattern were identified at the grain boundaries:

(a) The fringes crossed the boundaries without deviation, so that the step height was zero.

(b) The fringes were curved at the boundary, usually on one side only but occasionally on both sides. There was no sharp offset, as would occur with sliding, and the step height was again recorded as zero.

(c) The fringes were apparently sharply offset at the magnification used, and a positive reading was therefore recorded.

In each case a total of 300 readings was taken to give a mean value of $\bar{v}_{av}$ at the different strains, and this was then plotted against the total extension, as shown in fig. 4.15. After a small initial rise, it was found that $\bar{v}_{av}$ levelled off at a finite value of the order of 0.1μ . During the course of this test it was also found that the proportion of boundaries showing sharp offsets was gradually decreasing, since a number of boundaries which appeared to be of type (c) at low strains became obviously of type (b) at the higher strains. An analysis of the measurements showed that the percentage of boundaries appearing as type (c) was 79% at a strain of 0.2% and only 47% at a strain of 0.5%. The apparent sharpness of a step was found to depend on the fringe spacing and magnification employed, and an obvious curvature of type (b) at high magnification might easily be mistaken for a sharp offset of type (c) at low magnification.

Three magnox specimens of similar grain size were tested under the same stress, but at temperatures of 21°C , 75°C and 125°C respectively (See Table 4.3). A standard fringe spacing and magnification was used to arbitrarily define offsets of type (c).

For the tests at 21°C and 75°C , measurements were taken to determine the mean vertical step height $\bar{v}_{av}$ for strains in the range 1.1 - 4.1%. The occurrence of a curvature of

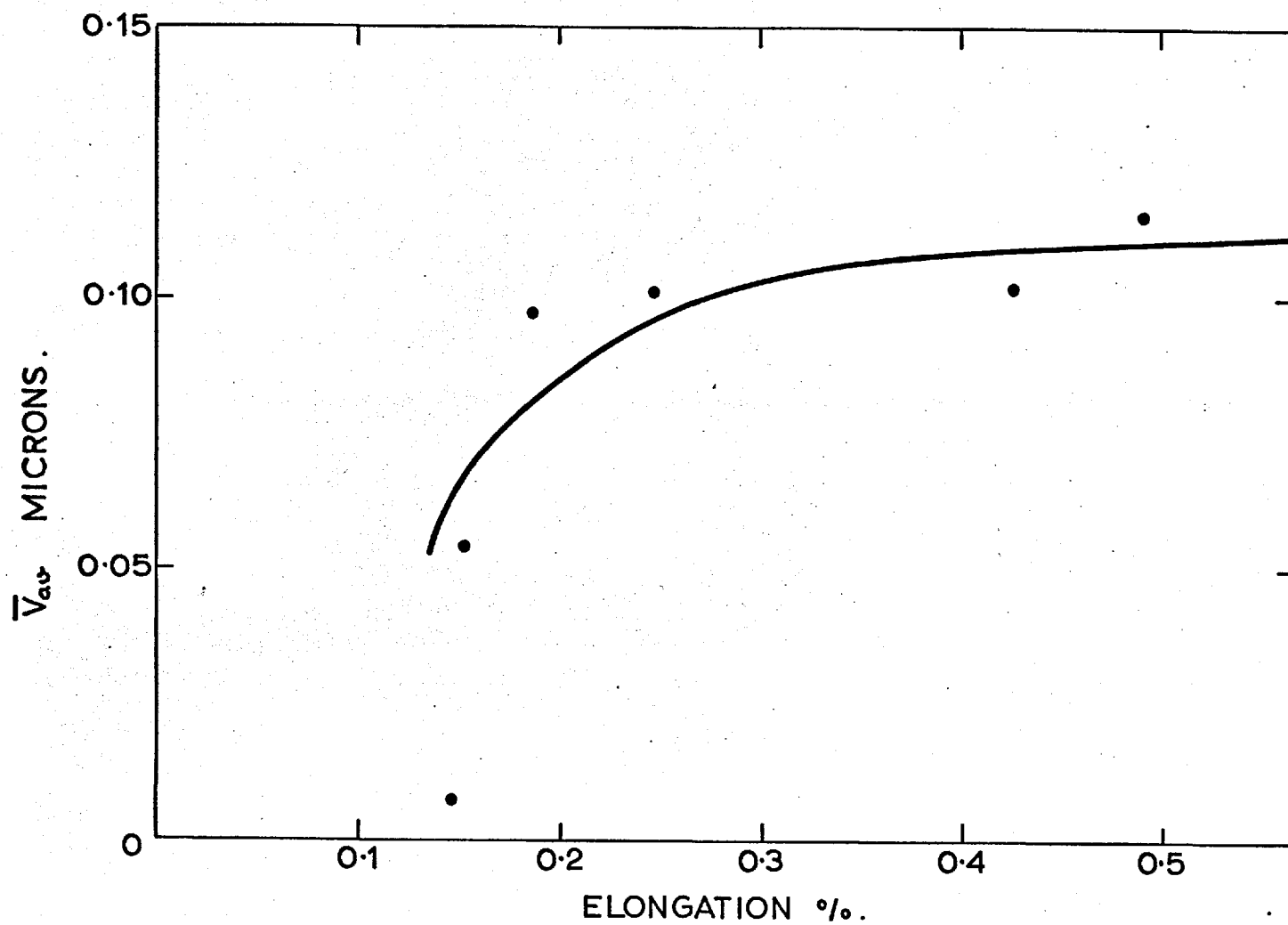


FIG. 4.15. Apparent sliding at 21°C.

type (b) at the boundary is clearly shown in fig. 4.16, after straining specimen MX15 to 4.1% at 21°C. In these tests, only offsets of type (c) were recorded. At both temperatures, the mean step height was found to remain constant at approximately 0.03 μ , as shown in fig. 4.17, and, within the limits set by the error bars at the 95% confidence level, there was no measurable difference between the two curves. It was also found that the percentage of readings showing sharp offsets was approximately $24 \pm 2\%$ at both temperatures. Similar measurements were also taken on the specimen tested at 125°C, and at this temperature the value of $\bar{v}_{av}$ was found to rise from the level of the other two curves as the extension increased. It was also found that the percentage of readings of type (c) increased slightly at each strain, rising from approximately 24% at a strain of 1% to approximately 35% at a strain of 4%.

These results show that at temperatures of 75°C and below, the apparent sliding is independent of strain, at least for strains greater than 1%, is unaffected by temperature, and occurs at a fixed proportion of the boundaries. At 125°C, a temperature-sensitive effect is superimposed on this low temperature phenomenon, and subsequent tests at temperatures in the range 125°C - 200°C, described in section 4.3, indicated this second effect to be genuine grain boundary sliding.



FIG. 4.16. Curvature of interference fringes at boundary. $T = 21^{\circ}\text{C}$.
Specimen MX 15 at 4.1% strain (X 860).

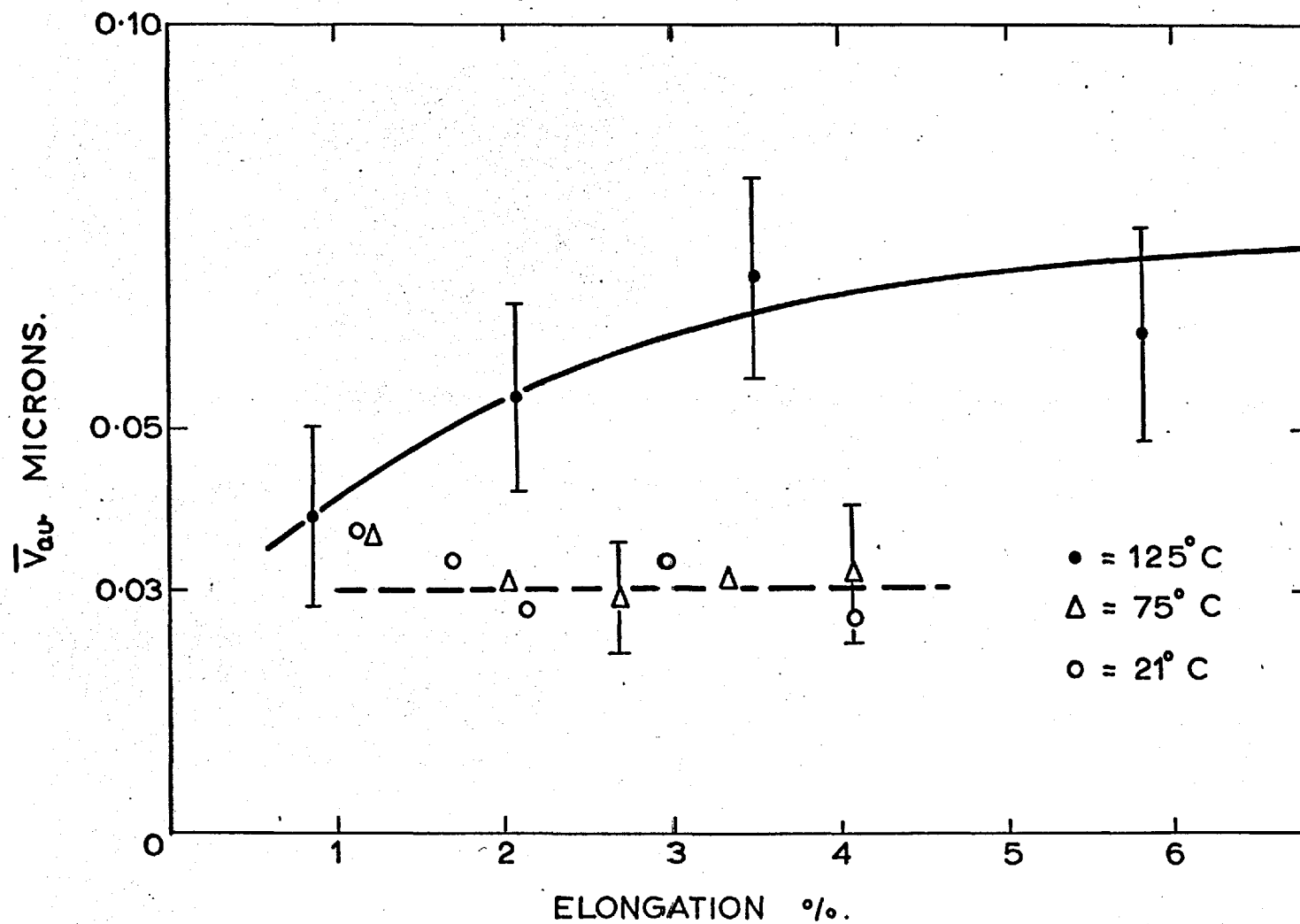


FIG. 4.17. Sliding-extension curves at 21°C, 75°C and 125°C.

Using the results of specimens MX18 and MX19 (See Tables 4.3 and 4.4), a stress dependence for sliding was calculated from the general formula

$$\dot{\bar{v}}_{av} = A \sigma^n \exp(-Q/RT) \quad 4.3.$$

where $\dot{\bar{v}}_{av}$ = rate of sliding

σ = stress

Q = activation energy of sliding

R = gas constant

T = temperature in $^{\circ}\text{K}$

A, n = constants

A value of $n = 4.0$ was obtained, and this was then used with the results of MX31 and MX18 (See Tables 4.1 and 4.3) to calculate an activation energy of sliding, Q . The value thus obtained was $Q = 23$ kcal/mole, which, although subject to large error because of the uncertainty in the curve for MX18, served to indicate that the result obtained for MX18 at 125°C was at least of reasonable magnitude. Using this value for the activation energy, it was estimated that the amount of high-temperature sliding occurring at room temperature after an extension of 3% would be of the order of $10^{-6}\mu$, and, since this is very much smaller than the observed apparent sliding of $\bar{v}_{av} = 3 \times 10^{-2}\mu$, it was

concluded that the latter must be attributable to some other process.

It therefore appears that there are two distinct processes which occur independently:

(i) thermally activated high temperature sliding. This takes place essentially at the boundary.

(ii) localised shear which is not thermally activated. Figs. 4.14b and 4.16 indicate that this occurs in a zone immediately adjacent to the boundary. It is probable that this process takes place at all temperatures, but only becomes obvious at low temperatures where true sliding is virtually absent.

4.2.3. Metallographic Observations.

When fringes were observed to be bent at the boundary, they were usually bent on one side only, although in a few isolated cases the bending was found to pass through the boundary region. Etching of both magnesium and magnox specimens deformed at room temperature showed that boundary migration had not occurred. Considerable twinning was observed at room temperature, but this decreased at higher temperatures, in agreement with the results on magnesium by Barrett and Haller¹⁵⁷. Occasionally, triple point folds were observed in the specimen deformed at 21°C, but they only extended a short distance into the grain. This

contrasted with the specimen deformed at 125°C, where folding occurred at a number of triple points and some sub-grains were formed at the grain edges.

4.2.4. Mechanism of Low Temperature Shear.

Consider two adjacent grains A and B, with their basal planes orientated such that grain A can extend readily under an applied stress but grain B only extends with difficulty. Under conditions of continuity of strain, this will give rise to a localised zone of accommodating deformation close to the boundary, either in grain B, as shown in fig. 4.18, or by inhibition of deformation in grain A. After some finite amount of strain, apparently of the order of 0.5% for Mg and less than 1% for magnox, work hardening will occur, thereby stabilising the step height in the manner found experimentally, and leading to an equality of the deformation rates in each grain. Evidence for this mechanism is provided by the constant proportion of boundaries showing low temperature shear at 21°C and 75°C, since this would be expected with specimens having a similar distribution of grain orientations. The same proportion was also obtained for specimen MX35 of a coarser grain size (See Table 4.3) which was tested to check this relationship. With this specimen, slopes were again visible on only one side of the boundary, and $\bar{v}_{av}$ was 0.045 μ at a strain of 1.17%.

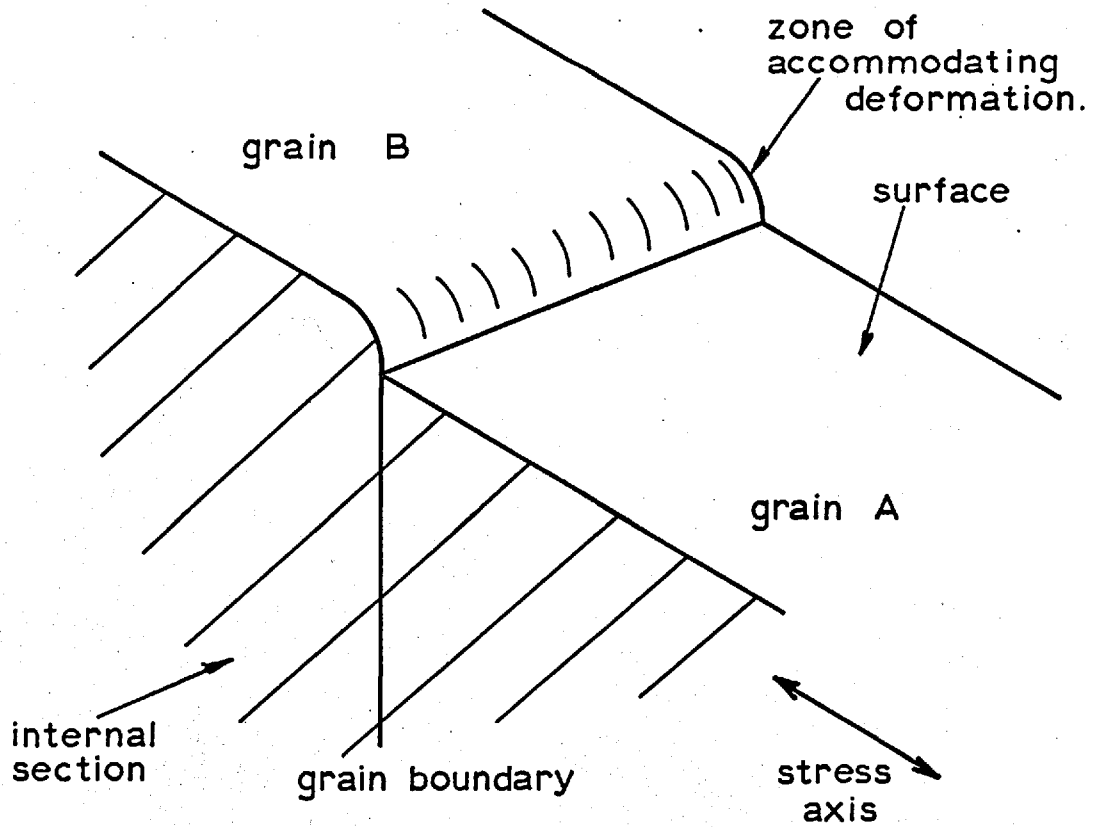


FIG. 4.18. Schematic representation of low temperature shear.

The stabilised step height therefore increases with an increase in grain size.

Urie and Wain¹⁵¹ also reported localised shear adjacent to the boundary, after studying the deformation of aluminium at room temperature, but they found the zone of accommodation to occur on both sides of the boundary. It therefore seems likely that a difference exists between h.c.p. and f.c.c. metals, probably due to the difficulties of initiating slip in h.c.p. metals on systems other than the basal planes.

4.2.5. Conclusions.

The present results indicate that it is confusing to associate low temperature phenomena with that found under high temperature creep conditions. It appears that at low temperatures accommodating slopes are formed between grains due to initial inhomogeneous deformation. These slopes are also clearly resolvable in some of the published photographs.

Prior to this work, the most convincing evidence of sliding at low temperatures had been furnished by the electron micrographs of Cuff and Grant¹⁶⁸. An attempt was made to repeat their experiment on magnox, by taking surface replicas of specimens deformed at room temperature. The results were unsatisfactory, however, since the Al specimen used by Cuff and Grant had carried a special surface marking

due to chemical polishing, in the form of a cellular sub-structure which crossed the grain boundaries. Since it was not possible to use this polishing technique on magnox, it was necessary to continue the investigation on Al, and this was undertaken by Dr. R.C. Gifkins at the University of Melbourne. Full details are published elsewhere¹⁷², but, in brief, the results indicated that the apparent sliding observed by Cuff and Grant was due to cracking in the surface oxide film.

4.3. Tests in the Temperature Range 125°C - 200°C.

In an attempt to correlate the results obtained at high and low temperatures, two additional tests were carried out at 125°C and 150°C. These specimens, together with specimen MX31 tested at 200°C, were also used to investigate the effect of repolishing during the test, since there was some evidence, from work on bi-crystals⁹⁴, that it may be possible to remove any "slide hardened" surface layer by repolishing or etching.

4.3.1. The Effect of Repolishing on Sliding Measurements.

4.3.1.(a) Repolishing After the Deviation from Linearity.

A stress of 8000 p.s.i. was chosen for the specimens tested at 125°C and 150°C, since it afforded a direct comparison with specimen MX31 (See Table 4.1). The experimental details are given in Table 4.4.

To check the occurrence of any surface effect, specimen MX21 was tested in the normal way, and in addition the specimen was repolished at intervals throughout the test. A similar experiment had previously been carried out by Gittins⁹⁸, by repolishing two Mg specimens, creep tested at 300°C, at strains of about 8% and 13% respectively. The results obtained were inconclusive, however, since there was a marked increase in the sliding rate for one specimen but not for the other, although a study of the results shows that it would have been possible to draw a small increase for the second specimen also. The apparent inconsistency between specimens may have been due to the removal of an insufficient quantity of material. This is partly substantiated by Gittins' report that he removed less than one grain diameter during the repolishing, although later work on the same material showed that it was necessary to go down about two grain diameters to obtain grain configurations typical of the bulk material. Previous results by Rachinger¹¹³, using Al specimens of a grain size similar to that of specimen MX21, had also indicated a depth effect equivalent to two grain diameters, and it was decided to get well below this surface layer in the present work. At each repolish the specimen was therefore initially abraded on 400 SiC paper, and then taken through the polishing procedure in the usual way.

By weighing the specimen before and after repolishing, the loss in weight over the gauge length could be used to determine by simple proportion the slightly reduced load required to give the same strain rate after repolishing. This method was used in preference to determining the difference in specimen width, since it was not possible, especially at high strains, to measure this accurately before repolishing, owing to the gross deformation on the surface. By measuring the width after repolishing, and allowing for the extension that had taken place, it was estimated that about 3-4 grains were removed during the repolish. This did not significantly reduce the number of grains in the cross-section, which was initially about 60.

Using this procedure, it was found that the repolishing and subsequent load reduction produced no marked irregularities in the creep curve, as indicated in the curve for MX21 shown in fig. 4.19, where the three repolishing points are indicated by R_1 , R_2 and R_3 respectively. The resultant sliding-extension curve, shown in fig. 4.20, was found to be initially of a similar form to those obtained at 200°C, yielding a linearity followed by a subsequent decrease in the sliding rate at some low but finite strain. At the first repolishing point R_1 , after the end of the linear portion, the value of $\bar{v}_{av}$ was read off the graph as $\bar{v}_{av} = 0.49\mu$. It should be noted that this value was subject

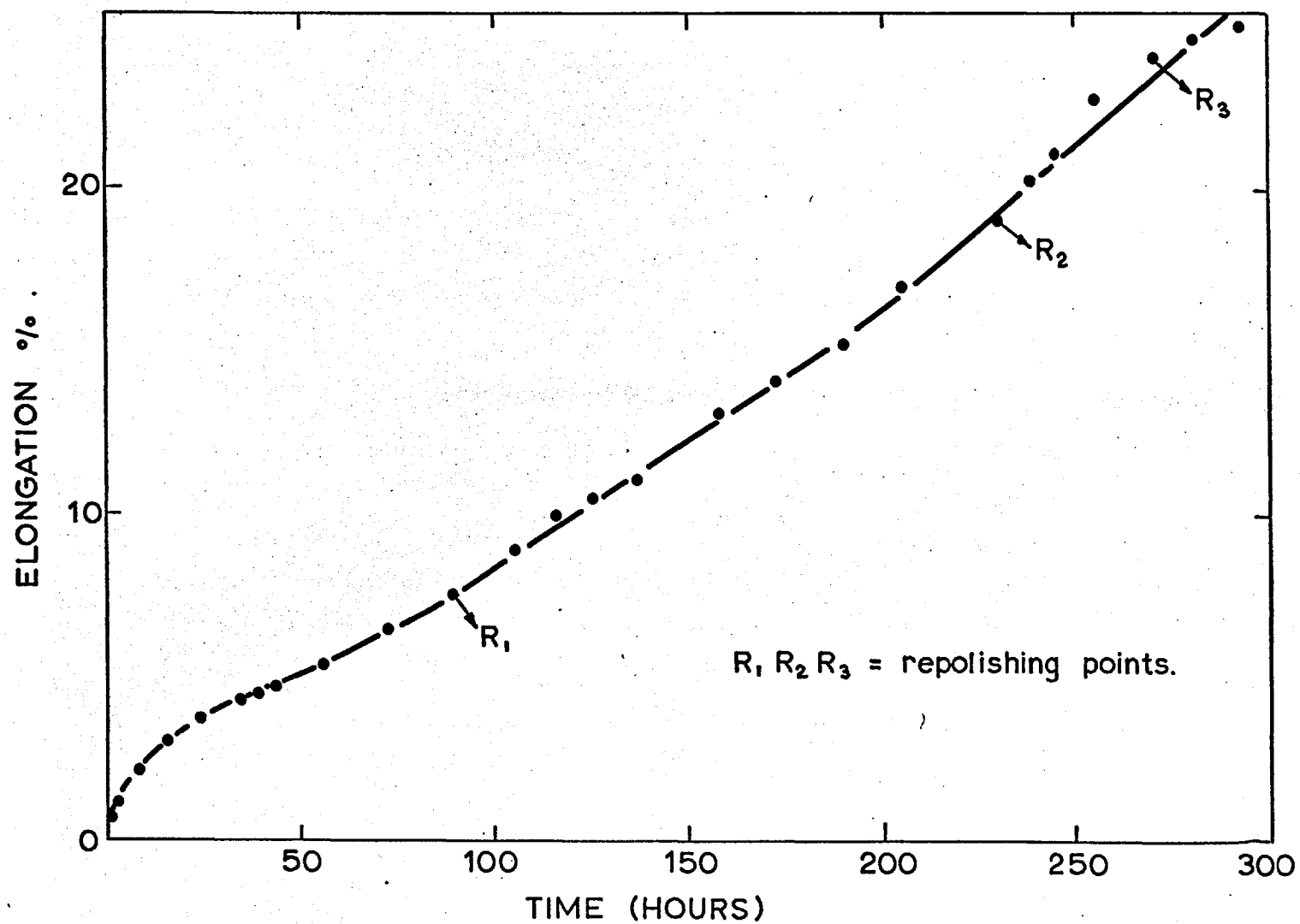


FIG. 4.19 Creep curve for specimen MX 21.

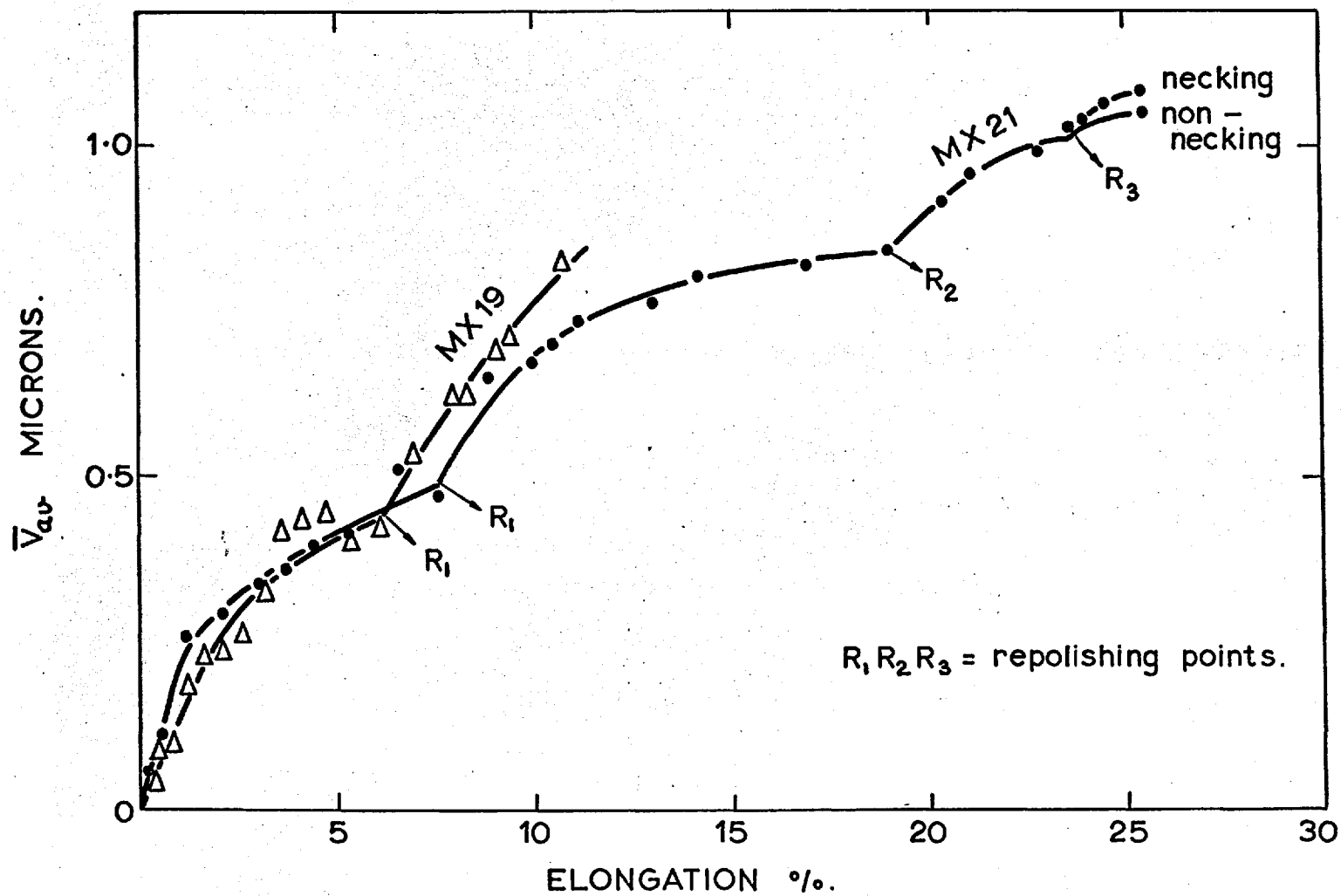


FIG. 4.20. Effect of repolishing during creep.

to a fairly large error bar, since variations in the individual values of v increase with increasing strain. Subsequent values of $\bar{v}_{av}$, obtained after repolishing, were then added to this to obtain an overall value of the step height. Since the points immediately after the repolish had much smaller error bars, the shape of the curve was obtained with a good degree of accuracy, although the overall values of $\bar{v}_{av}$ were subject to this larger cumulative error.

A similar process was carried out at each repolishing point, and the resultant graph showed there was always an initial increase in the sliding rate immediately after repolishing, and a decrease after a further strain of about 2%, similar to that observed in the initial test. Some necking was apparent at a total strain of 25.4%, and it was found that the individual values of v were often very much higher in the necked region. To check this, 300 readings of $\bar{v}_{av}$ were taken in this area and a further 300 in an area remote from this region. Both values are shown in fig. 4.20.

Using this figure, the average rate of sliding was calculated for the initial strain of 1%, and for a similar increment of strain after each repolish. The rates of sliding were also calculated for the points immediately prior to repolishing. The results are shown below:

Rates of Sliding Before and After Repolishing.

	<u>$\frac{d\bar{v}_{av}}{dt}$ initially.</u>	<u>$\frac{d\bar{v}_{av}}{dt}$ prior to repolishing.</u>
Before Repolish 1:	0.07 μ /hour	0.002 μ /hour
After Repolish 1:	0.006 μ /hour	0.001 μ /hour
After Repolish 2:	0.007 μ /hour	0.002 μ /hour
After Repolish 3:	0.006 μ /hour	-

This clearly shows that there was an initial rapid rate of sliding, which fell off to some lower value after about 2% strain. After repolishing, the sliding rate at first increased, although not to the rapid rate that was attained initially, and then fell off again to the same low value.

Similar results were also obtained with specimen MX19, tested at 125°C, and in this case a large number of measurements of $\bar{v}_{av}$ were taken both before and after repolishing so that the sliding-extension curve was well defined. This curve is also shown in fig. 4.20. The result again showed a resurgence of sliding after repolishing, although $\frac{d\bar{v}_{av}}{dt}$ for the second linear region was again lower than initially. The calculated rates of sliding for the first 1% strain (0.008 μ /hour), and for an additional

1% strain after repolishing ($0.0006\mu/\text{hour}$), were in a similar ratio to those obtained at 150°C .

4.3.1.(b) Repolishing Before the Deviation from Linearity.

Specimen MX31 (See Table 4.1) was strained at the same stress but at 200°C , giving a short term test of just over 33 hours to fracture. The creep curve is shown in fig. 4.21. Repolishing was carried out at four stages during the test, but for this specimen the initial repolish was made before the deviation from linearity in the sliding-extension curve.

This specimen was also used to investigate the possibility of enhanced sliding within the region of necking, since there had been reports of this for Mg^{98} , and earlier measurements on specimen MX21 had indicated a preferentially high value of $\bar{v}_{av}$ within this region. Necking was first observed at an overall strain of about 24%, and at this point lines were scribed on the specimen surface dividing the original gauge length into four approximately equal sections. During subsequent creep, the strain was measured for each section individually, and $\bar{v}_{av}$ determined for (a) the section including the necked portion, and (b) a section distinct from the area of necking.

The resultant sliding-extension curve, shown in fig. 4.22, exhibited a number of interesting features. Firstly, the linear portion continued through the first

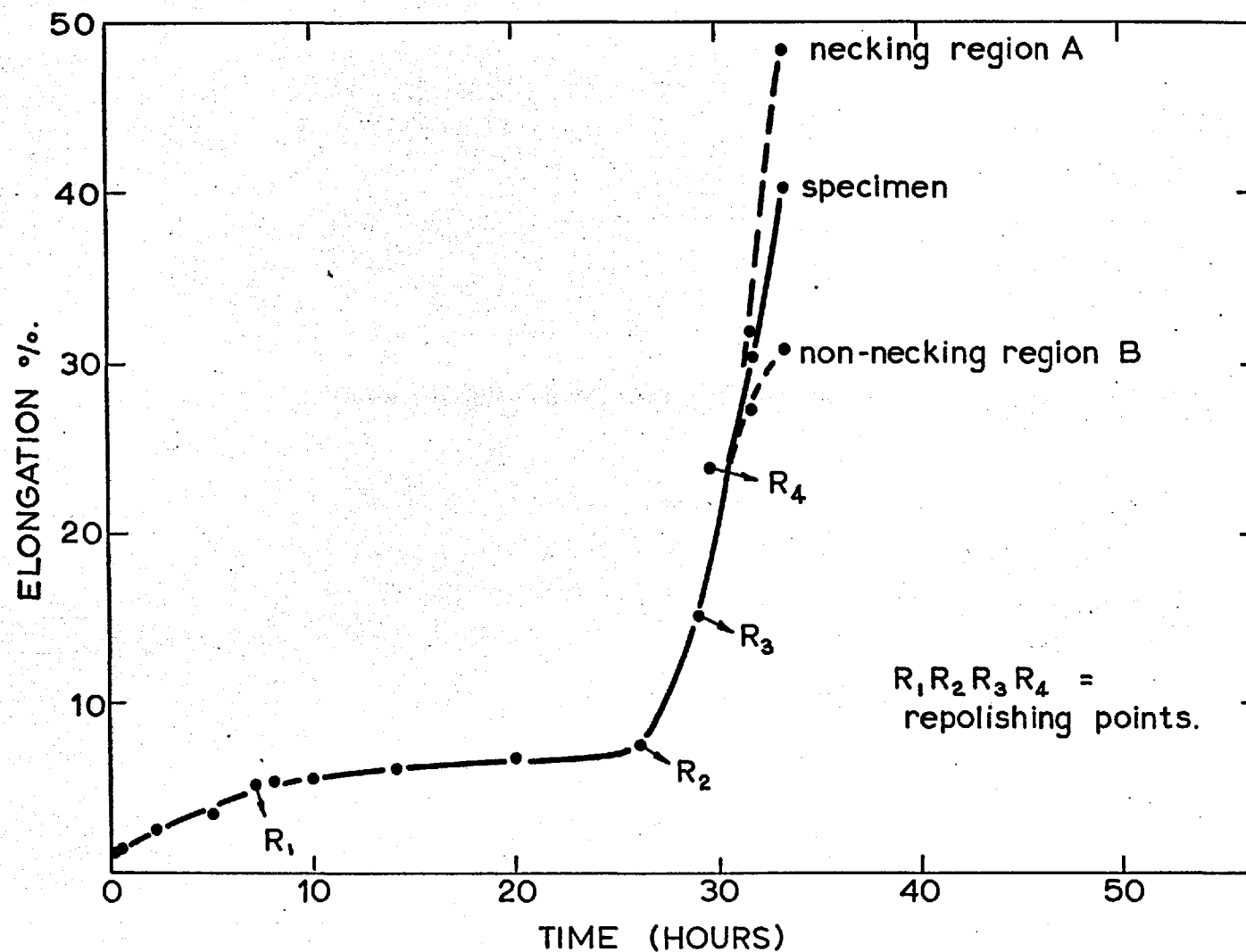


FIG. 4.21. Creep curve for specimen MX 31.

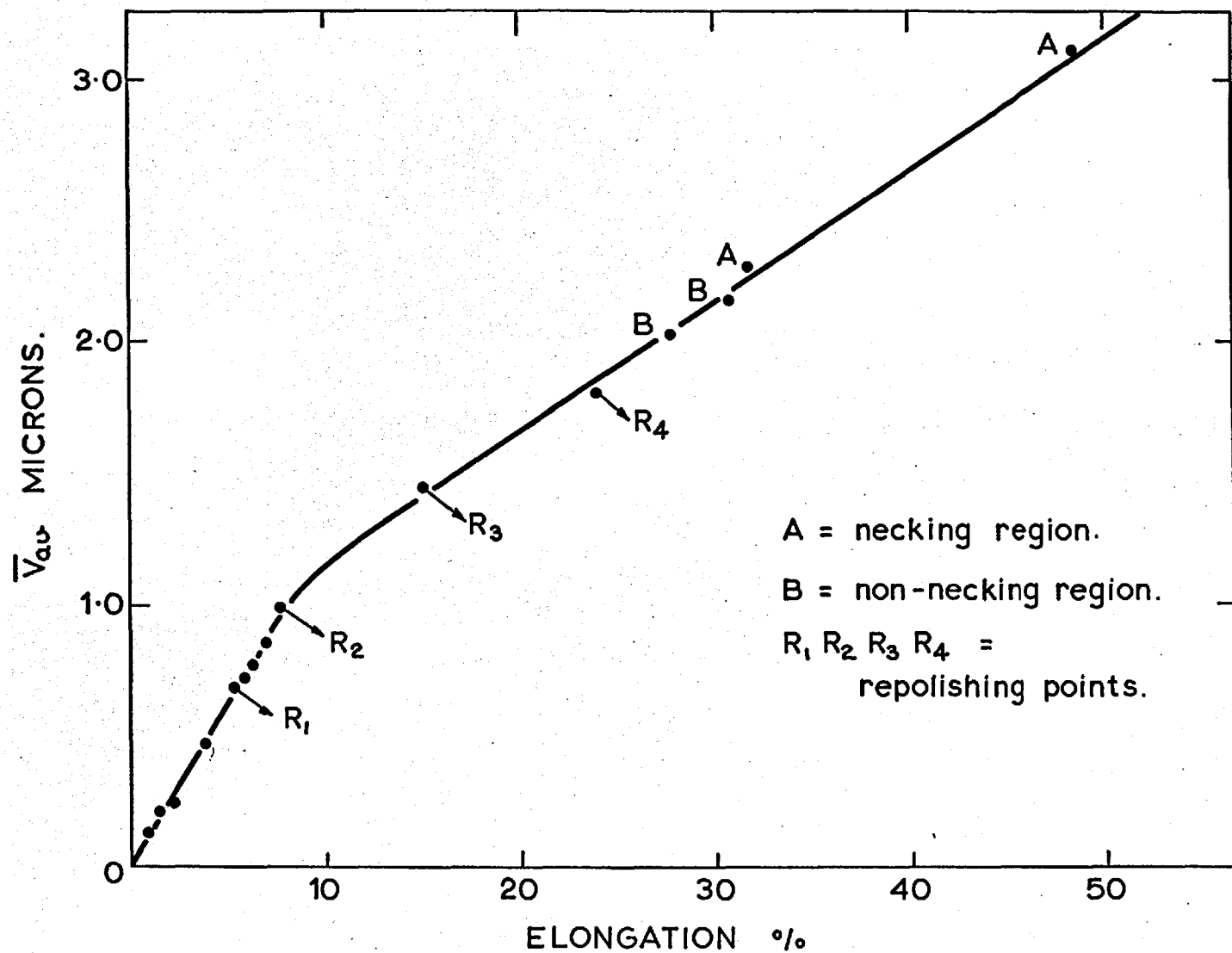


FIG. 4.22: Sliding-extension curve for specimen MX 31.

repolishing point, and ultimately deviated at a strain approximately equivalent to that at which the creep curve changed from secondary to tertiary creep. In this case, therefore, there was no resurgence of sliding after the first repolish, but this was consistent with the results obtained for the previous two specimens since, owing to the nature of the creep curve, $d\bar{v}_{av}/dt$ decreased from an initial value of $0.42\mu/\text{hour}$ to a value of $0.05\mu/\text{hour}$ after R_1 . The observed deviation from linearity in the sliding-extension curve after R_2 is explicable, since this point marked the transition from secondary to tertiary creep, and thus, owing to the faster strain rate then operative, the sliding contribution would be expected to decrease. A rough calculation showed that it would be necessary for the sliding rate to increase by a factor of $\times 10^2$ between secondary and the later stages of tertiary creep if sliding were to keep in step with the overall deformation throughout the test. In addition, no increase in the sliding rate was observed after the third and fourth repolish, but again this was probably because the specimen was then undergoing very rapid strain in tertiary creep, and enhanced sliding would not be expected under these conditions.

The apparent increase in sliding observed in the necking region was found to be entirely due to the much greater strain accommodated in the area adjacent to the

necking point, as shown by the two points for the necking and non-necking regions in fig. 4.22. This result is therefore in agreement with that obtained by McLean and Farmer¹⁰⁰ on an Al alloy.

4.3.2. Metallographic Observations after Repolishing.

With each of these specimens (MX19, MX21 and MX31), it was observed that the grain boundary configuration was corrugated after the first repolish. This is clearly demonstrated for specimen MX31 by a comparison of figs. 4.23 and 4.24. The first figure shows the straight boundaries on the original surface after a strain of 5.2% but before repolishing. The second figure, taken at a depth of about 3-4 grain diameters, shows the wavy boundaries on the new surface created by repolishing without further strain. This new surface was lightly etched to show up the grain configuration. After further straining, an examination of these boundaries with interference fringes showed that the irregularities led to variations in step height from point to point along the boundaries. Polygonisation was also observed along some grain boundaries, as shown in fig. 4.25. Triple point folds occurred in only a few isolated grains, and were usually very short. With specimen MX21, continued etching of the original surface showed that there was a transition from smooth to irregular boundaries over a depth



FIG. 4.23. Grain boundary configuration
at surface.
Specimen MX 31 at 5.18%
strain. (570).

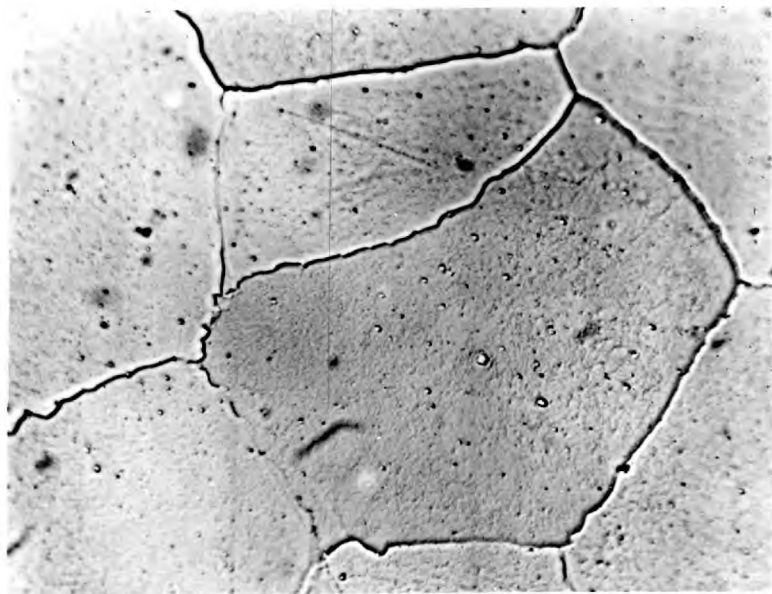


FIG. 4.24. Grain boundary configuration
internally.
Specimen MX 31 at 5.18 %
strain. (X 570).



FIG. 4.25. Internal polygonisation.
Specimen MX 21 at 8.89%
strain. (X 325).

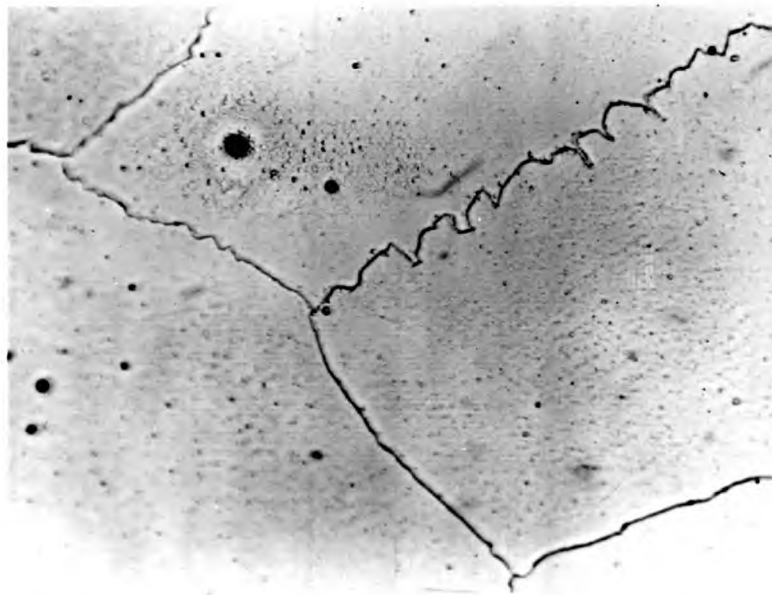


FIG. 4.26. Highly corrugated internal
boundary.
Specimen MX 31 at 5.18%
strain. (X 570)

of about half a grain diameter. Occasionally an exceptionally corrugated boundary was observed, as shown in fig. 4.26, giving the appearance of a boundary whose migration has been held up at numerous locking points. However, less than 1% of the boundaries were this corrugated. It was also a general impression that the higher values of v usually occurred on the straighter boundaries, although no quantitative measurements were made to substantiate this.

4.4. Tests at 250°C and 300°C.

To extend the sliding data to a higher temperature, tests were carried out in an argon atmosphere at 250°C ($0.57 T_m$) and 300°C ($0.62 T_m$). The experimental details are given in Table 4.5.

4.4.1. Sliding Measurements.

The results obtained at these higher temperatures were basically similar to those at 200°C. Measurements of the dependence of $\bar{v}_{av}$ on extension again yielded curves having an initial linearity, as shown in fig. 4.27 for the two specimens tested at 250°C.

Specimen MX26 was repolished at a strain of 9%, in a manner similar to that carried out at the lower temperatures, and the result again showed an increase in $d\bar{v}_{av}/dt$ with

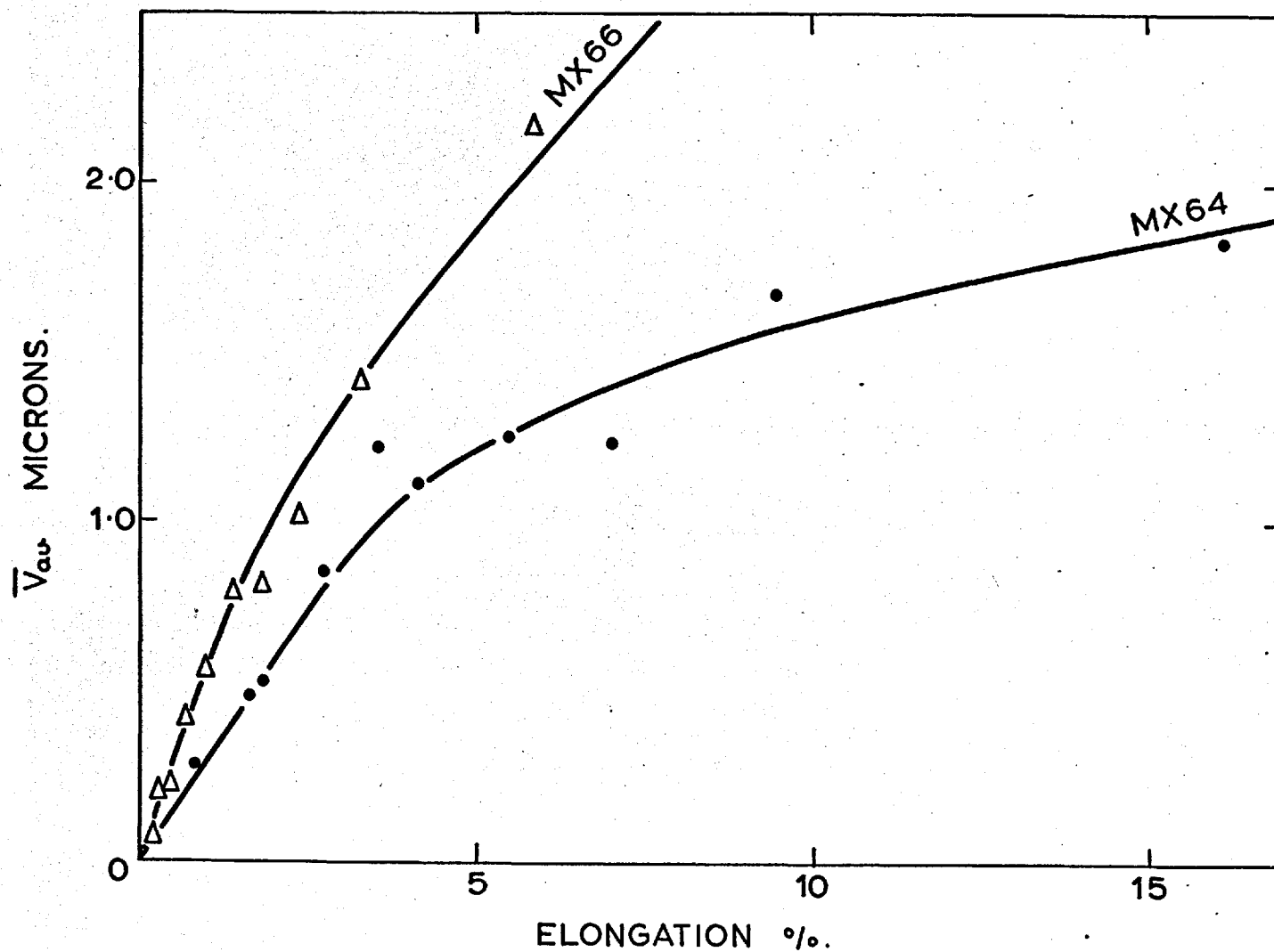


FIG. 4.27. Sliding-extension curves at 250°C.

subsequent straining. However, owing to the high rate of strain occurring in tertiary creep, only three points were obtained for $\bar{v}_{av}$ after repolishing, and it was therefore not possible to accurately assess the new rate of sliding.

The values of E_{gb}/E_{tot} for specimens MX26 and MX43 showed an increase with decreasing stress, in conformity with the results obtained at 200°C. However, a comparison of specimens MX7 and MX26 revealed that the grain size effect, outlined in section 4.1.3., was apparently reversed, so that the coarser-grained specimen now exhibited the larger sliding contribution. It seems unlikely that this is a genuine effect, since the slope of the sliding-extension curve for specimen MX7 is defined by two points only, and thus the absolute value of $\bar{v}_{av}$ at any given strain is subject to a large error bar.

A comparison of the values of E_{gb}/E_{tot} obtained at these higher temperatures with those obtained at 200°C (Table 4.1) shows that, under similar conditions of stress and grain size, the amount of sliding per unit extension decreased with increasing temperature through the range 200 - 300°C. This is contrary to the results obtained in the range 125 - 200°C (Tables 4.1 and 4.4), where E_{gb}/E_{tot} appeared to be independent of temperature, and also contrary to the widely accepted opinion^{124,131,132} that the grain boundary sliding contribution increases with an increase in temperature.

Some previous workers^{108,110,114} have found E_{gb}/E_{tot} to be invariant with increasing temperature under conditions of constant stress. On the other hand, McLean and Farmer¹⁰⁰ reported an invariance in Al by reducing the stress at the higher temperatures to give a constant rate of strain. The results reported here agree in principle with those of McLean and Farmer, since it follows from their work that an increase in temperature at constant stress should lead to a decrease in E_{gb}/E_{tot} , and in fact they specifically noted that an increase in the strain rate at constant temperature yielded a lower value of E_{gb}/E_{tot} . A closer analysis of the results of Fazan et al¹¹⁴ revealed that in each case they found a slight decrease in E_{gb}/E_{tot} with increasing temperature, but since the tests were all of an extremely short duration the values of E_{gb}/E_{tot} were always less than 10%. Similarly, the experiments of Martin et al¹¹⁰ were also carried out under fast rates of strain, such that even at the lowest temperature the strain rate was 0.7%/hour. It therefore seems likely that the last two results may not apply to long-term high-temperature creep conditions. The work of Rozenberg¹⁰⁸ on Ni at constant stress was carried out over a wider temperature range (600 - 750°C), but, since this only corresponds to a range of 0.51 - 0.59 T_m , it is possible that this was insufficient to produce any marked decrease in E_{gb}/E_{tot} . Even so, Rozenberg obtained a low

value of E_{gb}/E_{tot} at the highest temperature, but made no comment on this.

In the present work, the situation is somewhat different owing to the use of an h.c.p. metal. As the temperature-sensitivity of the rate of grain boundary sliding is very much greater than that of slip on the (0001) plane, it would be expected that E_{gb}/E_{tot} should increase with increasing temperature. In fact, since this was not observed, it is necessary to account for the experimental results by invoking an additional mode of deformation which has a greater temperature-sensitivity than that of sliding. It is suggested that this additional mode is slip on the non-basal planes, since some evidence for this already exists.

At 200°C, for both high and low rates of strain, the dominant modes of deformation of Mg^{132,161} and magnox¹⁶⁰ are basal slip and grain boundary sliding. However, Bakarian and Mathewson¹⁷³ have shown that at temperatures greater than about 225°C non-basal slip becomes operative due to slip on the pyramidal planes, and Chaudhuri et al¹⁷⁴ have suggested this is due to cooperative slip occurring consecutively along the $\{10\bar{1}0\}$ and $\{10\bar{1}1\}$ planes in a common slip direction. They also found that the non-basal slip bands developed progressively during creep, and it was suggested that the type of slip occurring may depend on the strain rate, since at room temperature the higher rates

would be accommodated by twinning and kinking. Jones and Harris¹⁴⁶, investigating the deformation of polycrystalline Mg, found that non-basal slip traces became more frequent with increasing temperature and strain rate, until, at a temperature of 426°C, they were characteristic of every grain for specimens tested under rapid rates of strain ($\geq 10^{-6} \text{ sec}^{-1}$).

In the present experiments, non-basal slip traces were only seen occasionally in a small number of the larger grains at 200°C, in agreement with the results of other workers¹⁷⁵, and usually only in those tests conducted at fast rates of strain. At 250°C, non-basal traces, in the form of irregular bands, were especially evident in specimen MX64, tested at the larger stress, but at 300°C non-basal slip was observed in all three specimens. This was in agreement with the work of Jones and Harris¹⁴⁶, since the minimum creep rates were fairly high in each case*. It is therefore concluded that non-basal slip becomes an increasingly important mode of deformation as the temperature is increased through the range 200 - 300°C, and that the temperature-sensitivity is greater than that of sliding.

* about 10^{-5} sec^{-1} for specimens MX7 and MX26.

Although E_{gb}/E_{tot} was lower at the higher temperature, it should be noted that the minimum sliding rate was very much increased, as shown below:

$$\text{MX7:} \quad d\bar{v}_{av}/dt = 1.73 \times 10^{-4} \text{ cm/hour (200}^\circ\text{C)}$$

$$\text{MX4:} \quad d\bar{v}_{av}/dt = 8.16 \times 10^{-8} \text{ cm/hour (300}^\circ\text{C)}.$$

Since the increase in secondary creep rate between specimens MX4 and MX7 was of the order of 4.3×10^3 , the increase in sliding rate of 2×10^3 was therefore insufficient to compensate for this.

4.4.2. Metallographic Observations.

Polygonisation was observed along many of the grain boundaries during the initial stages of the tests, resulting in very small grains in the position of the original boundary. After repolishing specimen MX26, for example, it was estimated that, at a total strain of 10%, about 30% of the boundaries were polygonised. Sliding was often observed, by the displacement of interference fringes, at the new boundaries created by polygonisation, in a manner similar to that reported in magnox by Harris¹⁷⁶. It was also found that the internal boundaries were again corrugated at 300°C, in contrast to the results of Couling and Roberts¹²⁴, where such boundaries were observed on repolished Mg specimens at 149°C but not at 315°C. However, this apparent discrepancy is resolvable in terms of strain

rate, since their tests at 315°C were carried out at a low stress and a very much reduced rate of strain. Suiter and Wood¹⁶¹ have also reported the absence of corrugations in Mg at 350°C , but again their experiments at this temperature were carried out at a slow strain rate.

4.5. The Effect of Thermal Cycling.

The experimental procedure used in this investigation involved creep testing specimens at high temperature for a given length of time, cooling them to room temperature and taking measurements, and then re-heating for further creep. Thus the procedure involved thermal cycling, and it was essential to know if this had any effect on either the creep rate or the incidence of slip and sliding.

The possible effect of thermal cycling was first demonstrated by Boas and Honeycombe¹⁷⁷, who tested specimens of Sn, Cd, Zn and Pb, and showed that, in all but the last named cubic metal, the anisotropy of thermal expansion was sufficient to cause inter-crystalline stresses and a resultant plastic deformation. More recently, a number of workers, studying the effects of thermal cycling, have shown the occurrence of deformation phenomenon such as slip, twinning, boundary sliding and migration in both bi-crystal¹⁷⁸ and polycrystalline¹⁷⁹ specimens.

It seemed probable, however, that thermal cycling would have no effect on this work, since Kuznetsov et al¹⁸⁰ have shown that there was no measurable effect on Zn specimens after cycling through 175 cycles to an upper temperature of 130°C (0.58 T_m), and that it was necessary to go to a higher upper temperature. Further work¹⁸¹ revealed that the effects of thermal cycling on Mg were less than on Zn because of the smaller anisotropy of thermal expansion. Since the highest temperature used in this work was only 300°C (0.62 T_m), and the number of cycles was always very small, it seemed likely that there would be no measurable effect. However, this was checked by carrying out two thermal cycling tests.

In the first test, a specimen was thermally cycled between room temperature and 200°C for a total of 10 cycles, being held at the upper temperature for periods between 3 and 120 hours. There was no measurable extension after this treatment, but the majority of grain boundaries became visible, and about 20% of them showed very small displacements perpendicular to the surface, usually of the order of 0.05 μ . A critical examination of the surface revealed the presence of migration at only two grain boundaries, but some slip was visible in one or two of the larger grains.

A second test was carried out by subjecting a specimen to a similar cycling programme with an upper temperature of 300°C , and after 10 cycles there was a small but measurable increase in length ($< 0.1\%$). This was probably due to the preferred orientation. All boundaries were then visible, a number of them showing migration, and slip was evident in some grains. About 80% of the boundaries showed steps between grains, which were usually small, up to 0.1μ , but were occasionally larger than this, up to a maximum of 0.2μ .

The results of these tests therefore confirmed that, under the experimental conditions used in this investigation, the deformation due to thermal cycling was very much less than that due to creep.

4.6. The Configuration of Grain Boundaries at the Surface.

In an attempt to explain the discrepancy observed by Rachinger¹¹³ between surface and interior grains, Gifkins¹⁸² was the first to point out that a difference in grain topography exists between an annealed and an "as-cut", or polished, surface. This is because the boundaries of surface grains tend to an equilibrium position normal to the surface during annealing, whereas an as-cut surface, as with a plane through the interior, has a random distribution of boundary intersections. It was therefore suggested that polishing after the annealing treatment would give an as-cut

surface that is initially typical of the interior, but under creep conditions this may, as a result of migration, give the same distribution of surface angles as on annealing. To test this hypothesis, four sets of experiments were planned, and these are outlined in sections 4.6.1. - 4.6.4.

4.6.1. Annealed and As-cut Configurations after Heat Treating at 430°C.

An initial test was carried out to determine the difference between an annealed and an as-cut surface, by heat treating two polished specimens under the same conditions of temperature (430°C) and time (2 hours) to give similar grain sizes. One specimen was then repolished, by removal of about 5 grain diameters, but the second specimen remained in the annealed state. Both specimens were sectioned transversely using a piercing saw, and mounted in cold-setting resin. The transverse section, perpendicular to the original surface, was then polished and etched to show the boundary configuration.

Fig. 4.28 shows a typical transverse section normal to the surface in the annealed specimen, for which three sets of readings were taken

- (i) The angle β made by the boundary at the point where it intersected the surface.

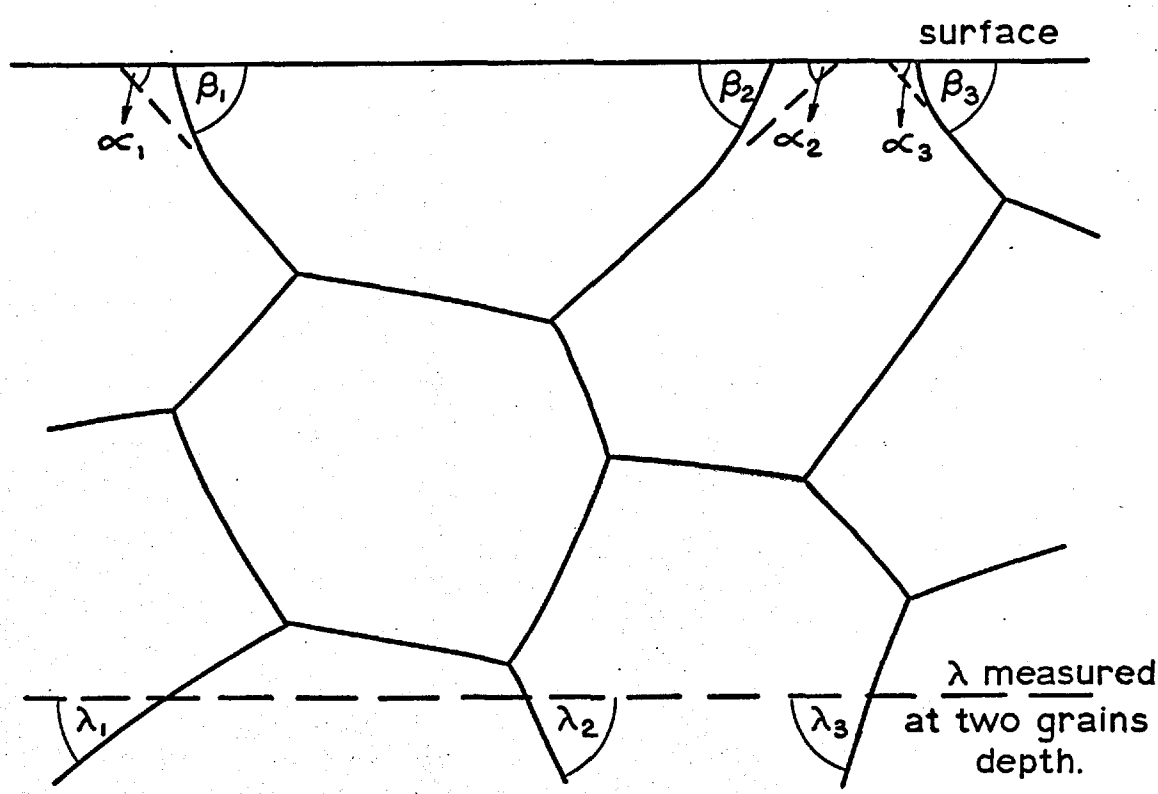


FIG. 4. 28. Transverse section of an annealed surface.

- (ii) The angle α between the surface and the extrapolated boundary at the first triple point below the surface.
- (iii) The angle λ between the boundaries and a line scribed parallel to the surface at a depth of the order of two grain diameters.

On the as-cut specimen, only the angle β between the boundary and the surface was measured. In each case, 400 readings were required to obtain smooth histograms, and it was therefore necessary to repolish the specimens several times, perpendicular to the surface at which the angles were being measured, to obtain this large number of readings. A depth of at least two grain diameters was removed between each set of readings, so that an entirely new boundary configuration was studied each time.

It should be noted that, as Davies and Wilshire¹⁸³ have pointed out for the case of slip planes, the observed distribution of the angles β along a given section does not represent the true distribution of angles with the surface. This can be seen by reference to fig. 4.29, where A, D and E are in the plane of the surface, and ABCD represents a grain boundary inclined at a true angle ϕ . If BEF is the random plane of sectioning, then the measured or observed angle β is less than ϕ . It can be seen that a boundary making a true angle of ϕ with the surface may appear on sectioning at any angle β where $\phi > \beta > 0^\circ$.

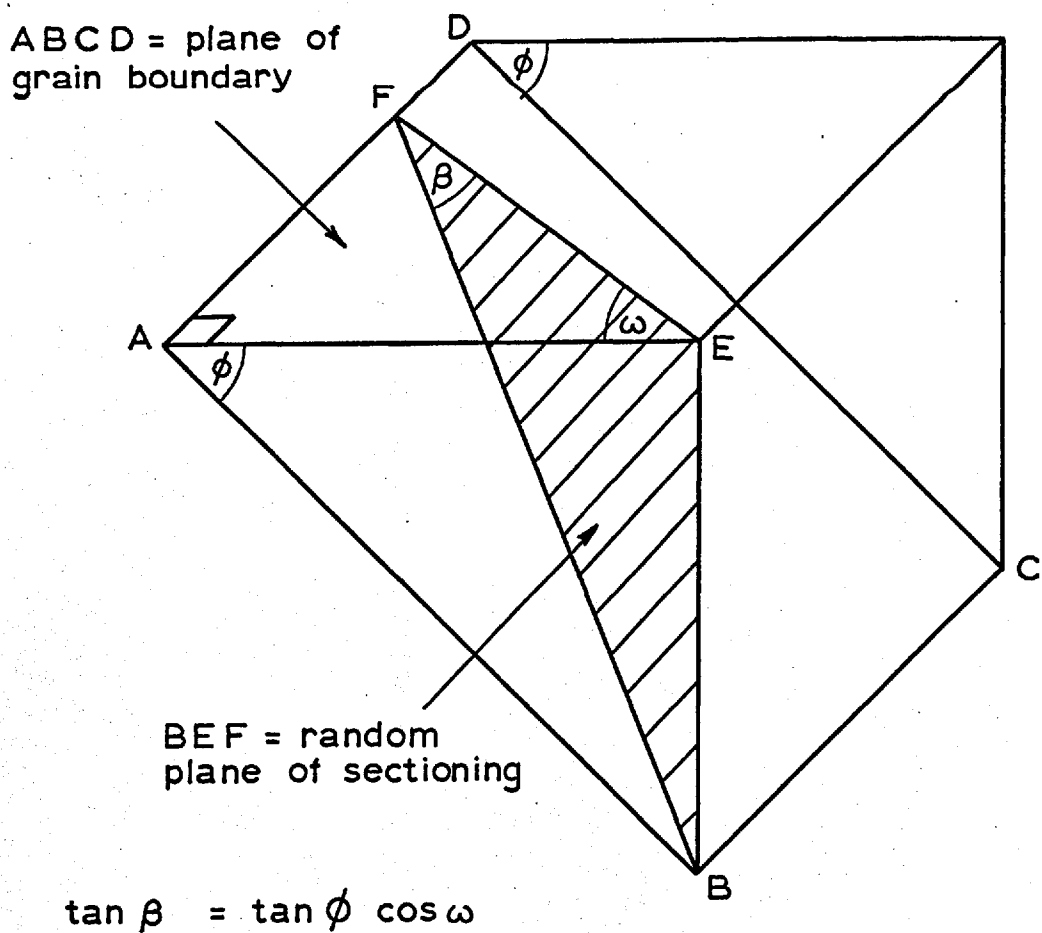


FIG. 4.29. Relationship between true (ϕ) and observed (β) angles.

From the diagram, it follows that

$$\tan \beta = \tan \phi \cos \omega, \quad 4.4.$$

where ω is the angle between the plane of sectioning and the normal to the grain boundary. Using this equation, it is therefore possible to calculate the true angle ϕ . No such correction was made in the present work, however, since the internal angle ψ , as defined in section 2.3.3, refers specifically to the angle measured on a particular plane of sectioning.

In fig. 4.30, the histograms are shown for (a) the observed angles β on the annealed surface, and (b) the observed angles β on the as-cut surface. The latter distribution is approximately sinusoidal. This was as expected, since it follows from Buffon's needle problem¹⁸⁴ that the distribution of angles intersected by a random line will follow a sine relationship, with an average angle equal to one radian (57.3°).

The average observed angles were calculated in each case, and the results obtained were as follows:

	$\overline{\beta}$	$\overline{\alpha}$	$\overline{\lambda}$
Annealed:	77°	61°	59°
As-cut:	58°		

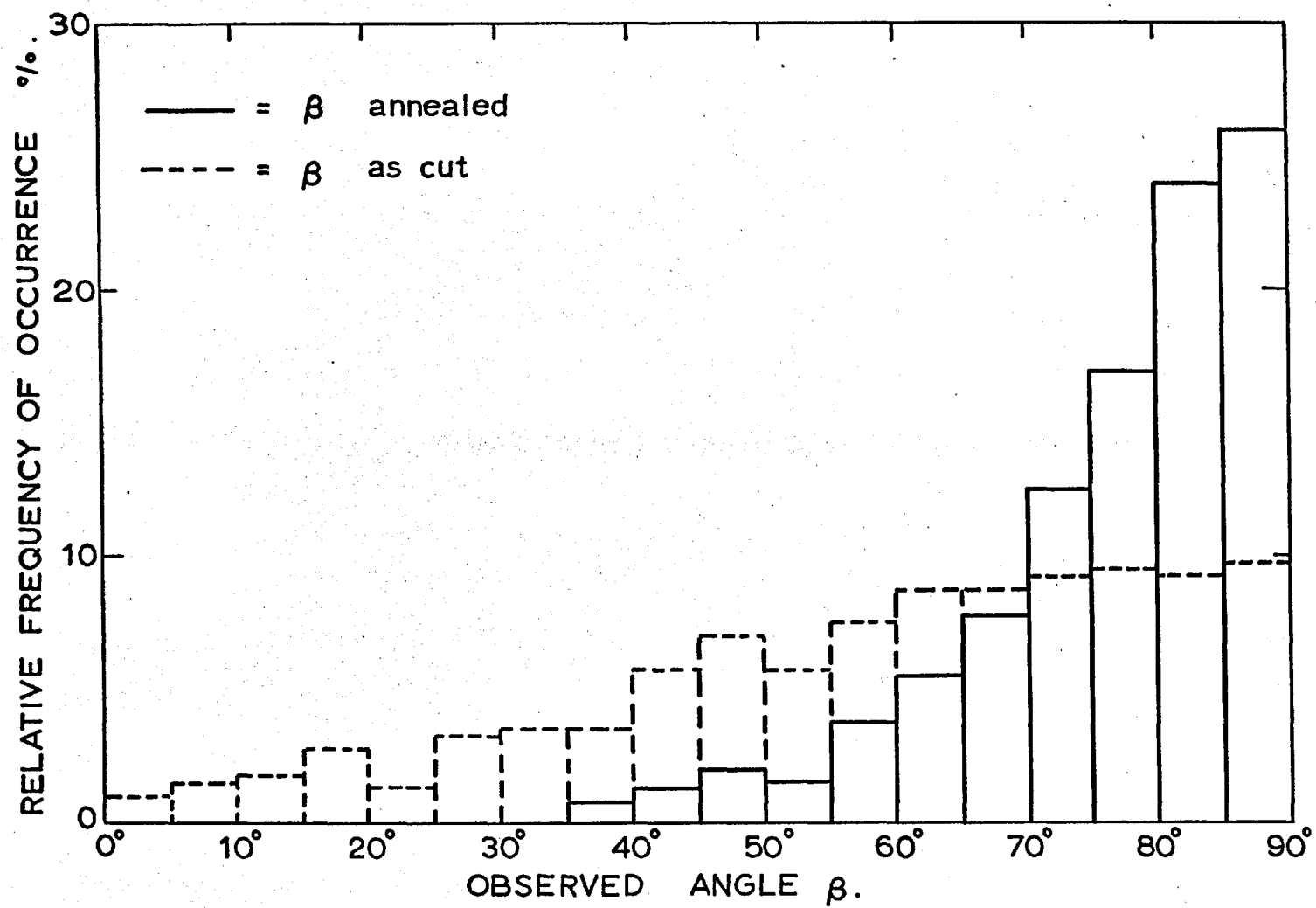


FIG. 4.30. Histograms of observed angles.

The value of 58° obtained for the as-cut surface is very close to the value of 57.3° predicted theoretically. The high value of $\bar{\beta}$ on the annealed surface confirms that the boundaries tend to an equilibrium position perpendicular to the surface during the annealing process, but, since the force pulling the boundaries to this position decreases as the angle approached 90° , the equilibrium value is only attained by a small proportion of the boundaries, and the average angle is 77° . The histogram of β for the annealed surface shows that no readings were recorded of less than 35° , and it was also observed that many of the lower values of β occurred when two boundaries intersected the surface from the same triple point situated just below the surface. The value of $\bar{\alpha}$, slightly higher than $\bar{\beta}$ for the as-cut surface, indicates that there is a depth effect due to the surface migration, although this may not be a genuine observation since it was difficult to measure this angle by extrapolation. The average curvature of the boundary from the point of intersection of the surface to the triple point is given by $\bar{\beta} - \bar{\alpha} = 16^\circ$, but, in general, most of the curvature was observed to be immediately beneath the surface. The similarity between $\bar{\lambda}$ on the annealed surface and $\bar{\beta}$ on the as-cut surface shows that an as-cut configuration was obtained at a depth of less than two grain diameters.

4.6.2. Sliding Measurements with an Annealed Configuration.

All tests in sections 4.1 - 4.4 were carried out on specimens having as-cut surfaces. However, since it has been established that there is a difference between an as-cut and an annealed boundary configuration, a test was undertaken to study the effect of using an annealed surface.

Two specimens, MX51 and MX54, were annealed to give a similar grain size to specimens MX25 and MX4 respectively. They were then tested under the same conditions as these specimens, at stresses of 6000 and 4000 p.s.i. respectively (See Table 4.6), but with annealed rather than as-cut surfaces. As was expected, the creep curves were unaffected by the presence of a different surface configuration, since the internal boundary structure remained unchanged. Measurements of $\bar{v}_{av}$ were taken at successive increments of strain throughout the test, in the usual manner, and the grain size was checked at a low strain when the boundaries first became visible as a result of the boundary offsets. In each case, the $\bar{v}_{av}$ values for the annealed surfaces were less than those for the as-cut surfaces at similar strains. In addition, the sliding-extension curves for MX51 and MX54 were fairly linear up to a high strain. This is shown for MX54 in fig. 4.31, in which the curve for the as-cut surface is also given. The curves for MX51 and MX25 were similar to these, although there was a smaller difference between the

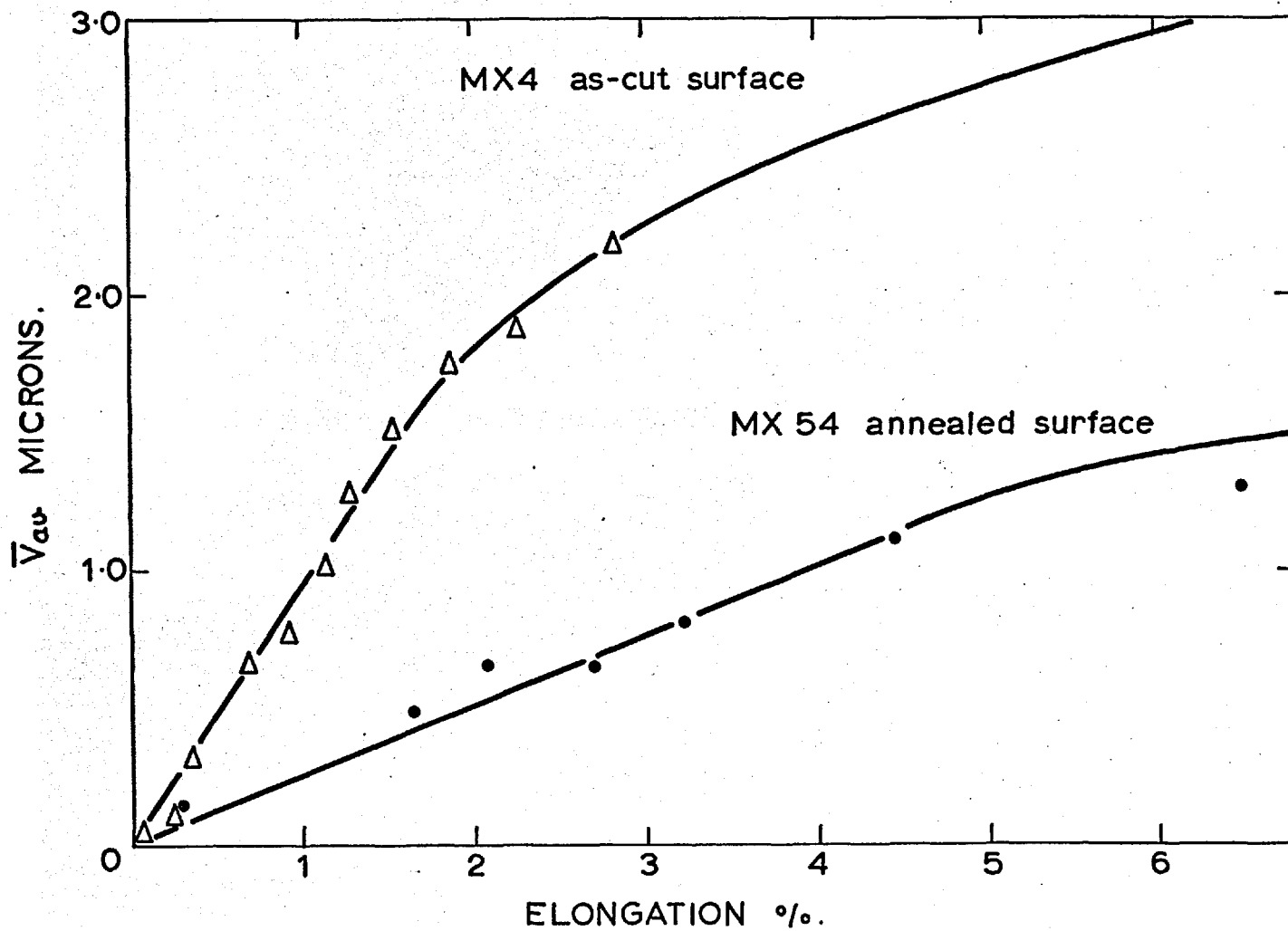


FIG. 4.31. Effect of using an annealed surface.

two types of surface at any given strain. The values of E_{gb}/E_{tot} for the annealed surfaces, shown in Table 4.6, were calculated by putting $k = 1.07$ in equation 3.1. However, this calculation may not be valid, since it seems likely that a different value of k will apply to an annealed configuration. This is discussed in more detail in Chapter 5.

Only a small amount of migration was observed on the annealed surfaces during deformation, in contrast to the large amounts often observed on as-cut surfaces. It was therefore an easy matter to take the individual readings of v . This lack of migration indicated that annealed surfaces were more stable than as-cut surfaces during creep, although it was also observed that, with the annealed configuration, small corrugations were often formed in the surface boundaries.

4.6.3. The Change of Boundary Configuration at an As-cut Surface During Creep.

A test was carried out to check the suggestion, made by Gifkins¹⁸², that the boundary configuration at an as-cut surface may change under prolonged creep.

A number of specimens was prepared having a grain size of the order of 100 grains/cm., and these were creep tested, under a stress of 4000 p.s.i. at 200°C, for varying lengths of time between 5 and 500 hours. The conditions were

therefore the same as those used for specimen MX2 (See Table 4.1). This test also served to check the reproducibility of the creep curve in the absence of the alternate heating and cooling that occurred during the routine tests. For the majority of specimens, the reproducibility was quite good within the primary and secondary regions of creep, although there were often large differences between the behaviour of identical specimens in tertiary and occasionally in the later stages of secondary creep. Since the main interest of this work was centred on the linear portion of the sliding-extension curve, which terminated towards the end of the secondary stage, this lack of reproducibility in the tertiary stage was unimportant. The final value of $\bar{v}_{av}$ was measured on some of the specimens which were strained without interruption, and there was fairly good agreement, within experimental error, with the value measured at a similar total extension in the interrupted test of specimen MX2.

Each specimen was sectioned transversely, mounted in resin, and then polished, perpendicular to the original surface, and etched. Readings were taken of the angle β made by every boundary with the surface, and in each case a total of 400 measurements was recorded, and the average angle $\bar{\beta}$ calculated. Fig. 4.32 shows that the observed angle changed almost linearly with strain, from an initial value

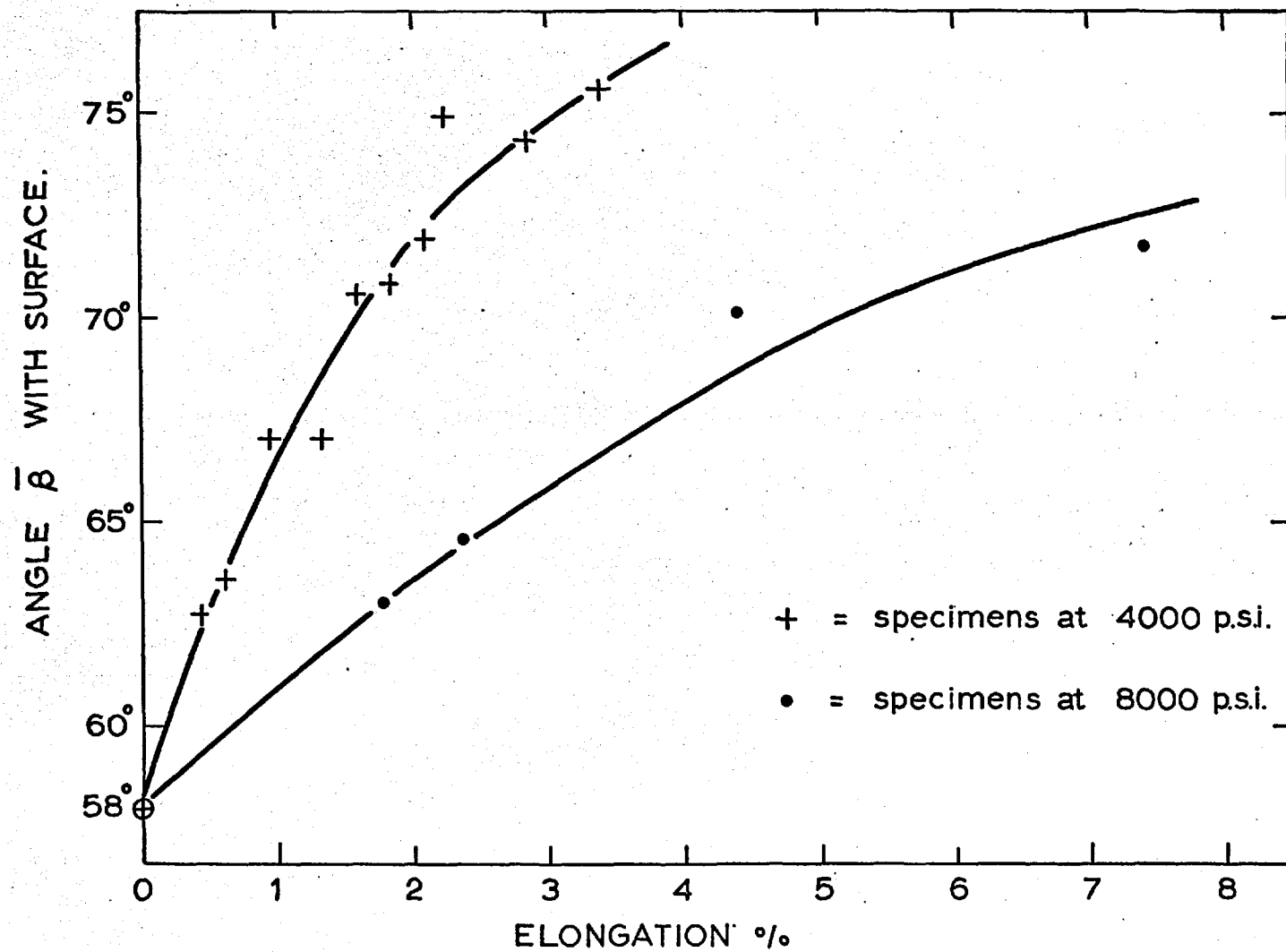


FIG. 4.32. Change of angle with strain.

of 58° for an as-cut surface, to a value of about 74° at a strain of 2-3%, after which there was only a gradual migration to higher angles. The initial rate of change of angle was quite rapid, as shown in fig. 4.33. For example, a specimen tested for only 5 hours, to a strain of 0.42%, yielded an average angle of 62.8° .

The result of this experiment suggests that the observed linearity between $\bar{v}_{av}$ and extension during the initial stages of creep is connected with the change of angle that is taking place concurrently, since the strain at which the sliding-extension curve deviates from the initial linearity appears to coincide approximately with the strain at which the internal angle saturates. This can be seen by comparing the curve for the specimens tested at 4000 p.s.i. in fig. 4.32 with the sliding-extension curve for specimen MX2 in fig. 4.2. At higher strains, the sliding is again approximately linear with extension, but with a smaller slope than the initial one, and similar to that obtained for an annealed surface.

If the high initial slope is due, in some way, to the presence of rapidly migrating boundaries, then it should also be possible to explain the observation that the linear portion of the sliding-extension curve extended to a higher total strain under a higher stress (fig. 4.2). A second test was therefore carried out, in which five specimens of

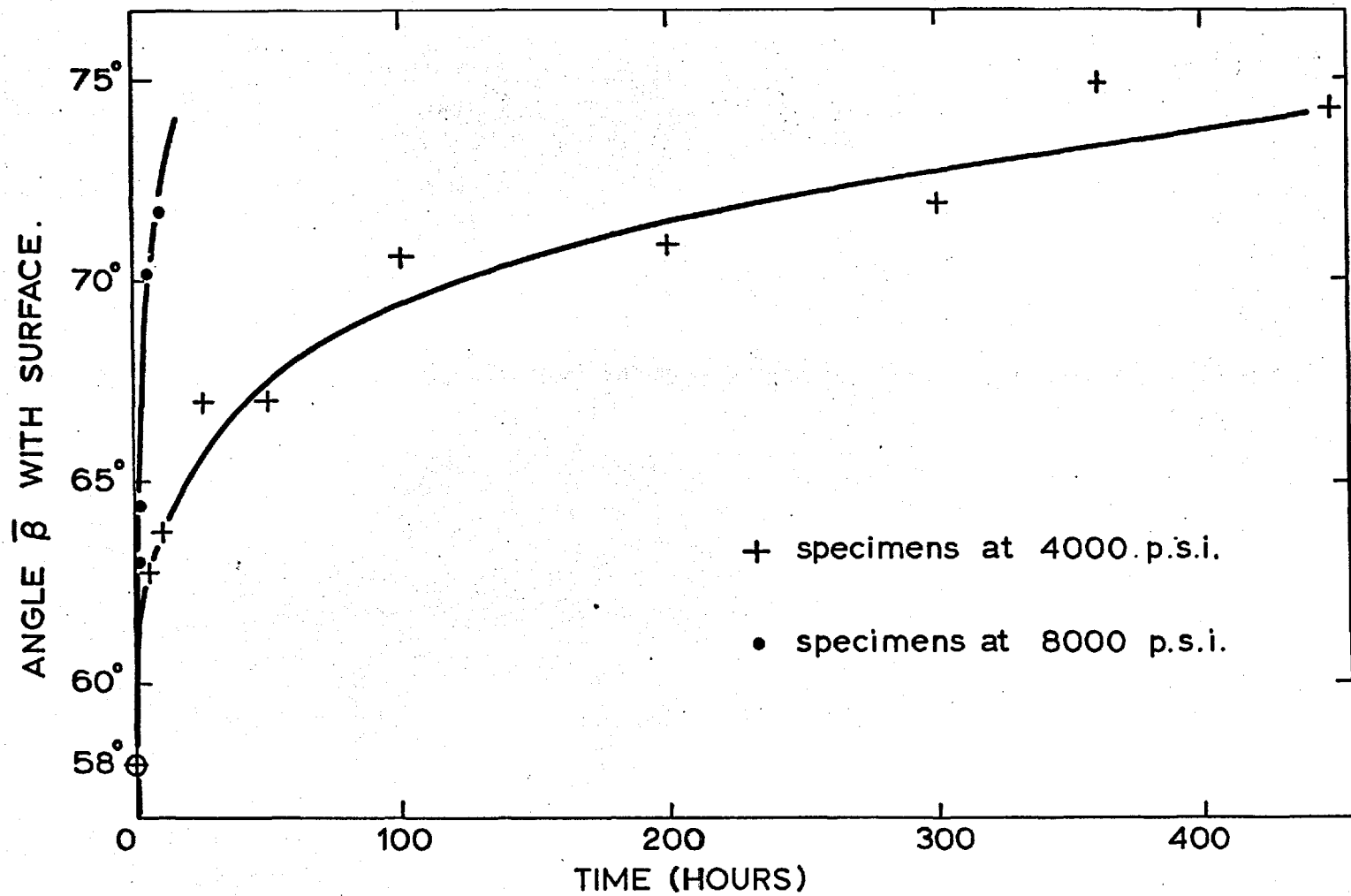


FIG. 4.33. Change of observed angle with time.

similar grain size were tested for varying lengths of time at a temperature of 200°C and under a stress of 8000 p.s.i. These specimens were therefore directly comparable with specimen MX31 (See Table 4.1). The measured average angle $\bar{\beta}$ was again plotted against extension, as shown in fig. 4.32, and it was found that there was a fairly linear change, as with the previous specimens, but this now extended to a higher strain. The rate of migration of the surface boundaries was very much faster at the higher stress, as shown in fig. 4.33, but, since this was not sufficient to compensate for the much faster creep rate, the change in angle took place over a wider range of strain. It was not possible to test whether the strain at which the angle saturated corresponded closely with the strain at which the sliding-extension curve deviated from linearity, since specimen MX31 was repolished after 5.2% elongation (fig. 4.22).

As an additional check on the above results, a specimen was creep tested and then sectioned both transversely and longitudinally. The average observed angles $\bar{\beta}$ and $\bar{\psi}$, made by the intersection of the boundaries with the free surface on the transverse and longitudinal sections respectively, were the same, within experimental error, in both cases, and thus indicated that representative measurements were obtained solely from transverse sectioning.

4.6.4. The Change of Boundary Configuration
at an As-cut Surface on Annealing
at 200°C and 300°C.

Tests were carried out to determine whether a change of angle occurred at an as-cut surface at temperatures of 200°C and 300°C respectively. The specimens used for this work were held at temperature for 24 hours without applying a stress, and then removed from the furnace, sectioned, and angle measurements taken in the usual way. The average surface intercept angle for the specimen treated at 200°C was found to be 59.5°, which, although slightly higher than that measured on an as-cut surface, was the same within experimental error. A similar result was also obtained on a specimen thermally cycled between room temperature and 200°C for a total of 10 cycles. This was consistent with the surface observation that there was only a very small amount of migration at one or two of the boundaries. At 300°C, the average intercept angle after 24 hours treatment was 69.5°, which showed that this temperature was sufficient to cause migration in the absence of a stress.

4.7. Measurements of Longitudinal and Transverse Offsets.

In the majority of tests undertaken in this work, the contribution made by grain boundary sliding was determined from a measure of the average boundary offset ($\bar{v}_{av}$)

occurring perpendicular to the surface. This parameter was chosen since, using interferometry, it was more accurately measured at very low strains than the average longitudinal ($\bar{u}$) or transverse ($\bar{w}$) offsets occurring in the plane of the surface*. However, for reasons outlined in Chapter 5, it became apparent during the course of this work that a more reliable value of E_{gb}/E_{tot} may be obtained from measurements of u or w . Some readings of these parameters were therefore taken, so that a comparison could be made between values of E_{gb}/E_{tot} obtained independently from u , v and w measurements. The results of this analysis are given in section 5.2.2.(b). In addition, a number of previous workers have measured the variation of u , v or w with respect to θ , the angle between the grain boundary and the stress axis in the plane of the surface, and their results show little agreement. The present measurements therefore provided a direct comparison with this other work.

4.7.1. Variation of u , v and w with θ .

Specimen MX63 was used for this investigation, and experimental details are given in Table 4.1. Prior to testing, a grid of fine lines was scribed on the specimen

* A definition of terms has already been given in section 2.3.3 (fig. 2.1).

surface using a diamond stylus attached to a micrometer stage. A total of 600 measurements was taken of both u and w , at an overall strain of 2.49%, and in each case the angle θ was also recorded. The appearance of typical offsets is shown in figs. 4.34 and 4.35. For ease of measurement, readings of u were only made from the offsets of transverse lines, and readings of w only from the offsets of longitudinal lines. Since the probability of a transverse marker crossing a grain boundary decreases as θ increases, no readings of u were obtained for angles of θ greater than about 80° . Similarly, no readings of w were obtained for angles less than about 10° . Thus the mean values of u in the range $60^\circ - 80^\circ$, and the mean values of w in the range $10^\circ - 30^\circ$, are subject to large error, since they represent the average of only a small number of readings. To determine the variation of v with respect to θ , 300 readings of v were taken in each 10° increment of θ , so that the mean value in each increment of angle, $\bar{v}_\theta$, was obtained with a high degree of accuracy. It was not possible to take such a large number of readings of u and w , since readings could only be taken at a point where the boundary was crossed by a scribed line.

Fig. 4.36 shows the resultant plot of $\bar{u}_\theta$, $\bar{v}_\theta$ and $\bar{w}_\theta$ versus θ , representing the average value obtained for each parameter in every 10° increment of θ . The general trend is

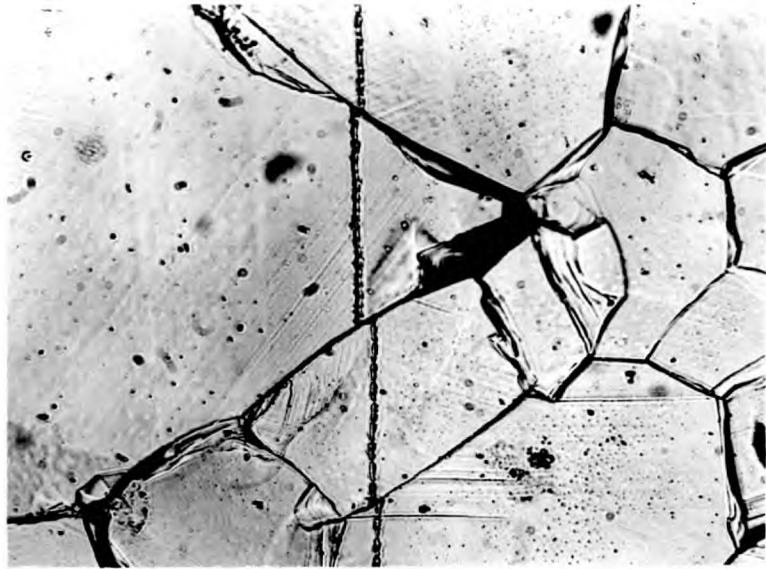


FIG. 4.34. Offsets revealed by scribed marker. Stress axis horizontal. Specimen MX63 at 2.49 % strain. (X 370).

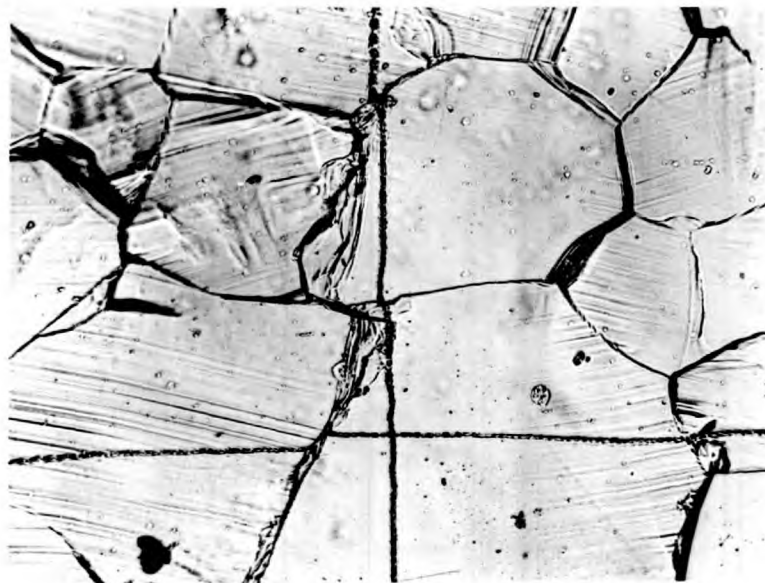


FIG. 4.35. As for fig 4.34. Specimen MX63 at 2.49 % strain. (X 270).

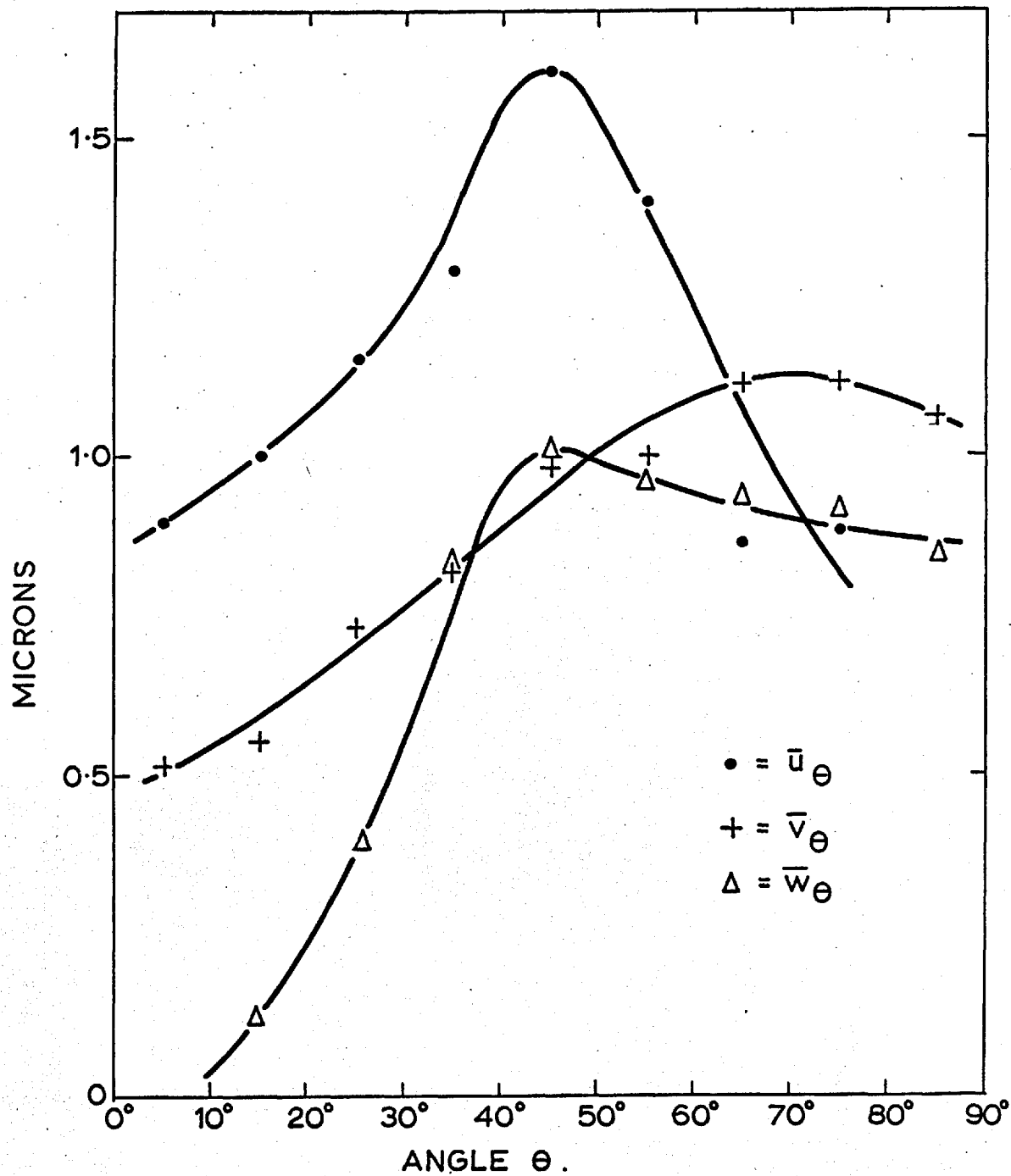


FIG. 4.36. Variation of u, v and w with θ .

for $\bar{u}_\theta$ to rise from some finite value at $\theta = 0^\circ$ to a maximum at $\theta = 45^\circ$, and thence to fall sharply at higher angles. In contrast, $\bar{w}_\theta$ rises from zero at $\theta = 0^\circ$ to a maximum at about $\theta = 45^\circ$, and then drops only slightly for higher values of θ . The mean vertical offset $\bar{v}_\theta$ rises slightly but significantly from $\theta = 0^\circ$ to $\theta = 90^\circ$, with the possible exception of a small drop for angles greater than about 70° .

At first sight it may appear that each curve should be of a symmetrical form about a peak at $\theta = 45^\circ$, since this angle represents the maximum resolved shear stress. However, this is incorrect, and the general trend of the curves is qualitatively explicable. The unsymmetrical nature of the $\bar{w}_\theta$ curve arises because the observed angle θ measured in the plane of the surface is not directly equivalent to the true angle γ between the plane of the grain boundary and the stress axis. This can be seen by reference to fig. 4.37, which is similar to that used by Davies and Wilshire¹⁸³ to analyse the case of slip planes. If the true angle is γ , then the observed angle on some random plane of sectioning, in this case the surface, is some angle θ such that $\gamma \leq \theta \leq 90^\circ$. Now w represents the transverse displacement of the sliding vector resolved into the plane of the surface, and the length of the sliding vector depends on the resolved shear stress. Since this is a maximum for $\gamma = 45^\circ$, it follows that $\bar{w}_\theta$ increases from

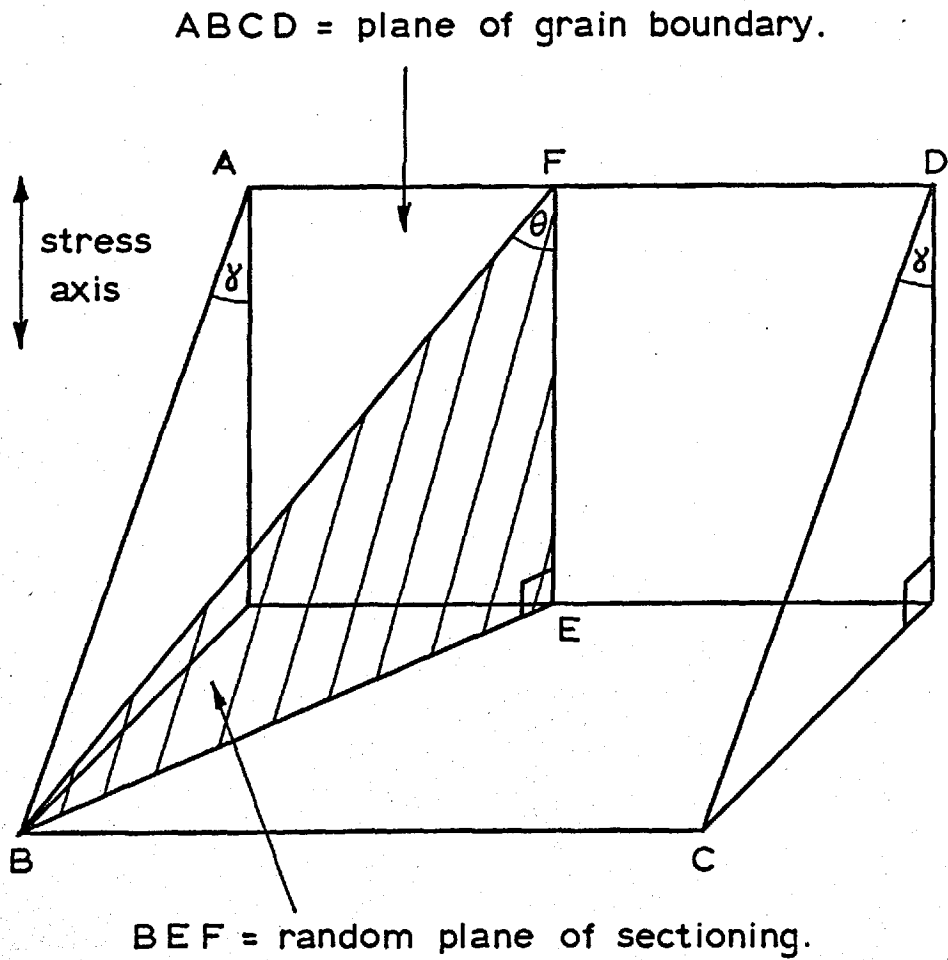


FIG. 4.37. Relationship between true (γ) and observed (θ) angles.

$\Theta = 0^\circ$ to $\Theta = 45^\circ$ because γ is also increasing. As Θ increases in the range from 45° to 90° , however, there will still be a number of boundaries for which the true angle γ is about 45° , but there will also be an increasing number for which γ has some higher value, thereby leading to a slight overall reduction in $\bar{w}_\Theta$. An analysis of this theory by Scriven and Williams¹⁸⁵ has shown that there should be an observed peak at about $\Theta = 50^\circ$, followed by a small fall for higher angles of Θ . This is similar, but not identical to the results obtained here, since their analysis predicts a slightly greater fall-off at higher angles.

The larger overall values of $\bar{u}_\Theta$ are explicable, since u is composed of both a v and a w component. This is discussed in more detail in section 5.1, and an equation (5.3) is derived relating u , v and w . Using this equation, together with the experimental values of $\bar{v}_\Theta$ and $\bar{w}_\Theta$, and by assuming $\bar{\psi} = 75^\circ$, it is possible to calculate the corresponding value of $\bar{u}_\Theta$ in any 10° increment of Θ . The resultant curve is of a similar form to that obtained experimentally, although there is some scatter on the individual points.

The shape of the $\bar{v}_\Theta$ curve is more difficult to interpret, since v represents the component of the sliding vector resolved perpendicular to the surface. The value of v therefore depends on the internal angle ψ between the

grain boundary and the surface, and there is no direct correlation between ψ and the observed angle Θ . Thus $\bar{v}_\Theta$ is essentially independent of Θ , but, at the same time, there is some dependence due to the inter-relation between Θ and the true boundary angle γ . Theoretically, this would indicate a modification of the Scriven and Williams analysis, to yield a curve that was only slightly dependent on Θ , with a peak at about 50° and a slight fall at higher angles. The experimental curve is in some agreement with this, although the maximum occurs at about 70° , and there is only a slight drop at larger angles.

A number of workers have taken measurements to determine the variation of u , v or w with Θ , and it is of interest to compare their results with those presented here. Couling and Roberts¹²⁴ measured u from transverse marker lines, and their plot of $\bar{u}_\Theta$ versus Θ yielded a curve of almost sinusoidal form, rising from $\bar{u}_\Theta = 0$ at $\Theta = 0^\circ$ to a maximum at $\Theta = 90^\circ$, although there was considerable scatter in the values at angles greater than 45° . This is a surprising distribution, and is completely inexplicable in terms of the present results. In contrast, Harper, Shepard and Dorn¹¹⁵ also measured u from transverse markings, and their $\bar{u}_\Theta$ curve was similar to the one reported here, being asymmetrical and rising to a peak at 45° . Rozenberg and Epshtein¹⁸⁶ measured the variation of the average vertical

offset with Θ , and obtained a curve in which $\bar{v}_\Theta$ peaked at 45° , but a large source of error was probably inherent in this work due to the taking of only a small number (unspecified) of readings. This result also conflicts with that presented here, and the authors erroneously reported agreement with the data of Dorn et al¹¹⁵, whilst overlooking the fact that they were measuring a different parameter. A more comprehensive survey was carried out by Gittins⁹⁷, who measured the variation of all three components with respect to Θ on β -brass. The results obtained for $\bar{u}_\Theta$ and $\bar{w}_\Theta$ were fairly similar to those reported here, but the variation of $\bar{v}_\Theta$ was different. Gittins observed a well defined linear relationship between $\bar{v}_\Theta$ and Θ , with $\bar{v}_\Theta$ rising from a minimum at 0° to a maximum at 90° . No explanation of this was given, and it is difficult to understand why linearity should occur.

From fig. 4.36, $\bar{u}_{av}$, $\bar{v}_{av}$ and $\bar{w}_{av}$ were calculated, representing the values obtained from a random distribution of boundaries with respect to the stress axis, by taking the mean of the average values in each 10° increment of Θ . In addition, the mean values $\bar{u}_{trans}$ and $\bar{w}_{long}$ were calculated directly from the readings taken for u and w along transverse and longitudinal traverses respectively. Because of the inherent experimental difficulty in measuring the longitudinal

offsets along a longitudinal marker line, no attempt was made to determine $\bar{u}_{\text{long}}$. Similarly, no readings were taken to determine $\bar{w}_{\text{trans}}$. A value was also obtained for $\bar{v}_{\text{long}}$, by taking readings of v along a longitudinal traverse.

The results obtained were as follows:

$\bar{u}_{\text{av}} = 1.395 \mu$	$\bar{u}_{\text{trans}} = 1.450 \mu$
$\bar{v}_{\text{av}} = 1.144 \mu$	$\bar{v}_{\text{long}} = 1.204 \mu$
$\bar{w}_{\text{av}} = 0.857 \mu$	$\bar{w}_{\text{long}} = 0.967 \mu$

The results show that the values of the three parameters are dependent on whether they are determined from random measurements, or from measurements taken by making a longitudinal or transverse traverse of the specimen. This is because a longitudinal traverse intersects boundaries inclined at an average angle of 57.3° with the stress axis, whereas the average angle with the stress axis intersected by a transverse traverse is 32.7° . A random selection of measurements refers to an average angle of $\theta = 45^\circ$. It is also apparent that, although $\bar{v}_{\text{long}}$ and $\bar{w}_{\text{long}}$ both represent the component of sliding measured perpendicular to the stress axis along a longitudinal traverse, the average offset is larger perpendicular to the surface. The significance of these results is discussed in more detail in Chapter 5.

4.7.2. The Occurrence of Negative Sliding.

When measurements are taken of the offsets perpendicular to the surface, using interference fringes or direct focussing, the actual direction of sliding is indeterminate, and it is therefore not possible to distinguish those cases in which the sliding makes no positive contribution to the overall extension. This effect, known as "negative sliding", may arise in two ways. Firstly, the grains may rotate, thereby producing offsets without contributing to the total strain. Secondly, under certain conditions, internal stresses may build up within the grains and cause sliding in a negative sense. It is therefore obvious that a large error could be introduced into the work if a substantial proportion of the readings were due to either of these factors. To check the incidence of negative sliding, u and w offsets were examined on a specimen having marker lines on the surface. Because of the presence of markers, it was then possible to distinguish directly those cases in which the sliding was in a negative sense.

Couling and Roberts¹²⁴ were the first workers to consider this, and they reported that 2 - 4% of their measured displacements were negative. If these were entirely due to grain rotation, then they must also be paired with the positive ones at the opposite sides of the

rotating grains⁶⁹, giving a possible redundancy of 4 - 8%. The same redundancy also applies to v measurements, since they may be subject to an error due to rotation about axes in the specimen surface. Mullendore and Grant⁸², investigating the creep of an Al-2% Mg alloy, reported that 20% of the grain boundaries showed negative sliding, but in this case the grain size was most irregular. In contrast, Gittins used β -brass specimens of a very uniform grain size and found negative sliding at only 2 boundaries in a total of 400 examined, whilst Evans¹⁸⁷, using Au of a regular grain size, found that 5% of the boundaries exhibited negative sliding.

In the present work, a study of 400 boundaries revealed that approximately 3% of them showed negative sliding. Thus the maximum possible redundancy on v readings was 6%. However, it appeared that it was invariably the smaller grains that rotated, and the vertical or horizontal offsets associated with these grains were usually small. It was estimated that the total percentage contribution to the $\bar{v}_{av}$ measurements made by negative sliding was only about 2 - 3%. It therefore appears that negative sliding only becomes important in specimens of varying grain size, and this is probably because, if very small grains are present, the possibility of accommodation by grain rotation is increased.

4.8. Determination of E_{gb}/E_{tot} from Grain Shape Measurements.

The first attempt to measure E_{gb}/E_{tot} in the interior of a specimen was made by Rachinger¹¹³ on pure Al, and his results are described in detail in section 2.3.3.(e). In brief, Rachinger determined E_{gb}/E_{tot} from grain shape measurements, and found that the value internally was very much larger than the value at the surface. However, Gittins⁹⁷ has recently repeated these experiments on the same material, tested under almost identical conditions, and reported a slightly lower value of E_{gb}/E_{tot} in the interior. These results are summarised in Table 2.2. Grant and co-workers¹¹⁷ have also taken grain shape measurements on pure Al, and they found that E_{gb}/E_{tot} decreased slightly below the surface, over a depth of about 1 grain diameter, and then remained constant.

Because of these anomalies, it was decided to carry out grain shape measurements on some of the creep specimens used in this work, and an initial test was undertaken to determine the number of readings required to give an acceptable error bar.

4.8.1. Statistical Analysis.

Specimen MX21 (See Table 4.4) was sectioned parallel to the stress axis at a total strain of 25.40%, and the maximum length L and maximum breadth B of 300

different grains were measured using a crossed grid in the eye-piece. E_s , the extension due to slip within the grains, was calculated for each pair of readings from a modified form of an equation due to Rachinger:

$$E_s = \left(\frac{bL}{2B} \right)^{2/3} - 1 \quad 4.5.$$

where ℓ and b , the original length and breadth before testing, were included to allow for the slight elliptical nature of the grains. It was then possible to calculate the average value of E_s , and hence obtain E_{gb} from the equation

$$E_{tot} = E_s + E_{gb} \quad 2.1.$$

The results derived for E_s/E_{tot} are shown below:

No. of grains measured.	E_s/E_{tot} calculated from	
	(i) $\left(\frac{\overline{L}}{\overline{B}} \right)$	(ii) $\left(\frac{\overline{L}}{\overline{B}} \right)$
100	96 $\pm$ 10%	95 $\pm$ 27%
200	94 $\pm$ 5%	93 $\pm$ 18%
300	93 $\pm$ 4%	94 $\pm$ 16%

The improved accuracy obtained by measuring the average L/B ratio can be seen by comparison of column (i) with column (ii), in which the results were calculated from the same figures but by using the ratio (average L/ average B). In the latter case, the absolute values were similar, because the L/B ratio was fairly constant, but the uncertainty was much greater due to variations in grain size. The errors represent the 95% confidence limits, and, in the second case, these were calculated by applying the formula for compounding variances.

Since measuring the length to breadth ratio of individual grains was a tedious, and time-consuming, task, readings were also taken using the original Rachinger technique of measuring the number of grains per unit length. This differed from the previous method (ii) in that it did not record the maximum diameter of each grain, and the same grains were not measured in each direction. The results obtained are shown below:

	<u>No. of grains counted.</u>	$\frac{E_s}{E_{tot.}}$
	500	81 $\pm$ 29%
	1000	87 $\pm$ 21%
Rachinger method:	1500	93 $\pm$ 17%
	2000	91 $\pm$ 16%

After a total of about 2000 intercepts, the absolute value by this method was similar to that obtained previously, but the error bars were still very large.

From these initial results, it was decided that the best method of determining E_{gb}/E_{tot} was from the average L/B ratio, and that a minimum of 150 readings was required to give an acceptable error bar.

4.8.2. E_{gb}/E_{tot} by Grain Shape.

Several creep specimens were sectioned parallel to the stress axis, polished and etched. In each case a total of 150 readings was taken of the length to breadth ratio of individual grains, and E_{gb}/E_{tot} was calculated in the manner indicated previously. For some specimens, measurements were also taken on the original surface, or, in the case of two specimens, on surfaces that had been repolished during the test. Full details of the results are given in Table 4.7. The error bars again represent the 95% confidence limits. No surface readings were taken for specimen MX31, since this specimen had been repolished at an intermediate strain of 23.97%.

The results reveal two interesting trends. Firstly, using the grain shape method, larger values of E_{gb}/E_{tot} were always obtained from readings taken internally, and, in those cases where no repolishing had been carried out during

the test, the difference between surface and interior was of the order of 10%. These results therefore show the same general trend as those of Gifkins¹⁸⁸ for a Pb-2.2% Tl alloy and Rachinger¹¹³ for Al, although in the latter case the variation between surface and interior was about 50%. However, the results conflict with those of Grant et al¹¹⁷ for Al, and Gittins⁹⁷ for Al, β -brass and β - γ brass, where a slightly lower value of E_{gb}/E_{tot} was obtained in the interior.

A second feature of the results is that the grain shape method, in comparison with results obtained by $\bar{v}_{av}$ measurements at the same strain, always appears to substantially overestimate the value of E_{gb}/E_{tot} . In general, the values obtained for E_{gb}/E_{tot} on the surface by the grain shape method are 2 - 4 times larger than those obtained from $\bar{v}_{av}$ measurements, although there is no obvious correlation between the two results. In those cases where the initial sliding contribution was known to be small, as in specimens MX21 and MX31 for example, there appears to be some agreement between the surface values obtained from $\bar{v}_{av}$ and the internal values obtained from grain shape. The large values of E_{gb}/E_{tot} obtained for some specimens by grain shape is almost certainly due to a "rounding-off" of the grains by migration, thereby invalidating this method of measurement. This is discussed in more detail in section 5.2.2.(c).

4.8.3. Comparison of E_{gb}/E_{tot} by Grain Shape and the Printed Grid Technique.

As an explanation of the large values obtained for E_{gb}/E_{tot} by the Rachinger method, it has been postulated⁴¹ that migration occurs to maintain the grains in an **equi-axed** configuration. If this is correct, it should be possible to distinguish the effect directly by measuring both the length to breadth ratio of individual grains, and the length to breadth ratio of printed grid lines contained within the grains. Thus, if migration occurs to maintain an equi-axed structure, the effect will be localised entirely at the boundary and will reduce the overall length to breadth ratio of the grain. It will not, however, affect the grain interior, so that the ratio obtained by the grid measurements will give a true indication of E_s .

Specimen MX74 was used for this test. The experimental details have already been given in Table 4.2. The specimen was strained to 16.77%, and surface readings were taken to determine E_{gb}/E_{tot} by two methods:

- (i) By the average L/B ratio of the grains.
- (ii) By the average L/B ratio of the printed grid lines within the grains.

Measurements were also taken to determine the average vertical offset $\bar{v}_{av}$. The results obtained were as follows:

Method.	$\left(\frac{L}{B} \right)$	E_{gb}/E_{tot}
By grain shape:	1.215	18.8%
By printed grid:	1.237	10.1%

The larger L/B ratio obtained from the grid measurements confirmed that migration was tending to "round-off" the grains, resulting in a higher value of E_{gb}/E_{tot} by the Rachinger method. The value of k calculated from the grid measurements for use in equation 3.1 was $k = 1.45$, which was surprisingly high since a value of $k = 1.00$ had been obtained at a strain of 2.1%. A similar value of k was also obtained when calculated solely from the L measurements. This value is discussed in more detail in section 5.2.2.(a).

4.9. Analysis of the Creep Data.

4.9.1. Determination of the Activation Energy.

Dorn^{11,12} has shown that the high temperature creep rate $\dot{\epsilon}$ of metals tested under low stress can be represented by the formula

$$\dot{\epsilon} = C \sigma^n \exp(-Q/RT) \quad 2.4.$$

where σ is the applied stress, Q is the activation energy of secondary creep, and C and n are constants.

In an investigation of Al and Mg over a wide range of temperature, Dorn and co-workers^{27,189} showed that low values of Q were obtained for temperatures less than about $0.5 T_m$, but a constant value was obtained¹¹ for temperatures greater than this. This has recently been confirmed for magnox¹⁹⁰ and Mg¹⁴⁶, under certain conditions of secondary creep rate.

In the present work, the minimum creep rate was calculated from the creep curves for the specimens tested over a range of temperatures at two different stresses*. The activation energy of secondary creep was then obtained by plotting $\log \dot{\epsilon}$ against $1/T$ for these specimens, as shown in fig. 4.38, and measuring the slope of the curves under conditions of constant stress. The result was two straight, almost parallel, lines, yielding an activation energy of the order of 50 kcal/mole. This was much higher than anticipated, since Harris and Jones¹⁹⁰ obtained a value for magnox of $Q = 33 \pm 8$ kcal/mole, which is comparable with the activation energy for self-diffusion of Mg¹⁹¹ (32 kcal/mole). The result is explicable, however, since high values of Q (50 - 55 kcal/mole) were also obtained by Tegart³⁴, whilst carrying out compression creep tests on polycrystalline Mg.

* specimens MX65, MX66, MX43 at 2000 p.s.i.; MX2, MX64, MX26 at 4000 p.s.i.; see Tables 4.1 and 4.5.

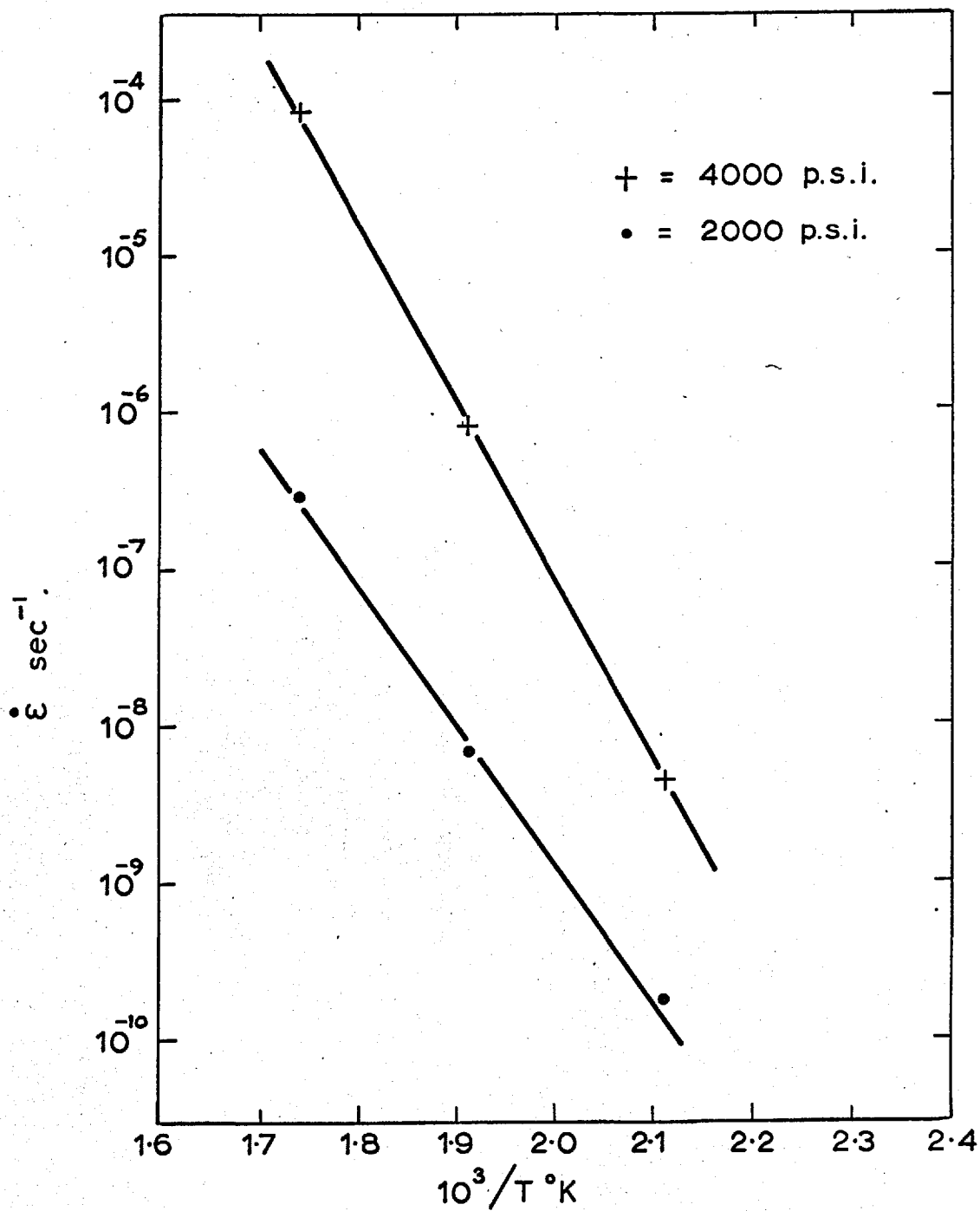


FIG. 4.38. Determination of activation energy.

Jones and Harris¹⁴⁶ have shown that these high values were due to the use of a very rapid strain rate (faster than about 10^{-6} sec^{-1}), so that non-basal slip became the dominant mode of deformation, and the high activation energy was identified with this process.

In the present work, the tests at 300°C were carried out at a very rapid rate of strain ($10^{-4} - 10^{-6} \text{ sec}^{-1}$), and the extensive occurrence of non-basal slip has already been cited. To overcome this difficulty, Q was calculated from the two lower points in the bottom curve in fig. 4.38, representing the lowest stress at temperatures of 200°C and 250°C respectively. A value of $Q = 36 \text{ kcal/mole}$ was obtained, which is in good agreement with the published figure. Unfortunately, insufficient results were available at very low rates of strain for an accurate determination of Q in the absence of non-basal slip.

4.9.2. Determination of the Stress Exponent.

The stress exponent n can be directly obtained from a logarithmic plot of the secondary creep rate against the stress. However, since $\dot{\epsilon}$ is a sensitive function of the applied stress, the range of stresses covered by this method is usually too small for an accurate determination of n to be made. It is therefore advantageous to be able to extend the stress range by plotting a temperature-compensated creep

rate against the stress. This is achieved by plotting $\dot{\epsilon} \exp^{Q/RT}$ against the stress, as originally proposed by Zener and Hollomon¹⁹², over a temperature range in which Q is constant.

It was shown previously that a constant value of Q , equal to 50 kcal/mole, was obtained for specimens tested at strain rates of greater than about 10^{-9} sec^{-1} . Using this value for the activation energy, a temperature-compensated strain rate was plotted against the stress for all specimens of similar grain size tested between 200°C and 300°C , and having strain rates of greater than 10^{-9} sec^{-1} . The result, shown in fig. 4.39, gave a stress exponent of $n = 6.8$. This is higher than the value predicted by the Weertman model²¹, for which the rate-controlling mechanism in a solid-solution alloy is dislocation glide, and the stress exponent is $n = 3.0$. Whilst a number of workers¹⁹³⁻¹⁹⁵ have found values of n in the range 3.0 - 3.5 for alloys, Harris and Jones¹⁹⁰ have shown that, for magnox tested at stresses greater than about 2240 p.s.i., an exponent of $n = 7.0$ is applicable, although a value of $n = 3.5$ applies for stresses lower than this. The value of n obtained here, for stresses in the range 2000 - 8000 p.s.i., is therefore in close agreement with their result, and is probably a consequence of non-basal slip becoming the dominant mode of deformation.

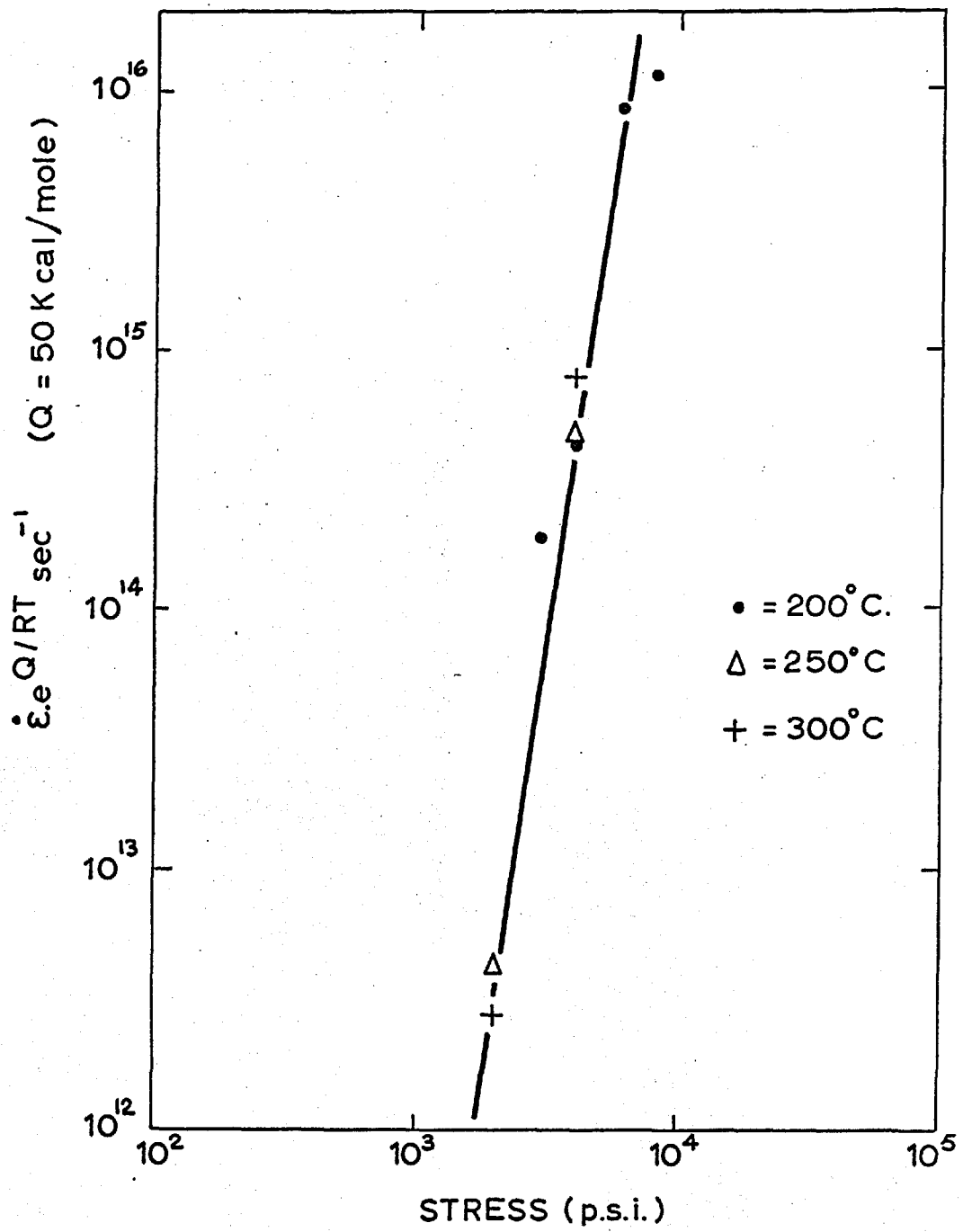


FIG. 4.39. Determination of stress exponent.

Table 4.1.

Results of Tests at 200°C.

Specimen Number	No. of Grains/cm.	Stress p.s.i.	$\bar{v}_{av}$ at $E_{tot} = 1\%$	E_{gb}/E_{tot} at $E_{tot} = 1\%$
MX65	110	2000	0.644 μ	75%
MX63	101	2500	0.581 μ	63%
MX29	96	3000	0.584 μ	60%
MX2	104	4000	0.566 μ	63%
MX25	104	6000	0.324 μ	36%
MX31	107	8000	0.131 μ	15%
MX3	84	6000	0.334 μ	30%
MX4	54	4000	0.935 μ	54%
MX8	53	6000	0.370 μ	21%
MX71	28	3000	1.536 μ	46%

Table 4.2.

Determination of k Using Printed Grid Technique.

(Temperature = 200°C).

Specimen Number	No. of Grains/cm.	Stress p.s.i.	Time hrs.	Elongation	Grain Strain	E_{gb}/E_{tot}	$\bar{v}_{av}$	k
MX33	54	3500	2495	2.013%	1.042%	48%	1.795 μ	1.00 $\pm$ 0.15
MX23	60	3750	1612	2.170%	0.901%	58%	1.842 μ	1.14
MX67	45	4000	323	2.397%	1.390%	42%	1.960 μ	1.13
MX68	54	4500	61.5	2.204%	1.257%	43%	1.725 μ	1.02 $\pm$ 0.17
MX69	52	6000	1.5	2.107%	1.559%	26%	0.908 μ	1.20
MX73	26	4000	258	2.078%	1.455%	30%	2.212 μ	1.03
MX74	29	6000	2.5	2.106%	1.853%	12%	0.858 μ	1.00

Table 4.3.

Details of Tests in the Temperature Range 21°C - 125°C.

Specimen Number	No. of Grains/cm.	Stress p.s.i.	Temperature
<u>Magnesium</u>			
M4	32	5800	21°C
<u>Magnox</u>			
MX15	107	18000	21°C
MX10	100	18000	75°C
MX18	104	18000	125°C
MX35	55	18000	21°C

Table 4.4.

Results of Tests at Constant Stress at 125°C and 150°C.

Specimen Number	No. of Grains/cm.	Stress p.s.i.	Temperature	$\bar{v}_{av}$ at $E_{tot} = 1\%$	E_{gb}/E_{tot} at $E_{tot} = 1\%$
MX19	100	8000	125°C	0.131 μ	14%
MX21	100	8000	150°C	0.159 μ	17%

Table 4.5.

Results of Tests at 250°C and 300°C.

Specimen Number	No. of Grains/cm.	Stress p.s.i.	Temperature	$\bar{v}_{av}$ at $E_{tot} = 1\%$	E_{gb}/E_{tot} at $E_{tot} = 1\%$
MX66	110	2000	250°C	0.544 μ	64%
MX64	113	4000	250°C	0.281 μ	34%
MX43	108	2000	300°C	0.502 μ	58%
MX26	107	4000	300°C	0.227 μ	26%
MX7	55	4000	300°C	0.493 μ	29%

Table 4.6.

Results of Tests with Annealed and As-cut Surfaces.

Specimen Number	Surface Condition	No. of Grains/cm.	Stress p.s.i.	Temp.	$\bar{v}_{av}$ at $E_{tot} = 1\%$	E_{gb}/E_{tot} at $E_{tot} = 1\%$
MX51	Annealed	104	6000	200°C	0.144 μ	16%
MX25	As-cut	104	6000	200°C	0.324 μ	36%
MX54	Annealed	53	4000	200°C	0.300 μ	17%
MX4	As-cut	54	4000	200°C	0.935 μ	54%

Table 4.7.

Determination of E_{gb}/E_{tot} from Grain Shape Measurements.

Specimen Number	No. of Grains/cm.	Stress p.s.i.	Temperature	E_{tot}	Using $k = 1.07$ with $\bar{v}_{av}$.		E_{gb}/E_{tot} from average L/B ratio:	
					E_{gb}/E_{tot} at Surface:		Surface	Interior
					Initially	Finally		
MX21	100	8000	150°C	25.4%	17%	4%	-	$7 \pm 4\%$
MX2	104	4000	200°C	19.0%	63%	23%	31%	41%
MX25	104	6000	200°C	21.5%	36%	10%	20%*	29%
MX31	107	8000	200°C	48.5%)	15%	7%)	-	$8 \pm 7\%$
				30.8%)		8%)	-	$7 \pm 6\%$
MX3	84	6000	200°C	26.9%	30%	13%	$45 \pm 8\%$	$55 \pm 9\%$
MX8	53	6000	200°C	19.2%	21%	9%	$20 \pm 8\%$	$33 \pm 7\%$
MX43	108	2000	300°C	19.0%	58%	27%	50%*	68%
MX7	55	4000	300°C	35.9%	29%	8%	-	$45 \pm 12\%$

* Surface repolished during test (MX25 at 10.0%; MX43 at 2.5%).

CHAPTER 5: DISCUSSION.

In section 5.2 of this chapter, the more important experimental observations are discussed in detail, and suggestions are made for further work. Before this is possible, however, it is necessary to consider the theoretical relationship between u , v and w , and to analyse the possible methods of calculating E_{gb}/E_{tot} from boundary offsets. This is contained in section 5.1.

5.1. Relationships Between u , v and w :

Formulae for Calculating E_{gb} :

The definitions of u , v and w , and the angles θ and ψ , have already been given in section 2.3.3. In order to calculate E_{gb} , the extension due to grain boundary sliding, it is easiest to consider a longitudinal line drawn on the specimen surface before deformation, parallel to the stress axis, and from one end of the specimen to the other. After testing, E_{gb} can be obtained directly by measuring the longitudinal offset (u) at every boundary intersected by this line, since it follows that

$$E_{gb} = \frac{1}{l} \sum_{\text{length}} u \quad 5.1.$$

where l is the length of the longitudinal traverse.

If $\bar{u}_{\text{long}}$ refers to the average longitudinal offset u when measured along a longitudinal traverse, and n is the number of grains/cm., then equation 5.1 can be rewritten as

$$E_{\text{gb}} = n \bar{u}_{\text{long}} \quad 5.2.$$

It should be noted, however, that $\bar{u}_{\text{long}}$ is not the same as $\bar{u}_{\text{trans}}$, the average longitudinal offset measured along a transverse traverse. This is discussed in more detail later.

From fig. 2.1 it follows that⁹⁷

$$u = \frac{v}{\tan \psi} + \frac{w}{\tan \theta} \quad 5.3.$$

If v and w are also measured at every point of intersection on a longitudinal traverse, then

$$\sum_{\text{length}} u = \sum_{\text{length}} \left(\frac{v}{\tan \psi} + \frac{w}{\tan \theta} \right) \quad 5.4.$$

$$= \sum \left(\frac{v_{\text{long}}}{\tan \psi} \right) + \sum \left(\frac{w_{\text{long}}}{\tan \theta} \right) \quad 5.5.$$

where $\sum v_{\text{long}}$ and $\sum w_{\text{long}}$ again refer to the sum of the values of v and w measured along a longitudinal traverse.

It was shown during the course of this work that the average internal angle $\bar{\psi}$ between the grain boundary and the surface increased with increasing strain. If, however, we consider the situation as it exists internally, then no change in $\bar{\psi}$ occurs, and $\bar{\psi} = \bar{\theta} = 57.3^\circ$ since both are the result of the intersection of random boundaries by a longitudinal line. Similarly, in the interior, $\bar{v}_{\text{long}}$ and $\bar{w}_{\text{long}}$ are also equivalent, since both represent components of the sliding vector measured perpendicular to the stress axis, and both are measured at boundaries making the same average angle of intersection with the stress axis. Although the two ratios occurring in equation 5.4 vary independently at any one boundary, the average values will be identical, so that

$$\sum \frac{v_{\text{long}}}{\tan \psi} = \sum \frac{w_{\text{long}}}{\tan \theta} \quad 5.6.$$

Thus, from equation 5.4,

$$\sum_{\text{length}} u = 2 \sum \frac{v_{\text{long}}}{\tan \psi} \quad 5.7.$$

$$= 2 \sum \frac{w_{\text{long}}}{\tan \theta} \quad 5.8.$$

But since

$$\bar{u}_{\text{long}} = \frac{\sum u}{n \ell} \quad 5.9.$$

it follows from equation 5.2 that

$$E_{gb} = n \bar{u}_{\text{long}} \quad 5.2.$$

$$= 2 n \left(\frac{v_{\text{long}}}{\tan \psi} \right) \quad 5.10.$$

$$= 2 n \left(\frac{w_{\text{long}}}{\tan \theta} \right) \quad 5.11.$$

where the average bar refers to the average of the quotient.

Having established the relationship between $\bar{u}_{\text{long}}$, $\bar{v}_{\text{long}}$ and $\bar{w}_{\text{long}}$, it is interesting to consider the effect of measuring the parameter w from the offsets occurring along a transverse traverse, giving $\bar{w}_{\text{trans}}$. The observed relationship between $\bar{w}_{\theta}$, representing the average value of w obtained in 10° increments of θ , and θ in the range $0^{\circ} - 90^{\circ}$ (fig. 4.36), indicates that the measured offset w is dependent on the resolved shear stress along the boundary,

and thus on the true angle γ between the boundary and the stress axis. The average angles of intersection in the plane of the surface for a longitudinal and transverse traverse are 57.3° and 32.7° respectively, and these angles are symmetrically disposed with respect to 45° , the angle of maximum resolved shear stress. However, the values of $\bar{w}_{\text{long}}$ and $\bar{w}_{\text{trans}}$ will not be the same, because of the relationship, shown in fig. 4.37, between the true angle γ and the observed angle θ . Since $\gamma \leq \theta \leq 90^\circ$, a transverse traverse, in which $\bar{\theta} = 32.7^\circ$, will intersect, on average, boundaries inclined at low true angles with the stress axis. On the other hand, a longitudinal traverse, in which $\bar{\theta} = 57.3^\circ$, will intersect a number of boundaries having a true angle which is close to that of the maximum resolved shear stress. Thus, $\bar{w}_{\text{long}}$ will be larger than $\bar{w}_{\text{trans}}$.

So far in this analysis, it has been assumed that the average angles $\bar{\theta}$ and $\bar{\psi}$ remain constant throughout the test. This is approximately true in the interior at low strains, since the reduction in angle with increasing grain strain is only very small. However, at the surface the effect of change of angle cannot be neglected, since it has been shown that $\bar{\psi}$ increases from an initial value of about 58° for an as-cut surface to a value of about 75° at some low but finite strain. The effect of this change of angle is two-fold. On the one hand there is a continuing reduction

in the resolved shear stress, which tends to reduce the amount of sliding along the boundary. On the other hand, as a result of the increase in angle, the offset v perpendicular to the surface is greater for a smaller amount of sliding. It is not immediately obvious which of these two opposing effects will predominate.

To determine this, it is necessary to assume in the first instance that the variation of v with ψ is the same as that of w with θ . This is reasonable since both represent components of sliding resolved perpendicular to the stress axis. It is then possible to calculate $\bar{v}_{\text{long}}$ for a specimen for which $\bar{\psi}$ has saturated, such as MX63 at a strain of 2.49% (See section 4.7.1), by determining

- (i) the frequency of occurrence of internal angles along a longitudinal section, in 10° increments of ψ , from the experimentally derived histogram for an annealed configuration (fig. 4.30),
- and (ii) the value of $\bar{w}_\theta$ for this specimen in each 10° increment of θ (fig. 4.36).

A combination of these results therefore yields $\bar{v}_{\text{long}}$. A similar calculation can also be made to determine $\bar{w}_{\text{long}}$, in this case using the histogram for an as-cut surface since this has the same distribution of angles as for a longitudinal traverse. The result of this analysis shows that the change in $\bar{\psi}$, and consequent decrease in resolved

shear stress, should give rise to a value of $\bar{v}_{\text{long}}$ that is approximately equal to, or slightly less than, $\bar{w}_{\text{long}}$. The significance of this calculation in terms of the experimental results is discussed in detail in section 5.2.1.

Having determined the relationships between u , v and w , it is necessary to consider the methods of calculating $E_{\text{gb}}/E_{\text{tot}}$ from each parameter. A comprehensive list was given in Table 2.1 of the various materials for which $E_{\text{gb}}/E_{\text{tot}}$ has been quoted, but it was emphasised that a direct comparison between different sets of results is usually not possible since wide variations exist in the method of obtaining the ratio. The basic requirement of such a calculation is a formula relating E_{gb} to either $\bar{u}$, $\bar{v}$ or $\bar{w}$, but a difficulty arises since, as already indicated, the values of these averages vary depending on whether they are measured randomly, or along a longitudinal or transverse traverse. This variation was overlooked by some previous workers, and accounts for many of the discrepancies. However, Brunner and Grant¹⁹⁶ took this variation into account, and correctly showed that

$$E_{\text{gb}} = n \bar{u}_{\text{long}} \quad 5.2.$$

$$= n (\overline{u_{\text{trans}} \cdot \tan \theta}) \quad 5.12.$$

Equation 5.2 has little practical application since it is not easy to measure longitudinal offsets at positions along a longitudinal traverse, because this would involve the measurement of u from the displacement of the intersections of a longitudinal line with the grain boundary. In theory this is perfectly feasible. In practice it is often impossible because of boundary migration or other topographical changes in the immediate vicinity of the boundary. The second equation is therefore the more useful, and in this case readings are taken, at every point of intersection along a transverse line, of both the longitudinal offset u and the angle θ between the boundary and the stress axis.

In a similar manner, the average transverse offset $\bar{w}$ is best obtained from measurements taken along a longitudinal line, to yield $\bar{w}_{\text{long}}$. It was shown earlier that E_{gb} can then be calculated using equation 5.11, where w and θ are again recorded at every point of intersection on a longitudinal traverse. This equation is correct for use with interior measurements, but may not be correct at the surface since it makes no allowance for any difference between the sliding components in the plane of (w) , and perpendicular to (v) , the surface.

In the present work, it was decided to attempt to calculate E_{gb}/E_{tot} from measurements of the average offset $\bar{v}$ perpendicular to the surface. There were two reasons for choosing this parameter:

(i) Unlike u or w , it does not require any form of scribed line or visible oxide stringer on the surface.

(ii) Using an interference technique, vertical offsets of the order of 0.05μ were readily measurable. It was therefore the most accurately determined parameter, and was particularly advantageous at low strains, or with specimens of very fine grain size, when the individual offsets were extremely small.

One disadvantage of using $\bar{v}$, which was not foreseen initially, was that the offsets perpendicular to the surface were directly affected by the change in the internal angle ψ , and therefore by the presence of a free surface. As a result, it was not possible to equate $\bar{v}_{long}$ and $\bar{w}_{long}$, and equation 5.10 could not be used. In any event, this equation is not used easily, since it involves sectioning of the specimen to obtain the individual values of ψ . The calculation of E_{gb} was therefore made through the equation

$$E_{gb} = k n \bar{v}_{av}, \quad 5.13.$$

using an empirical value of k obtained via a printed grid

technique for determining grain strain. Measurements of v were taken randomly, to yield $\bar{v}_{av}$, since this represented the most convenient experimental method. The value of k thus obtained is discussed in more detail in section 5.2.

To summarise, the correct formulae to use in calculating E_{gb} from measurements of $\bar{u}_{long}$, $\bar{u}_{trans}$ or $\bar{w}_{long}$ are shown in equations 5.2, 5.12 and 5.11, although the latter equation is probably only applicable in the interior. If the offsets are measured perpendicular to the surface, readings are best taken randomly to give $\bar{v}_{av}$. Equation 5.13 should then be used, and a separate investigation conducted to determine the correct values of k under different experimental conditions. Many previous workers have calculated E_{gb} using incorrect formulae, and these are examined in detail in the Appendix.

5.2. Discussion of the Experimental Results.

It is convenient at this stage to summarise briefly the results presented in Chapter 4:

(i) Measurements of the average vertical offset $\bar{v}_{av}$ occurring at grain boundaries on the surface of specimens subjected to creep testing were shown to increase linearly with increasing strain, up to a strain in the range 1 - 6%. Beyond this point, the vertical component of sliding increased at a slower rate than the overall extension.

The strain at which the deviation from linearity occurred was shown to be stress dependent, such that it occurred at a higher strain for increasing stresses.

(ii) Repolishing of specimens after the end of the linear region, by removal of about 3 - 4 surface grains, was found to give enhanced sliding perpendicular to the surface, and the occurrence of a second linear portion.

(iii) This effect was shown to be closely associated with the average internal angle $\bar{\psi}$ made by the boundaries with the surface. During creep the boundaries migrated to a position of lowest energy configuration perpendicular to the surface. It was found that $\bar{\psi}$ changed from a value of about 58° initially to about 75° at some finite strain, after which little further migration occurred. The strain at which this saturation angle was attained was found to be stress dependent, and closely related to the point at which the sliding-extension curve ceased to be linear.

(iv) During creep, the internal boundaries were often found to become corrugated, and this effect was especially noticeable in specimens in which E_{gb}/E_{tot} was small.

(v) Grain boundary sliding, measured in terms of the average offset occurring perpendicular to the surface at a strain of 1%, was investigated over a wide range of temperature. At low temperatures ($\sim 0.3 T_m$), real sliding did not occur, but, because of differences in grain strain,

a zone of accommodation was often formed immediately adjacent to the boundary. Grain boundary sliding became an ~~important~~ mode of deformation at temperatures greater than about $0.4 T_m$.

(vi) E_{gb}/E_{tot} was found to decrease at temperatures greater than about $0.55 T_m$, and it was suggested that this was due to the greater temperature-sensitivity of non-basal slip.

(vii) The dependence of sliding on stress and grain size was investigated. In general, the results confirmed those of other workers, which have shown that the value of E_{gb}/E_{tot} increases with a decrease in stress or grain size.

(viii) Measurements were taken to determine the variation of the longitudinal (u), transverse (w) and vertical (v) offsets with the angle θ in the plane of the surface between the boundary and the stress axis. The result showed some agreement with those of other workers, but there were also a number of differences. An explanation of the observed distributions was presented.

(ix) A method was developed to photographically print an accurately spaced grid on to the surface of specimens, and this was used to measure the strain within individual grains. Using this technique, an average value of $k = 1.07$ was obtained for use in the equation $E_{gb} = k n \bar{v}_{av}$ (5.13). This is lower than the value calculated by some previous workers.

(x) Results obtained for E_{gb}/E_{tot} by the Rachinger grain shape technique were found to be generally larger than the results derived from $\bar{v}_{av}$ measurements, although some agreement was obtained when E_{gb}/E_{tot} was small and the boundaries were very corrugated. This suggested that migration occurred in the specimens having a high value of E_{gb}/E_{tot} , thereby maintaining the grains in an equi-axed configuration.

5.2.1. The Mechanism of Sliding at the Surface.

In section 4.7.1, the results were given for measurements of u , v and w taken on specimen MX63 at a strain of 2.49%. The value obtained for the ratio $\bar{v}_{long}/\bar{w}_{long}$ was 1.25, in contrast to the result of the analysis given in section 5.1, in which it was concluded that, because of the increase in $\bar{\psi}$, this ratio should be equal to, or slightly less than, unity. Other workers have also reported larger offsets occurring perpendicular to the surface, and their results are summarised in Table 5.1. In each case the type of surface is specified, since this governs the average distribution of internal angles with the surface. The present results are in agreement with those reported elsewhere for magnox and a Pb-2.2% Tl alloy, but the ratio of $\bar{v}_{long}/\bar{w}_{long}$ for β -brass with an as-cut surface is substantially higher. It is possible that this

Table 5.1.

Results Obtained for the Ratio $\bar{v}/\bar{w}$.

Material.	Type of Surface.	Parameter Measured.	Value.	Reference.
<u>Present Results:</u>				
Magnox	As-cut	$\bar{v}_{\text{long}}/\bar{w}_{\text{long}}$	1.25	
"	As-cut	$\bar{v}_{\text{av}}/\bar{w}_{\text{long}}$	1.18	
<u>Results of Other Workers:</u>				
Magnox	As-cut	$\bar{v}_{\text{av}}/\bar{w}_{\text{long}}$	1.25	137
Pb-2.2% Tl	As-cut	$\bar{v}_{\text{av}}/\bar{w}_{\text{long}}$	1.2	188
β -brass	Annealed	$\bar{v}_{\text{long}}/\bar{w}_{\text{long}}$	1.51	97
"	Annealed	$\bar{v}_{\text{av}}/\bar{w}_{\text{long}}$	1.28	97
"	As-cut	$\bar{v}_{\text{long}}/\bar{w}_{\text{long}}$	1.7-1.9	97

difference may be partly ascribed to the unusual creep behaviour of β -brass, since the material exhibits no primary stage. These results show that it is not possible to account for the initial relationship between $\bar{v}_{av}$ and extension solely in terms of the change in $\bar{\psi}$, and an additional factor must be invoked to explain the large "vertical" component of sliding.

To account for this, it is necessary to re-examine the specialised conditions existing at the specimen surface. It seems likely that the large offsets occurring perpendicular to the surface are due to the extra degree of freedom that exists there, since surface grains are able to accommodate pressure from grains in the second layer by moving perpendicular to the surface without restriction. Movement in the plane of the surface, however, is impeded by the triple points.

This does not entirely account for the experimental observations, since it was found that $\bar{v}_{av}$ increased at a slower rate on a specimen with an annealed surface than on a specimen with an as-cut surface tested under the same conditions (fig. 4.31). With an annealed surface, it was observed that very little migration occurred during the tests, and the average internal angle $\bar{\psi}$ remained constant within experimental error. The slope of the sliding-extension curve for the annealed surface was similar

to that for the as-cut surface after the deviation from linearity had occurred, except possibly at very high strains, when the rapid strain rate occurring during tertiary creep, and the large error bars on the individual $\bar{v}_{av}$ points, made it difficult for any comparison to be made. It is therefore concluded that the enhanced sliding on the as-cut surface is intimately connected with the migration that occurs to change the average internal angle $\bar{\psi}$, since, when the boundaries have reached a stable position, the surface then resembles, and behaves as, an annealed configuration. Evidence for this is provided by the close association between the strain at which the linearity ceases in the sliding-extension curve, and the strain at which the angle saturates (figs. 4.2 and 4.32).

Some other workers^{124,131,132,197} have also suggested a close connection between the processes of sliding and migration, and, in particular, the results of Gifkins¹⁵⁴ on high-purity Pb show that both follow similar trends. For example, Gifkins found that a plot of the mean migration measured in the plane of the surface against extension yielded linearity up to about 3 - 4%, in a manner similar to the sliding-extension curves presented earlier. Gifkins also showed that an increase in stress gave a straight line of decreased slope in the migration-extension plot, which is again in agreement with the present results for sliding.

The experimental results suggest that sliding and migration occur cyclically, both internally and at the surface. In the interior, corrugated boundaries may be formed, possibly due to the formation of sub-grains in the boundary region in the manner suggested by Suiter and Wood¹⁶¹, and these inhibit the internal sliding. If, however, migration occurs, due to a difference in dislocation density on either side of the boundary, the corrugations are eliminated and sliding can continue. This is consistent with the observation that serrations on the internal boundaries were most prevalent in specimens in which E_{gb}/E_{tot} was small, for example, in specimens MX19, MX21, MX26 and MX31*. However, this does not agree with the conclusions of Mullendore and Grant¹⁶², who suggested, after a study of the formation of boundary corrugations during the creep of Al-Mg alloys, that corrugations only occurred in conjunction with sliding and migration. This may have been due to their use of creep ruptured specimens obtained from very short term tests.

At the surface, it is suggested that a stress builds up along the boundary, and this leads to sliding, partly in the plane of the surface, where it is restricted by adjacent triple points and may give rise to triple point folds, and

* See Tables 4.1, 4.4 and 4.5.

partly in a plane perpendicular to the surface, where no such restriction exists. At some later point the sliding becomes blocked by interlocking of the grains, and migration of the boundary must occur before further sliding is able to take place. With an annealed surface, migration will occur as a result of the same kind of driving force as that present in the interior of the specimen, so that the formation of any corrugations in the boundary will inhibit the sliding. At an as-cut surface, however, migration also occurs under the action of a second driving force due to the minimisation of boundary energy which occurs when the boundaries become almost perpendicular to the free surface. Thus, if corrugations are formed near an as-cut surface, they can be eliminated easily by boundary migration, and sliding can continue as before. Evidence for this is provided by the experimental observation that, if a new as-cut surface is created by repolishing during the test, the rate of sliding perpendicular to the surface again increases. In addition, small boundary corrugations were observed at the surface of specimen MX51, tested with an annealed surface (See Table 4.6), although none were observed at a similar strain at the surface of specimen MX25, tested with an as-cut surface under the same experimental conditions. With an as-cut surface, however, it would be difficult to distinguish very small corrugations due to the extensive migration.

From this analysis, it seems likely that a more representative value for sliding in the specimen as a whole would be obtained by measuring offsets in the plane of the surface, since these are restricted in a manner similar to that occurring internally. However, owing to the greater migration at an as-cut surface, it is possible that these offsets would also over-estimate internal sliding to a small extent. Some evidence for this is now available in the recent work of Grant et al¹¹⁷. Using an internal marker technique, they found that internal values of $\bar{w}_{\text{long}}$ were slightly lower than values on the surface, the decrease occurring over a depth of about 1 grain diameter.

This adequately explains the observed difference between an annealed and an as-cut surface, and the effect of re-polishing an annealed configuration. It does not, however, explain the initial linearity between sliding and extension for an as-cut surface, which is more difficult to interpret. The experimental results show that the component of sliding perpendicular to the surface increases linearly with extension, despite the decrease in the resolved shear stress along the boundary due to the change in $\bar{\psi}$. They also show that the deviation from linearity in the sliding-extension curve occurs at approximately the same strain as that at which the internal angle $\bar{\psi}$ saturates at about 75° . The test with the stable annealed surface

suggests that the internal sliding probably initially increases linearly with extension (fig. 4.31). Since the average internal angle $\bar{\psi}$ also appears to change fairly linearly with increasing strain, to a value of about 75° (fig. 4.32), it is possible that the linear relationship observed between sliding and extension on an as-cut surface is due simply to the continuous pressure from internal grain movement on the new boundary traces created at the surface.

During the course of this work, it was also noticed that boundaries on an as-cut surface frequently migrated away from their centres of curvature. Similar reports have also been made elsewhere^{124,154,198}. A simple explanation of this follows if the driving force is due to the tendency for grain boundaries to meet the surface at right angles, since the direction of migration will then depend entirely on the plane of sectioning of the grain. For example, if we consider an idealised spherical grain, as shown in fig. 5.1, the boundaries will migrate towards their centre of curvature if the plane of sectioning is AA', but away from their centre of curvature if the surface is created at BB', since in both cases the boundaries are tending towards the equilibrium position. There is thus, on average, no direct correlation between the direction of surface migration and the apparent centre of curvature of the boundary.

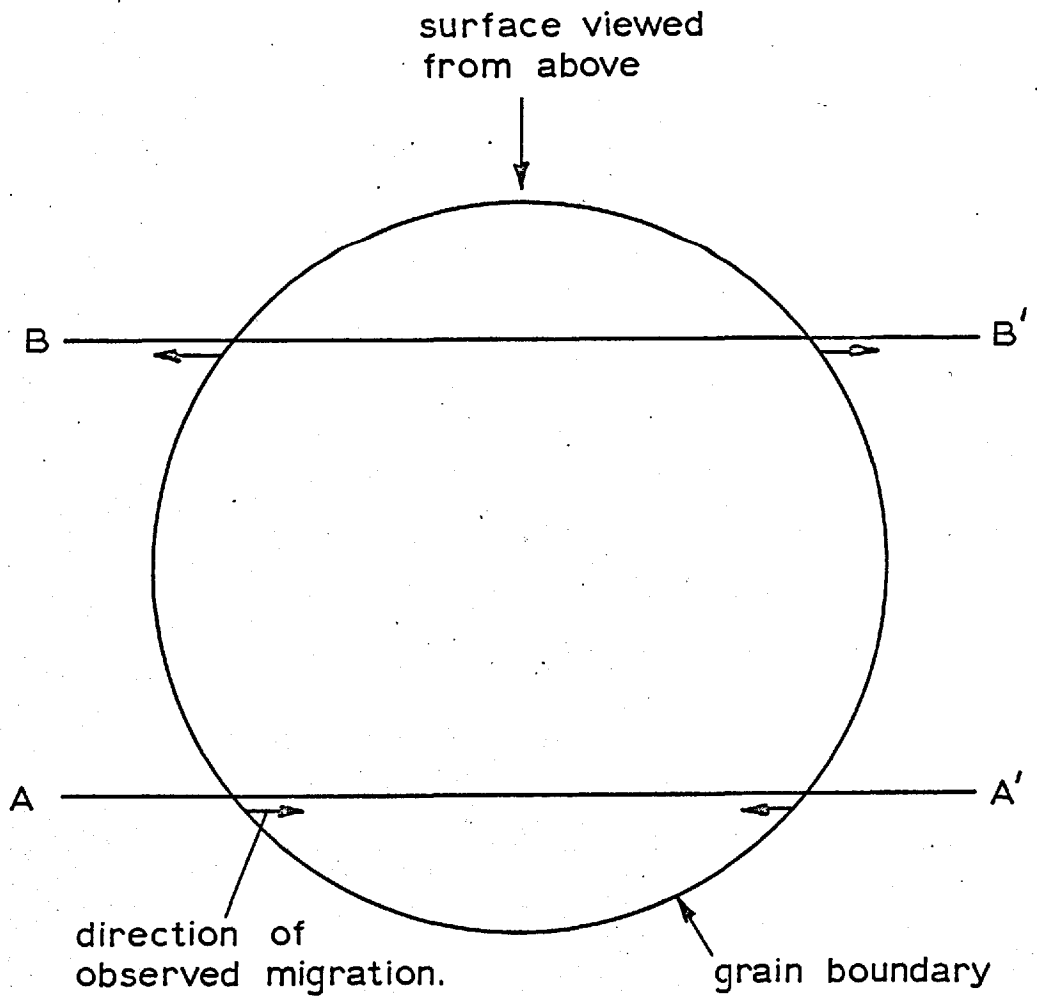


FIG. 5.1. Schematic illustration of direction of migration.

To sum up, it is suggested that migration occurs cyclically with sliding, and this eliminates small irregularities formed in the boundary. At an as-cut surface the migration is enhanced due to the existence of an additional driving force, and this may lead to a slight increase in offsets in the plane of the surface, but, more important, results in a large increase in offsets perpendicular to the surface due to the lack of hindrance on vertical movement. Two steps are therefore required before it is possible to relate measurements of the vertical (v) offsets with the values of E_{gb}/E_{tot} applicable to the specimen as a whole. Firstly, if measurements are taken to determine $\bar{v}_{av}$, a value of k must be measured for use in equation 5.13 before an accurate assessment of E_{gb}/E_{tot} can be obtained for the surface. Secondly, the relationship between E_{gb}/E_{tot} at the surface and E_{gb}/E_{tot} internally must be thoroughly investigated, using some form of internal marker line. Only the first of these prerequisites was examined in this work. The results are discussed in detail in section 5.2.2.

5.2.2. Experimental Determination of E_{gb}/E_{tot} :

5.2.2.(a) E_{gb}/E_{tot} from $\bar{v}$ Measurements.

In the preceding analysis, it was shown that, as a result of the additional migration occurring at an as-cut surface, sliding as measured by $\bar{v}$ was enhanced. Allowance for this must therefore be made in any formula utilised to calculate E_{gb} . Basically, an equation of the form $E_{gb} = k n \bar{v}_{av}$ (5.13) is required, where k is directly dependent on the angle δ between the sliding vector and the stress axis, and v is measured randomly. This latter method is preferable to using $\bar{v}_{long}$ or $\bar{v}_{trans}$, since it requires no surface marking of the specimen. Due to the increase in $\bar{\psi}$ with increasing strain, there is a consequent increase in $\bar{\delta}$, and the contribution made by the vertical offsets to the overall extension thus decreases, until, in the limit, $\bar{\delta} = 90^\circ$, so that the offsets make no contribution to the strain and k is therefore zero.

One problem of using an as-cut surface is therefore the change in $\bar{\psi}$, and consequent decrease in k , occurring during the initial stages of the test. This difficulty may not arise if an annealed surface were used, but again there would be no direct correlation with the interior. Unfortunately, this was not appreciated when the work was started, and the majority of tests were carried out on specimens having as-cut surfaces, since this gave a boundary

configuration that was typical of the interior. The experimental determination of k was therefore made on specimens having as-cut surfaces, so that the value obtained related directly to the routine tests.

Full details of the method used to derive values of k were given in section 4.1.3, but two additional observations should now be made. Firstly, since k is expected to change with the change in angle, the value obtained at any given strain will be some average of the values of k up to that point. Secondly, it should be noted that all specimens were taken to a similar strain of slightly greater than 2%, as individual grain extensions could not be measured with any degree of accuracy at very low strains. Since it has already been shown that the strain at which the average angle $\bar{\psi}$ saturates is stress dependent, it is therefore expected that the values of k would increase from a minimum at the lowest stress, where the angle may well have saturated, to a maximum at the highest stress, where this saturation had not occurred. Reference to Table 4.2 shows that this prediction is only partially fulfilled: for the specimens of the smaller grain size, there is a trend for k to increase with increasing stress, with the exception of specimen MX68 for which k is exceptionally low. No such effect was observed in the values of k obtained for the two specimens tested with the larger grain size.

The difficulty of observing this change of k is almost certainly due to the small number of specimens tested, and the inherent scatter in every result. Furthermore, the difficulty of obtaining consistency between different specimens has already been amply demonstrated. However, the appreciable difference in k between the two specimens (MX33 and MX69) at either end of the stress range, in which the times of testing differed by greater than two orders of magnitude, is probably significant.

If k decreases because of the change in angle, reaching a constant value after $\bar{\psi}$ has saturated, then it is expected that a measure of k at high strain would yield a lower value than that obtained initially. A value of k was determined from specimen MX74 at a strain of 16.77%, details of which were given in section 4.8.3. The value derived was $k = 1.45$, in contrast to the low value ($k = 1.00$) determined when the same specimen had been strained only 2.11%. This value is surprisingly high and is probably a direct result of using a specimen tested at a very rapid rate of strain, so that the sliding contribution was very small. The value obtained for the slip contribution from the grid measurements was $E_s/E_{tot} = 89.9\%$, resulting in a value of E_{gb}/E_{tot} of 10.1% by difference. However, since the absolute error in E_s/E_{tot} was of the order of $\pm 10\%$, the error introduced into E_{gb}/E_{tot} was very much larger. To test this hypothesis

realistically, more results are therefore required on specimens tested at a much lower rate of strain.

The conclusions reached from a determination of E_{gb}/E_{tot} from $\bar{v}$ measurements can be summarised briefly as follows:

(i) Since $\bar{v}_{av}$ is the easiest parameter to measure, it is desirable to have some method of converting it to E_{gb} .

(ii) Using a formula of the type $E_{gb} = k n \bar{v}_{av}$ (5.13), a value of k can be obtained experimentally using a printed grid technique to measure the strain within individual grains.

(iii) If an as-cut surface is used, the average angle $\bar{\psi}$ increases during the test, and k would be expected to decrease. However, the evidence for this needs confirming.

(iv) Using specimens of two different grain sizes, values of k were obtained in the range 1.00 - 1.20. An average value of $k = 1.07$ was used to calculate E_{gb}/E_{tot} for all specimens tested in the range 125°C - 300°C. This value, which is lower than that used by many previous workers, gave no values of E_{gb}/E_{tot} greater than 75%, and the majority of values were considerably less than this.

(v) More reliable measurements of E_{gb} would probably be obtained by using the grid technique on an annealed surface, since $\bar{\psi}$, and presumably k also, would then remain constant throughout the test. This was not done in the

present work, and all measurements were taken on as-cut surfaces.

(vi) The values of k obtained in this way, whether from annealed or as-cut surfaces, refer essentially to the surface grains. More work is required before it is known whether the values of E_{gb}/E_{tot} are also applicable to the internal conditions.

5.2.2.(b) E_{gb}/E_{tot} from $\bar{u}$ and $\bar{w}$ Measurements.

In section 5.1, formulae were given for calculating E_{gb}/E_{tot} from measurements of $\bar{u}_{trans}$ and $\bar{w}_{long}$ (equations 5.12 and 5.11). To test the validity of these relationships, E_{gb}/E_{tot} was calculated from each equation using the results obtained for specimen MX63 at a strain of 2.49% (see section 4.7.1). In addition, a calculation was also made from $\bar{v}_{av}$ measurements, using equation 5.13 with a k value of 1.07. The results obtained are shown below:

	Formula Used.	E_{gb}/E_{tot} .
(5.12)	$E_{gb} = n \cdot (\bar{u}_{trans} \cdot \tan \Theta)$	$44 \pm 6\%$
(5.11)	$E_{gb} = 2 n \cdot (\bar{w}_{long} / \tan \Theta)$	$58 \pm 7\%$
(5.13)	$E_{gb} = k n \bar{v}_{av}$	$49 \pm 5\%$

The values of E_{gb}/E_{tot} calculated from the equations for $\bar{u}_{trans}$ and $\bar{v}_{av}$ are in agreement within experimental error. The value obtained using $\bar{w}_{long}$, however, is significantly higher. This is because, as outlined in section 5.1, the equation is only strictly applicable to internal measurements, since it makes no distinction between the w and v sliding components. This same problem is overcome with the measurements of $\bar{v}_{av}$, by directly relating this parameter to E_{gb} through a value of k determined experimentally.

Grant et al¹¹⁷ have reported that values of $\bar{w}_{long}$ measured internally on Al are slightly lower than values measured at the surface. If this is also true for magnox, it suggests that E_{gb}/E_{tot} determined for the surface from measurements of $\bar{u}_{trans}$ or $\bar{v}_{av}$ may be of a similar magnitude to the value applicable internally. To check this, it would be interesting to compare surface and internal measurements of $\bar{u}_{trans}$.

5.2.2.(c) E_{gb}/E_{tot} from Grain Shape Measurements.

The results contained in section 4.8 indicate that values of E_{gb}/E_{tot} determined by grain shape are often about 2 - 4 times larger than those obtained from measurements of $\bar{v}_{av}$, although there appears to be some agreement for those specimens in which the ratio is initially very small.

Similar results have also been reported by Gittins⁹⁷, Grant et al¹¹⁷ and Garofalo et al^{123,129}. However, it is shown in the Appendix that it is necessary to increase the results of Grant et al obtained from marker lines by a factor of two. When this is done, the discrepancy between grain shape and the marker technique is again of the order of 2 - 4 times.

Since the values of E_{gb}/E_{tot} obtained from offset measurements are entirely consistent, as shown in the last section, it appears that the grain shape measurements give a false impression of the grain strain. This may be due to either the occurrence of extensive migration, or, as suggested by Grant et al¹¹⁷, to the preferential direction of grain growth during creep. The latter explanation must be accepted with some reserve, however, since Rachinger¹¹³ specifically noted that grain growth only occurred in his tests at 350°C, whereas very high values of E_{gb}/E_{tot} were obtained at temperatures as low as 250°C.

Some indirect evidence for spheroidization of the grains by migration was found in the present experiments. It has already been shown that corrugated boundaries can be formed during creep, especially under test conditions where E_{gb}/E_{tot} is relatively low. The presence of such boundaries indicates an absence of any appreciable migration on a large scale, and in those cases some agreement was obtained between the grain shape and $\bar{V}_{av}$ measurements. On the other

hand, in those specimens having a large sliding contribution, in which the boundaries remained fairly smooth, probably under the action of migration, the discrepancy between the two methods was greatest.

Table 4.7 shows that slightly lower values of E_{gb}/E_{tot} were always obtained on the surface, although the error bars are sufficiently large to give some agreement between the surface and internal values. It is not clear whether this represents a genuine effect, since some other workers^{97,117} have reported slightly higher values of E_{gb}/E_{tot} at the surface using grain shape measurements.

Davies and co-workers¹²⁶ attempted to explain any observed difference between surface and interior values of E_{gb}/E_{tot} by postulating that sliding was controlled by the size and distribution of ledges in the boundaries, and that surface boundaries may possess a different ledge configuration from those in the interior. Since there were indications that ledges only formed in the early stages of creep¹⁹⁹, they attempted to test this hypothesis by creep testing a nickel specimen to a strain of 2.5%, repolishing, and then continuing the test to fracture, which occurred at 14.3% strain. A value of $E_{gb}/E_{tot} = 86\%$ was obtained from measurements taken of the offsets perpendicular to the surface after fracture, and this was contrasted with the value of 35% obtained on the surface of nickel specimens

by Rozenberg¹⁰⁹. However, this comparison was not justified, since the specimens used by Rozenberg had annealed surfaces, in contrast to the as-cut surface produced by repolishing on the specimen used by Davies et al. In addition, there were wide variations in the testing conditions used in the two cases.

Details were given in section 2.3.3.(e) of the conflicting results obtained from grain shape measurements on Al, since Rachinger¹¹³ obtained a much larger value of E_{gb}/E_{tot} internally, whereas Gittins⁹⁷ and Grant et al¹¹⁷ found slightly larger values at the surface. The apparent discrepancy is again partly resolvable in terms of surface preparation, since Rachinger used specimens having annealed surfaces but Gittins and Grant et al used specimens with as-cut surfaces. This would satisfactorily explain the difference in surface values of E_{gb}/E_{tot} between the similar tests of Rachinger and Gittins, but it would not account for the difference in the internal values.

5.2.3. Variation of Values Obtained for E_{gb}/E_{tot} :-

5.2.3.(a) Variation of E_{gb}/E_{tot} with Stress, Temperature and Grain Size.

By testing a number of specimens of similar grain size at a temperature of 200°C, it was conclusively shown that the ratio E_{gb}/E_{tot} increased with a decrease in stress

(Table 4.1). Similar but less comprehensive results were also obtained at other temperatures in the range $125^{\circ}\text{C} - 300^{\circ}\text{C}$. A plot of E_{gb}/E_{tot} against stress (fig. 4.12) was found to extrapolate to approximately 100% at zero stress, thereby indicating that at very low stresses the sliding contribution can be very large. It should be noted, however, that two independent sets of workers^{115,116} have reported a reversal to occur at very low stresses, such that E_{gb}/E_{tot} decreases with a further decrease in stress. A similar extrapolation to zero stress by McLean¹⁰¹, using results obtained from Al specimens tested at 200°C , yielded a maximum value for E_{gb}/E_{tot} of about 40%. It is not possible to say whether this indicates a genuine disparity between Al and Mg, since McLean was using specimens having annealed surfaces, and it has already been shown that this would give substantially lower values of $\bar{v}_{av}$. On the other hand, this may be partly, but not necessarily entirely, compensated by the use of an erroneously high value of k in the formula $E_{gb} = k n \bar{v}_{av}$ (See Appendix).

Insufficient readings were taken in the temperature range $0.4 - 0.5 T_m$ to indicate whether E_{gb}/E_{tot} increased with increasing temperature, in a manner similar to that reported for Pt¹²⁷ in the range $0.42 - 0.62 T_m$. However, at temperatures greater than about $0.55 T_m$, E_{gb}/E_{tot} was found to decrease with increasing temperature, and it is

suggested that this was due to the occurrence of an additional mode of deformation, namely slip on the non-basal planes, which had a greater temperature-sensitivity than that of sliding. In support of this postulate, there was much visible evidence of non-basal slip at the higher temperatures.

Table 4.1 shows that, under conditions of constant stress and temperature, E_{gb}/E_{tot} increases with a decrease in grain size, although the amount of sliding per individual boundary at any given strain is actually decreased. This is in agreement with the results of McLean^{101,104} and Gifkins^{87,99}, but not with Brunner and Grant¹¹⁶, where no size dependence was observed. The results also show that, under the same conditions of stress and temperature, the finer grain size gives a faster minimum creep rate, although the greater contribution from grain boundary sliding is insufficient to account for this entirely.

5.2.3.(b) Variation of E_{gb}/E_{tot} in Different Metals.

All of the present high-temperature experiments were carried out on magnox, and the question therefore arises as to whether these results are only typical of a hexagonal material. At present there exists insufficient results on other materials for any conclusive statement to be made, but it does appear that results on magnox are sufficiently

related to those on other metals for at least the general trends to be typical. An examination of the values obtained for E_{gb}/E_{tot} by workers using different metals reveals that very large values are often associated with the hexagonal metals. There are some exceptions to this, however, since large values have also been reported for Cu^{100} , Ni^{126} , Au^{120} and $Pb-2.2\% Tl^{87,99}$, even after variations in the method of calculation have been taken into account.

Gifkins⁶⁹ attempted to rationalise this problem by plotting E_{gb}/E_{tot} determined by a number of workers for different metals against the number of grains in the smallest cross-sectional dimension of the specimen, under conditions of constant minimum creep rate and constant ratio of test temperature to T_m . The result showed a distinct tendency for high values of E_{gb}/E_{tot} to be associated with a large number of grains in the thickness, and it was therefore concluded that the high values obtained with the hexagonal metals were merely a consequence of the finer grain size used for those specimens. In fact, a plot of this type is not strictly valid unless allowance is made for the various methods of calculating E_{gb}/E_{tot} employed by the different workers. For example, in the results plotted by Gifkins, two sets of workers^{114,115} attempted to calculate E_{gb}/E_{tot} from measurements of $\bar{u}_{trans}$, and they used equation 2.12 with k values of 1.00 and 1.57 respectively.

It is also difficult to understand why the number of grains per specimen thickness should affect the contribution of sliding, after some initial minimum number of grains has been exceeded.

An attempt was made by Davies et al¹²⁰ to compare E_{gb}/E_{tot} obtained for Au with that found by other workers for different f.c.c. metals, but this was not satisfactory since the values of E_{gb}/E_{tot} were not all obtained under the same experimental conditions.

In the absence of a large number of measurements all utilised in the same manner to calculate E_{gb}/E_{tot} , it is not possible at this stage to reach even qualitative conclusions concerning the variation of E_{gb}/E_{tot} from one material to another.

5.2.4. Grain Boundary Sliding -

An Independent or Secondary Process?

Investigations over a wide temperature range have established a comprehensive picture of the temperature dependence of sliding. At temperatures below about $0.4 T_m$, thermally activated sliding does not occur. In place of it, however, a zone of accommodation may be formed immediately adjacent to the boundary, to compensate for inhomogeneous deformation in the two grains. Due to work hardening, this slope stabilises at some low but finite strain ($<1\%$ for

magnox), giving rise to an equality of deformation rates in either grain. Under low magnification, these accommodating slopes may be mistaken for genuine sliding offsets, and some have been reported as such by previous workers. Thermally activated sliding takes place, under conditions of low rates of strain, at temperatures greater than about $0.4 T_m$.

The activation energy of high temperature sliding was calculated by plotting $\log \dot{\bar{v}}_{av}$, the sliding rate during steady-state creep, against $1/T$, for those specimens of similar grain size tested at the same stress in the temperature range $200^\circ\text{C} - 300^\circ\text{C}^*$. In each case, the sliding rate thus obtained referred to the initial linear portion of the sliding-extension curve. The result was two straight lines for the specimens tested at 2000 p.s.i. and 4000 p.s.i., and the activation energies were 34 kcal/mole and 44 kcal/mole respectively. These values are slightly lower than the activation energy derived for creep (50 kcal/mole), although there are insufficient results for any definite conclusions to be drawn. At the lower stress, the value shows reasonable agreement with the activation energy for self-diffusion of Mg^{191} (32 kcal/mole).

* These specimens are listed in section 4.9.1.

A determination was made of the stress exponent of sliding from a log-log plot of the sliding rate during steady state creep against the stress, for specimens of similar grain size tested at 200°C (Table 4.1). The result yielded an exponent of $n = 4.2$, which is similar to that derived by Weertman¹⁷ for crystal slip controlled by dislocation climb. This exponent is almost the same as that obtained for the total creep of those specimens tested solely at 200°C, for which, from fig. 4.39, the exponent was $n = 5.0$.

The close similarity between the activation energies of sliding and creep, together with the observed linear relationship between sliding and total strain, suggests the existence of a single rate-controlling mechanism. The results of other workers^{100,105,110}, outlined in section 2.3.4, indicate that sliding is probably controlled by the rate of deformation within the grains.

Mullendore and Grant⁸² relegated sliding to a secondary process by showing that the amount of sliding on individual boundaries in an Al-2% Mg specimen was more closely related to the relative crystallographic orientations of the grains than to the orientation of the boundary with respect to the stress axis. They therefore put forward a model of slip-induced grain boundary sliding, in which it was assumed that sliding represented the unresolved shear component when

slip crossed the boundary from one grain to the next. At large extensions, it was suggested that no sliding took place independently of slip, although they concurred that, in the very early stages of deformation, up to about 2% strain, independent sliding may occur to give a large initial value of E_{gb}/E_{tot} . In their tests, and in other work also¹¹⁶, it was found that E_{gb}/E_{tot} decreased with increasing extension, and levelled off at strains greater than about 4%.

It is difficult to compare their results with those presented here, since the major interest in the present work was the contribution made by sliding at very low total strains. However, the observed linearity between $\bar{v}_{av}$ and extension on an annealed surface (fig. 4.31), up to at least 6% strain, suggests that, since k is probably constant under these conditions, E_{gb}/E_{tot} remains unchanged through the initial stages of deformation. An additional aspect of their theory is that it predicts little or no correlation between the u , v or w components of sliding and the angle between the boundary and the stress axis. This is also incompatible with the present results, as shown by the marked orientation dependence in fig. 4.36. Furthermore, the very high values obtained for E_{gb}/E_{tot} under certain experimental conditions make it difficult to consider sliding as other than an independent deformation process.

5.3. Suggestions for Further Work.

From the results presented in Chapter 4, and subsequent analysis in this chapter, it is now clear that specimens having as-cut surfaces exhibit enhanced migration, with a consequent increase in the sliding offsets measured perpendicular to the specimen surface. The first essential feature of any future work is to repeat some of the tests using specimens with annealed surfaces, and to determine, using the printed grid technique, the values of k . If, as it would appear, k is directly dependent on the average internal angle $\bar{\psi}$, then the constancy of ψ on an annealed surface should lead to a constant value of k independent of the total strain. If this is correct, then it will be possible to accurately calculate values for E_{gb}/E_{tot} at the surface.

Other experiments then suggest themselves. A comprehensive investigation of the effect of grain size, for example, using grain sizes that differ by at least an order of magnitude, and an extension of the present work to cover other classes of metals. In addition, it is necessary to compare the results obtained from surface observations with those in the interior, the latter being derived from some form of oxide marker. This is an essential feature of the work since, even with a stable annealed configuration, the presence of a free surface may materially affect the sliding components measured at the surface.

The present results indicate that, under certain conditions, values of E_{gb}/E_{tot} may be as high as 70 - 80%. Further work is now required to investigate whether large values of E_{gb}/E_{tot} are always associated with a high degree of cavitation; the results discussed in section 4.1.2 suggest that such a correlation may exist. If this is correct, much additional work is required to investigate ways of reducing grain boundary sliding, and thereby preventing cavitation failure. One possibility, in this respect, is by the introduction of a precipitate at the boundary. Some recent results by Gittins⁹⁷ have shown that the presence of γ precipitate along the boundary in a two-phase β - γ specimen inhibits sliding to a considerable extent. On the other hand, Grant et al¹¹⁹, investigating sliding in an Al-3% Cu alloy, concluded that boundary precipitates were not a primary factor in determining the amount of sliding, since the boundary may migrate away from these precipitates at an early stage in the test. Further work is required before the effect of grain boundary precipitates on sliding is fully understood.

5.4. Conclusions.

Grain boundary sliding is an important mode of deformation in metals subjected to creep at temperatures greater than about $0.5 T_m$. Under conditions of small grain

size and slow rate of strain, sliding may account for 70 - 80% of the total deformation during the early stages of creep, up to about 2% total strain. Three formulae have been presented (equations 5.12, 5.13, 5.11) for calculating E_{gb}/E_{tot} from measurements of $\bar{u}_{trans}$, $\bar{v}_{av}$ and $\bar{w}_{long}$ respectively. In general, $\bar{v}_{av}$ is the easiest, and most accurate, parameter to measure at the surface, but a reliable value of k is then required for use in equation 5.13. These values were obtained by determining the strain within individual grains, using a grid photographically printed on to the specimen surface. The results suggest that values of E_{gb}/E_{tot} are best obtained from measurements of $\bar{v}_{av}$ on an annealed surface, since this offers a stable boundary configuration and k should therefore be constant throughout the test. This was not done in the present work, however, since initially it was thought advantageous to use specimens having as-cut surfaces. With the latter, allowance must be made for the change in internal angle occurring during the test, which results in a continuously changing value of k . An attempt was made to determine the internal values of E_{gb}/E_{tot} from grain shape, but the results indicated that this was not a reliable technique. Most of the results reported here refer specifically to surface conditions, and a further investigation is required to correlate the observations with internal sliding.

APPENDIX.

An Analysis of the Methods Used by Previous Workers to Calculate E_{gb}/E_{tot} .

The correct equations to use in calculating E_{gb}/E_{tot} from the components $\bar{u}_{trans}$, $\bar{v}_{av}$ and $\bar{w}_{long}$ have already been given in section 5.1. However, many previous workers have utilised other formulae, so that their results are not directly comparable. A summary of these formulae is given in Table A.1. The basic equation is $E_{gb} = k n \bar{x}^*$, where $\bar{x}$ is the average of one component of sliding, such as $\bar{u}_{trans}$ or $\bar{v}_{av}$, and the geometrical factor k depends on the parameter used for $\bar{x}$. The individual formulae will now be examined in detail.

One of the earliest techniques for calculating E_{gb}/E_{tot} , put forward by McLean⁶, involved measuring, at the same point, both the vertical step height v and the component of sliding along the grain boundary in the plane of the surface. This was then used to calculate the total sliding displacement, but, since there was a large inaccuracy in the latter measurement, a method was later developed⁷ whereby E_{gb}/E_{tot} could be calculated directly from $\bar{v}$ measurements

* See section 2.3.3.(b)

Table A.1.

Formulae Used by Previous Workers to Calculate E_{gb} .

Workers.	Reference.	Component Measured.	Formula Used.
McLean	7	$\bar{v}_{av}$	$E_{gb} = \frac{\sqrt{5}}{\sqrt{2}} n \bar{v}_{av} (1 + E)^{1/2}$
Fazan, Sherby and Dorn	114	$\bar{u}_{trans}$	$E_{gb} = n \bar{u}_{trans}$
Harper, Shepard and Dorn	115	$\bar{u}_{trans}$	$E_{gb} = \frac{\pi}{2} n \bar{u}_{trans}$
Harper and Dorn	112	$\bar{v}_{trans}$	$E_{gb} = n \bar{v}_{trans}$
Ishida, Mullendore and Grant	117	$\bar{w}_{long}$	$E_{gb} = n \left(\frac{\bar{w}_{long}}{\tan \theta} \right)$
Rachinger	113	$\bar{u}_{trans}$	$E_{gb} = n \bar{u}_{trans}$
"	"	$\bar{w}_{long}$	$E_{gb} = 2 n \bar{w}_{long}$
"	"	$\bar{v}_{long}$	$E_{gb} = 2 n \bar{v}_{long}$
Couling and Roberts	124	$\bar{u}_{trans}$	$E_{gb} = 1.45 n \bar{u}_{trans}$
Gittins	97	$\bar{v}_{long}^*$	$E_{gb} = 0.85 n \bar{v}_{long}$

* Measured on an annealed surface.

alone, and this was made use of in subsequent work^{100,101,103}. To obtain a relationship between E_{gb} and $\bar{v}_{av}$, McLean assumed that the angle between the sliding vector and the stress axis could take all values between 0° and 90° with equal frequency. This is correct, but McLean overlooked the fact that his $\bar{v}$ measurements were made on a planar surface parallel to the stress axis, where the angles of intersection follow a sinusoidal relation. Also, no allowance was made for the change of average angle $\bar{\psi}$ with the surface, due to the tendency for boundaries to migrate to an equilibrium position. A number of other workers have computed E_{gb}/E_{tot} using the McLean relationship shown in the Table, which includes a correction factor of $(1 + E)^{1/2}$ to compensate for the reduction in angle between the boundary and the stress axis as the specimen elongates. Some workers have included this correction^{105,108,109,120,126,127}, but others have not^{87,98,99}.

In an attempt to calculate E_{gb}/E_{tot} for aluminium specimens, Fazan, Sherby and Dorn¹¹⁴ measured $\bar{u}_{trans}$. They then calculated E_{gb} by assuming $E_{gb} = n \bar{u}_{trans}$, so that the k factor was effectively 1. This is incorrect since $\bar{u}_{trans}$ obtained from a transverse traverse is not equal to $\bar{u}_{long}$ obtained from a longitudinal traverse, because the average angle of intersection of boundaries with the stress axis is not the same in the two cases.

Harper et al¹¹⁵ measured $\bar{u}_{trans}$, and assumed, without explanation, a k value of $\pi/2$. There appears to be no justification for this, since a transverse traverse intersects, on average, boundaries more nearly parallel to the stress axis, and thus $\bar{u}_{trans}$ is greater than $\bar{u}_{long}$ *. Since $E_{gb} = n \bar{u}_{long}$ (5.2), it therefore follows that the correct value of k must be less, and not greater, than unity. The same workers¹¹² also assumed a k factor of unity for use with measurements of $\bar{v}_{trans}$, but again this was unsubstantiated.

Ishida, Mullendore and Grant¹¹⁷ distinguished between longitudinal and transverse traverses, but they overlooked the fact²⁰⁰ that measurements of w , unlike u , included no contribution from the sliding component v perpendicular to the specimen surface. The equation they used, shown in the Table, is incorrect for their internal measurements because it underestimates E_{gb}/E_{tot} by a factor of two. This can be seen by reference to equation 5.11. When this is taken into account, their values of E_{gb}/E_{tot} are compatible with those obtained at the surface in the present investigation, under similar rates of strain. For surface values of E_{gb}/E_{tot} , it has already been shown in section 5.1 that a more accurate result would be obtained from measurements of the longitudinal offset u .

* Shown experimentally by fig. 4.36.

Rachinger¹¹³ attempted to determine E_{gb}/E_{tot} on the surface by measuring both the displacement of grid lines and the offsets perpendicular to the surface. He showed theoretically that the average gap at a grain boundary ($\bar{u}$), measured parallel to the stress axis, between the ends of a longitudinal grid line was given by

$$(E_{tot} - E_s) = n \bar{u} \quad A.1.$$

This is correct provided $\bar{u}$ is determined from a longitudinal traverse. However, Rachinger incorrectly assumed that the value obtained for $\bar{u}$ was independent of the direction of traverse, and measurements were taken to determine $\bar{u}_{trans}$ from a transverse traverse. The value thus obtained was then incorrectly substituted into equation A.1. As outlined in section 5.1, measurements should also have been made of the angle θ at every point of intersection of the grid line with a boundary, and he should then have used the equation

$$(E_{tot} - E_s) = E_{gb} = n (\bar{u}_{trans} \cdot \tan \theta) \quad 5.12.$$

In a similar manner, Rachinger theoretically showed that the average displacement ($\bar{w}$), measured perpendicular to the stress axis, between the ends of a transverse grid line

was given by

$$(1 + E_s)^{-1/2} - (1 + E_{tot})^{-1/2} = n \bar{w} \quad A.2.$$

Gifkins⁹⁹ has shown that, when E_s and E_{tot} are both small compared with unity, the latter expression reduces to

$$E_{gb} = 2 n \bar{w} \quad A.3.$$

Rachinger measured $\bar{w}_{long}$ for use in equation A.2, and again made no distinction for $\bar{w}$ obtained from a particular traverse. In fact, the angle Θ should also have been recorded for each value of w , and the results substituted into equation 5.11.

To utilise measurements of the offsets perpendicular to the surface, Rachinger assumed that $\bar{v}$ and $\bar{w}$ were equal, so that equation A.2 reduces to

$$E_{gb} = 2 n \bar{v} \quad A.4.$$

The present results show that, because of the change in $\bar{\psi}$, this assumption is incorrect. In addition, Rachinger measured $\bar{v}$ using a Talysurf surface analyser along a longitudinal traverse, and thus in reality obtained $\bar{v}_{long}$.

To summarise, in each case Rachinger used an invalid formula for his surface measurements. The agreement he found for the different methods was therefore probably fortuitous. The value of $k = 2$, which is a direct consequence of Rachinger's formula A.2, merely results from the fact that u consists of both v and w components, as shown by equation 5.3. Later calculations^{87,99} of E_{gb}/E_{tot} from $\bar{v}_{av}$ measurements using $k = 2$ are therefore not justified.

Couling and Roberts¹²⁴ attempted an experimental determination of k . They measured $\bar{u}_{trans}$, and fully appreciated that E_{gb} was best calculated from the equation $E_{gb} = n \bar{u}_{long}$ (5.2). To convert from the transverse to the longitudinal component, they measured the average value of $\bar{u}$ in each 10° increment of θ , and determined the frequency of occurrence of each increment on a longitudinal traverse. This method is essentially correct, but their result is dubious since the measured distribution of u with θ is unlike that obtained both in the present work and by other investigators. The distribution, which surprisingly peaked at $\theta = 90^\circ$, has been discussed in section 4.7.1. From this plot, they calculated a value of $k = 1.45$ for use with $\bar{u}_{trans}$, but, since $\bar{u}_{trans}$ should be larger than $\bar{u}_{long}$, reference to equation 5.2 shows that the relevant value of k will be less than unity.

More recently, Gittins⁹⁷ attempted to determine E_{gb}/E_{tot} by showing that

$$u = \frac{v}{\tan \psi} + \frac{w}{\tan \theta} \quad 5.3.$$

However, he incorrectly assumed that it was possible to take the independent average of two variables appearing in a fraction, so that he obtained

$$E_{gb} = \left(\frac{2n}{\tan \bar{\theta}} \right) \bar{w}_{long} \quad A.5.$$

Since, in the interior, $\bar{w}_{long} = \bar{v}_{long}$, he put

$$E_{gb} = \left(\frac{2n}{\tan \bar{\psi}} \right) \bar{v}_{long} \quad A.6.$$

Note also that he failed to distinguish between $\overline{\tan \theta}$, which should appear in the equations, and $\tan \bar{\theta}$, and he reasoned that, since $\bar{\theta} = \bar{\psi} = 57.3^\circ$ initially, the geometrical factor for the interior was $k = 2/\tan 57.3^\circ = 1.28$. Because of the change of angle occurring at an as-cut surface, Gittins measured the ratio $\bar{v}_{long}/\bar{w}_{long}$ for an annealed surface, and obtained a value of 1.5. Thus the k value for use with $\bar{v}_{long}$ on the surface was $k = 1.28/1.5 = 0.85$. It should be noted that since Gittins obtained a higher value of $\bar{v}_{long}/\bar{w}_{long}$ for an as-cut

surface (~ 1.8), the k value would be even smaller in that case.

In fact, this analysis is incorrect, since it is not valid to take the average of the two variables w_{long} and θ independently. This is shown by some results obtained in the present work. Measurements of w_{long} and θ were recorded for specimen MX63, and, after a total of 300 readings, the values obtained were as follows:

$$\begin{aligned}\overline{w_{\text{long}}} &= 0.872 \mu \\ \overline{\theta} &= 58.0^\circ\end{aligned}$$

$$\left(\frac{\overline{w_{\text{long}}}}{\tan \overline{\theta}} \right) = 0.628$$

Therefore,

$$\begin{aligned}E_{\text{gb}} &= 2 n \left(\frac{\overline{w_{\text{long}}}}{\tan \overline{\theta}} \right) \\ &= 2 \times 0.628 n.\end{aligned}$$

If the variables were taken separately, and $\tan \overline{\theta}$ used in place of $\overline{\tan \theta}$, then, by the Gittins analysis,

$$\begin{aligned}E_{\text{gb}} &= \left(\frac{2 n}{\tan \overline{\theta}} \right) \overline{w_{\text{long}}} && \text{A.5.} \\ &= \frac{2 n}{\tan 58^\circ} 0.872 \\ &= 2 \times 0.545 n.\end{aligned}$$

The true value of k to use with individual values of $\bar{w}_{\text{long}}$ in this case is therefore $k = (2 \times 0.628)/0.872 = 1.44$, which is higher than the value of 1.28 used by Gittins. Results on other specimens also indicate that the value of k derived in this manner is substantially greater than 1.28, although the average intercept angle $\bar{\theta}$ is always of the order of $57^\circ - 58^\circ$.

The conclusions to be drawn from this analysis are that all workers, with the exception of Brunner and Grant^{116,196}, have used an incorrect method to calculate $E_{\text{gb}}/E_{\text{tot}}$. These methods have been examined in detail, and it has been shown that the discrepancies can all be resolved in terms of invalid assumptions. Reference to Table A.1 shows that the range of magnitude of these discrepancies is often quite large. The method used to determine $E_{\text{gb}}/E_{\text{tot}}$ from measurements of $\bar{v}_{\text{long}}$ by Gittins⁹⁷, for example, would yield a value less than half that obtained by the Rachinger¹¹³ analysis from the same readings. The present results indicate that the true value is between the two. The methods used by different workers to calculate $E_{\text{gb}}/E_{\text{tot}}$ from measurements of $\bar{u}_{\text{trans}}$ range from the use of k values of 1.00 to 1.57 in equation 2.12. However, it was shown earlier that, if this equation were used with $\bar{u}_{\text{trans}}$, the correct value of k should be less than unity. This suggests that the values of $E_{\text{gb}}/E_{\text{tot}}$ obtained by Dorn et al¹¹⁵, for

which $k = \pi/2 = 1.57$, and Couling and Roberts¹²⁴, for which $k = 1.45$, may overestimate the true value by almost a factor of two. In this respect it is interesting to note that the values reported by Couling and Roberts were at all times very large, ranging from a minimum of 67% to a maximum of 93%.

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