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ON THE STRUCTURE OF TILT GRAIN BOUNDARIES IN CUBIC METALS. III. GENERALIZATIONS OF THE STRUCTURAL STUDY AND IMPLICATIONS FOR THE PROPERTIES OF GRAIN BOUNDARIES

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CONTENTS

The results of atomistic calculations of long-period tilt boundaries, which were reported in the preceding parts I and II, are generalized and represented concisely by using two-dimensional lattices, called decomposition lattices. The basis vectors of a decomposition lattice characterize the two fundamental structural elements composing all boundaries in a continuous series of boundary structures. Conversely, the governing condition on the basis vectors is that the boundary structure can change continuously throughout the misorientation range between the boundaries represented by the basis vectors. On assuming that no discontinuous changes in boundary structure occur at non-favoured boundary orientations, and that all boundaries considered are stable

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with respect to faceting, the governing condition may be used to deduce selection rules for adjacent favoured boundaries and the existence of other favoured boundaries in the misorientation range between two given favoured boundaries. The necessary condition for a discontinuous change in boundary structure to be possible at a non-favoured boundary orientation is formulated.

Various aspects of intrinsic and extrinsic grain boundary dislocations (g.b.ds) are treated. It is first shown that the observation of intrinsic g.b.d. networks in the transmission electron microscope does not necessarily imply that the reference structure, preserved by those g.b.ds, is a favoured boundary. Secondly, it is argued that extrinsic g.b.ds provide imperfect steps with Burgers vector components parallel to the boundary that do not exist in equilibrium high-angle tilt boundaries. Finally, an explanation of the physical basis of plane matching dislocations is proposed.

A general classification of grain boundary properties is introduced that is based on the results of this investigation of grain boundary structure. It is argued that only properties, such as grain boundary diffusion, that depend exclusively on the atomic structure of the boundary core may be used to detect favoured boundaries. Favoured boundaries exist at those misorientations where such a property is continuous but its first derivative, with respect to misorientation, is not. Grain boundary diffusion, the energy against misorientation relation and grain boundary sliding and migration are then discussed.

1. Introduction

The preceding parts I and II were concerned with the structure of tilt boundaries in pure cubic metals. In this paper we shall first generalize the results of those calculations by introducing a new concept, which we call the decomposition lattice. This lattice is a graphical means of representing the structures of all non-favoured boundaries in the misorientation range between two adjacent favoured boundaries. Conversely, the requirement that all non-favoured boundaries, between two adjacent favoured boundaries, can be represented on a decomposition lattice imposes selection rules, of a geometrical nature, on the adjacent favoured boundaries. Furthermore, provided certain assumptions are made it is possible to determine a minimum number of boundaries, between two given favoured boundaries, that must also be favoured to satisfy these geometrical rules. Consequently such favoured boundaries are not necessarily low energy boundaries.

Section 4 is concerned with grain boundary dislocations (g.b.ds). In parts I and II it was found that the most appropriate choice of reference structure, for defining the secondary dislocation content of a non-favoured boundary, is the favoured boundary, the units of which are the predominant fundamental structural elements of the non-favoured boundary. The use of alternative secondary dislocation descriptions is discussed and it is shown that secondary dislocations of these equivalent descriptions may sometimes be detected in the transmission electron microscope, rather than those based on the appropriate favoured boundary reference structure. Some distinctions are made between intrinsic and extrinsic g.b.ds in terms of their structure and properties. These include the occurrence of steps associated with g.b.d. cores and the direction of the Burgers vectors. The process of the absorption of an extrinsic g.b.d. into an array of intrinsic g.b.ds is discussed. Sutton (1982) has shown that the concepts of favoured and non-favoured boundaries are also applicable to the structures of (001) twist boundaries, calculated by Bristowe & Crocker (1978) using empirical potentials for copper and nickel. The extension of the present scheme to mixed tilt and twist boundaries is discussed and an explanation of the physical origin of 'plane matching' dislocations (Schindler *et al.* 1979) is proposed.

A general classification of the properties of grain boundaries is proposed in §5.1. This classification indicates which properties may be used to determine whether a boundary is favoured or non-favoured. The energy against misorientation relation is shown to be an unreliable method of determining favoured boundaries. Finally, self-diffusion along grain boundaries, the energy against misorientation relation, and sliding and migration of grain boundaries are discussed in the light of the results of the structural investigation.

2. The decomposition lattice

In this and the following section we shall be concerned with tilt boundaries sharing the same tilt axis and belonging to the same ξ-system (see part II). It is assumed that these boundaries are all stable with respect to faceting. Consider two adjacent favoured boundaries and let A and B label their units. Let $\boldsymbol{u}_{\mathrm{A}}$ and $\boldsymbol{u}_{\mathrm{B}}$ be the vectors characterizing those units respectively (see part I). For simplicity we assume that continuity of boundary structure exists throughout the misorientation range between these favoured boundaries. Hence all the intervening non-favoured boundaries are composed of A and B units. The generalization to the case where an isolated discontinuity occurs between two favoured boundaries is discussed below. Consider a non-favoured boundary in which there are x A units for every y B units, where x and y are relatively prime integers. The vector $\boldsymbol{l}$ bounding the primitive cell of this boundary (see part I), perpendicular to the tilt axis, is

$$\boldsymbol{l} = x\boldsymbol{u}_{\mathrm{A}} + y\boldsymbol{u}_{\mathrm{B}}. \tag{1}$$

Thus $\boldsymbol{l}$ characterizes a unit of this non-favoured boundary. If the boundary is not centred (see part I) then the period vector of the boundary, $\boldsymbol{p}$, equals $\boldsymbol{l}$; otherwise $\boldsymbol{p} = n\boldsymbol{l}$, where n is (an integer) equal to the number of atomic planes perpendicular to the tilt axis in one crystal period along the tilt axis. Therefore $\boldsymbol{l}$ is not a crystal lattice vector in centred boundaries. When x and y are allowed to take on any positive integer values, equation (1) defines a two-dimensional lattice with basis vectors $\boldsymbol{u}_{\mathrm{A}}$ and $\boldsymbol{u}_{\mathrm{B}}$. We call such a lattice a decomposition lattice because each lattice site corresponds to a specific decomposition into A and B units. The vector in the decomposition lattice joining the origin (at (0, 0)) and a node (x, y) in the lattice is given by equation (1), where x, y are positive integers. If x and y are relatively prime, then this vector is a primitive vector of the decomposition lattice (p.d.l. vector). Thus p.d.l. vectors characterize units of the intervening non-favoured boundaries. Straight lines in the decomposition lattice emanating from the origin pass through points that all represent the same boundary. We may choose to represent the decomposition in either the upper or lower grain, since all represented boundaries belong to the same ξ-system, and therefore p.d.l. vectors in the upper and lower grains are not independent. To illustrate the decomposition lattice it will be recalled that in part I, §4.2 it was shown that $\Sigma = 27\,(115)_1$, $31.59°/[1\bar{1}0]$ and $\Sigma = 11\,(113)_1$, $50.48°/[1\bar{1}0]$ are adjacent favoured boundaries in aluminium. Units of these boundaries are characterized by $\boldsymbol{u}_{\mathrm{A}} = \frac{1}{4}[55\bar{2}]$, and $\boldsymbol{u}_{\mathrm{B}} = \frac{1}{4}[33\bar{2}]_1$, respectively. Since continuity of boundary structure was found to occur throughout the intervening misorientation range these vectors are the basis vectors of a decomposition lattice. Vectors characterizing the units of all the intervening non-favoured boundaries are given by

$$\boldsymbol{l} = \tfrac{1}{4}x[55\bar{2}] + \tfrac{1}{4}y[33\bar{2}] \tag{2}$$

where x and y are relatively prime integers. Thus each $\boldsymbol{l}$, given by equation (2), is a p.d.l. vector of this decomposition lattice.

It is noted that the decomposition lattice does not provide the sequence of A and B units in non-favoured boundaries, but only their relative numbers. The sequence of units is determined uniquely by the requirement that it is continuous with the sequences of units in neighbouring boundaries in the misorientation range, as shown in part I, §4.3.

In general the larger the p.d.l. vector the higher the value of Σ associated with the corresponding boundary. By allowing x and y in equation (1) to become indefinitely large, but maintained relatively prime, the vector characterizing the unit of an irrational boundary may be approximated to any required accuracy. Thus, irrational boundaries, with infinite values of Σ, are 'represented' by nodes in the decomposition lattice that are infinitely far from the origin.

Isolated discontinuous changes in boundary structure between two adjacent favoured boundaries were discussed in part I, §6. It was shown that the boundary structures on either side of the discontinuity are composed of only two boundary units, but no units are common to both sides. Continuity of boundary structure exists, therefore, on either side of the discontinuity. Hence two decomposition lattices are required to represent all boundary structures when an isolated discontinuity exists between two adjacent favoured boundaries. Let the favoured boundary orientations be θ_A and θ_B and let the discontinuity occur at θ_t, where $\theta_A < \theta_t < \theta_B$. All boundaries in the range $\theta_A < \theta < \theta_t$ are composed of two units, one of which belongs to the favoured boundary at $\theta = \theta_A$. Thus all boundaries in this range may be represented on a decomposition lattice with basis vectors equal to the vectors characterizing the two boundary units appearing in that range. Similarly all boundaries in the range $\theta_t < \theta < \theta_B$ may be represented on another decomposition lattice with basis vectors equal to the vectors characterizing the two boundary units appearing in that range.

3. Selection rules for favoured tilt boundaries

Consider a decomposition lattice with basis vectors $\boldsymbol{u}_A$ and $\boldsymbol{u}_B$ corresponding to the vectors characterizing A and B boundary units. For the intervening boundary structures to change continuously with misorientation, it is necessary that they are all composed of A and B units, and may therefore be represented on this decomposition lattice. Therefore it must be possible to construct the vector characterizing the unit of any intervening boundary by taking the appropriate linear combination of $\boldsymbol{u}_A$ and $\boldsymbol{u}_B$, as in equation (1). This is the governing condition on the basis vectors of a decomposition lattice. It is emphasized that fulfilment of this condition is necessary but not sufficient for continuity of boundary structure, because, in addition, only one sequence of A and B units satisfies continuity of boundary structure, as described in part I, §4.3. However, in the absence of discontinuous changes in boundary structure at non-favoured boundary misorientations, the governing condition imposes certain requirements upon adjacent favoured boundaries.

The vector, $\boldsymbol{l}$, characterizing the unit of a centred boundary is never a crystal lattice vector in both grains, as explained in §2. Consider the case when A and B are units of non-centred boundaries. Then $\boldsymbol{u}_A$ and $\boldsymbol{u}_B$ are period vectors and therefore crystal lattice vectors. All lattice vectors of the corresponding decomposition lattice are therefore crystal lattice vectors. If centred boundaries occur for the tilt axis and crystal Bravais lattice considered†, the vectors characterizing the units of centred boundaries in the intervening misorientation range will not be lattice vectors of this decomposition lattice, and hence the governing condition is violated. Therefore

† Centred boundaries do not occur only for ⟨001⟩ tilt axes in simple cubic crystals.

at least one of the basis vectors of a decomposition lattice must characterize the unit of a centred boundary, whenever centred boundaries occur. Provided no discontinuous changes in the boundary structure exist at non-favoured boundary misorientations, the basis vectors of a decomposition lattice characterize units of adjacent favoured boundaries. In that case at least one of every two adjacent favoured boundaries must be centred. However, if a discontinuous change in boundary structure does occur between two adjacent favoured boundaries then they may both be non-centred. A condition exists that must be satisfied by non-centred favoured boundaries for such a discontinuity to be possible, and therefore for those boundaries to be adjacent. This condition is explained below.

If we assume that this type of discontinuity does not occur, the governing condition can also be used to deduce whether other favoured boundaries must exist between two known favoured boundary orientations, even if one of these known favoured boundaries is centred. Clearly two favoured boundaries cannot be adjacent if there exist any boundaries in the intervening misorientation range that cannot be represented on the corresponding decomposition lattice. In that case, at least the intervening boundary, the unit of which is characterized by the smallest vector, must be favoured. For example, suppose it has been determined in some f.c.c. metal that $\Sigma = 9\,(221)_1$, $141.06°/[1\bar{1}0]$ and $\Sigma = 27\,(115)_1$, $31.59°/[1\bar{1}0]$ symmetrical tilt boundaries are favoured. Units of these boundaries are characterized by $\frac{1}{2}[11\bar{4}]_1$ and $\frac{1}{4}[55\bar{2}]_1$ respectively. The vector $\frac{1}{4}[11\bar{2}]_1$ is the smallest one characterizing a unit of intervening boundaries, corresponding to $\Sigma = 3\,(111)_1$. Clearly $\frac{1}{4}[11\bar{2}]_1$ is not a p.d.l. vector of the decomposition lattice with basis vectors $\frac{1}{2}[11\bar{4}]_1$ and $\frac{1}{4}[55\bar{2}]_1$. Hence $\Sigma = 3\,(111)_1$ must also be favoured. Favoured boundaries $\Sigma = 3\,(111)_1$ and $\Sigma = 9\,(221)_1$ can be adjacent because all intervening boundaries may be represented on the decomposition lattice with basis vectors $\frac{1}{4}[11\bar{2}]_1$ and $\frac{1}{2}[11\bar{4}]_1$. But $\Sigma = 3\,(111)_1$ and $\Sigma = 27\,(115)_1$ cannot be adjacent favoured boundaries because the shortest vector characterizing a unit of an intervening boundary, i.e. $\frac{1}{4}[33\bar{2}]_1$, which characterizes $\Sigma = 11\,(113)_1$, is not a lattice vector of the decomposition lattice with basis vectors $\frac{1}{4}[11\bar{2}]_1$ and $\frac{1}{4}[55\bar{2}]_1$. Hence $\Sigma = 11\,(113)_1$ must also be favoured. It may be verified that any vector characterizing a unit of a symmetrical $[1\bar{1}0]$ tilt boundary in the range $31.59 \leqslant \theta \leqslant 141.06°$ may be represented on one of the three decomposition lattices with basis vectors $\frac{1}{4}[55\bar{2}]_1$, $\frac{1}{4}[33\bar{2}]_1$ or $\frac{1}{4}[33\bar{2}]_1$, $\frac{1}{4}[11\bar{2}]_1$ or $\frac{1}{4}[11\bar{2}]_1$, $\frac{1}{2}[11\bar{4}]_1$. Hence it is not necessary for any other boundaries in this range to be favoured. Nevertheless, other boundaries in this range may be favoured for reasons of energetics. Therefore, the above geometrical arguments determine the minimum number of favoured boundaries in the misorientation range between two known favoured boundaries. A boundary that is favoured in one material is not necessarily favoured in all materials with the same crystal structure. The only 'boundaries' that are certain to be favoured in all crystals with the same Bravais lattice are atomic planes in the ideal lattice. If the tilt axis is a symmetry rotation axis of the ideal crystal then as the misorientation of all non-equivalent boundary structures, in a given ξ-system, tends to zero the boundary plane tends to one of two distinct planes of the ideal crystal. The above geometrical arguments can then also be applied to these known favoured 'boundaries' in each ξ-system. In that case any boundaries that are necessarily favoured will be favoured in all materials with the same crystal structure. For example, as the misorientation of $[1\bar{1}0]$ symmetrical tilt boundaries tends to zero the boundary plane tends to (110) or (001) of the ideal crystal. However, neither of these 'favoured $[1\bar{1}0]$ symmetrical tilt boundaries' is centred in f.c.c. lattices. Therefore the centred $[1\bar{1}0]$ symmetrical tilt boundary, whose unit is characterized by the shortest vector, must be favoured. Thus $\Sigma = 3\,(111)_1$, $109.47°/[1\bar{1}0]$ is favoured in all f.c.c.

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crystals. It may be verified that the vectors characterizing units of all other $[1\bar{1}0]$ symmetrical tilt boundaries in f.c.c. crystals are p.d.l. vectors of the two decomposition lattices with basis vectors $\frac{1}{2}[110]$, $\frac{1}{4}[11\bar{2}]_1$ and $\frac{1}{4}[1\bar{2}1]_1$, $[00\bar{1}]$. Therefore there are no other favoured $[1\bar{1}0]$ symmetrical tilt boundaries that are geometrically necessary in all f.c.c. metals.

The energies of favoured boundaries, which have to exist between two known favoured boundaries for geometrical reasons, are not necessarily low compared with non-favoured boundaries. That is because the reasons why they are favoured are based entirely on geometrical considerations. Of course if the energy of a boundary is exceedingly high then the assumption of stability with respect to faceting may no longer be tenable. In that case the above considerations are inapplicable. We shall return to this point in §5.3 where the energy against misorientation relation is discussed.

It is emphasized that the above considerations regarding adjacent favoured boundaries are valid only when discontinuous changes in boundary structure do not occur at non-favoured boundary orientations. We shall now elucidate the necessary condition for the possible occurrence of a discontinuous change in boundary structure, at a non-favoured boundary orientation between two known favoured boundaries. Let the units, A and B, of two known favoured boundaries be characterized by vectors $\boldsymbol{u}_A$ and $\boldsymbol{u}_B$. Either of these favoured boundaries may be centred or non-centred. Similarly, let the shortest of vectors characterizing units from the intervening boundaries be $\boldsymbol{u}_C$ and the corresponding unit C. The necessary condition for a discontinuous change in boundary structure to occur between the favoured boundary orientations is the existence of a boundary in the same ξ-system (including the ideal crystal) with a unit, D, characterized by the vector $\boldsymbol{u}_D$, such that $\boldsymbol{u}_A + \boldsymbol{u}_D = \boldsymbol{u}_C$ for $\boldsymbol{u}_D \neq \boldsymbol{u}_B$. When this condition is satisfied, and it is energetically favourable for the discontinuous transition to occur, the two continuous series of boundary structures involved in the discontinuity will be (i) boundaries composed of A and D units and (ii) boundaries composed of B and C units. The discontinuous transition will occur in the range of misorientations between the boundaries that are composed of B and C units. On the other hand, the boundary composed of C units must always be favoured if the above condition cannot be satisfied and $\boldsymbol{u}_A + \boldsymbol{u}_B \neq \boldsymbol{u}_C$. As a first example assume that it has been determined in some f.c.c. metal that $\Sigma = 3\,(112)_1$ and $\Sigma = 17\,(223)_1$ symmetrical $[1\bar{1}0]$ tilt boundaries are favoured. Both of these boundaries are non-centred and they are characterized by $[11\bar{1}]_1$ and $\frac{1}{2}[33\bar{4}]_1$ respectively. The boundary $\Sigma = 43\,(335)_1$ is the intervening boundary whose unit is characterized by the smallest vector, i.e. $\frac{1}{4}[55\bar{6}]_1$. The vector $\frac{1}{4}[55\bar{6}]$ may be obtained by adding $\frac{1}{4}[11\bar{2}]$, which characterizes a unit of $\Sigma = 3\,(111)$ boundary, to $[11\bar{1}]$. Hence it is possible that a discontinuous change in boundary structure occurs between $\Sigma = 43\,(335)_1$ and $\Sigma = 17\,(223)_1$ boundary orientations. The discontinuity would involve the following two continuous series of boundary structures: (i) boundaries composed of units of $\Sigma = 3\,(112)_1$ and $\Sigma = 3\,(111)_1$ and (ii) boundaries composed of units of $\Sigma = 43\,(335)_1$ and $\Sigma = 17\,(223)_1$. If indeed the discontinuity did occur then $\Sigma = 3\,(112)_1$ and $\Sigma = 17\,(223)_1$ would be adjacent, non-centred, favoured boundaries. As a counter-example, assume that it has been determined that $\Sigma = 3\,(112)_1$ and $\Sigma = 9\,(114)_1$ symmetrical $[1\bar{1}0]$ tilt boundaries are favoured in some f.c.c. metal. These non-centred boundaries are characterized by the vectors $[11\bar{1}]_1$ and $[22\bar{1}]_1$. Then $\Sigma = 11\,(113)_1$ is the intervening boundary whose unit is characterized by the smallest vector, i.e. $\frac{1}{4}[33\bar{2}]_1$. No vector characterizing a unit of any $[1\bar{1}0]$ symmetrical tilt boundary can be added to either $[11\bar{1}]_1$ or $[22\bar{1}]_1$ to give $\frac{1}{4}[33\bar{2}]_1$. In addition $[11\bar{1}]_1 + [22\bar{1}]_1 \neq \frac{1}{4}[33\bar{2}]$ and therefore $\Sigma = 11\,(113)_1$ must be favoured.

4. Grain boundary dislocations

4.1. *Reference structures for the intrinsic secondary g.b.d. content of non-favoured boundaries*

Consider a non-favoured boundary in which the fundamental structural elements are A and B boundary units. Let there be yB units for every xA units where x and y are coprime integers and $x > y$. The atomistic calculations reported in parts I and II show that B units coincide with the centres of localized, distinct, stress fields of edge g.b.ds superimposed on the field of the ideal favoured boundary composed of A units. Since those sources of edge dislocation stress fields do not exist in the favoured boundary composed of A units, it was argued that the last boundary is the most appropriate choice of reference structure for describing the secondary g.b.d. (s.g.b.d.) content of the non-favoured boundary.

The elastic field of the boundary extends away from the boundary plane up to distances comparable with its period. If x/y is not an integer the spacing of B units is no longer uniform and there may then exist a number of possible reference structures for describing the elastic field far from the boundary. If x/y is close to an integer, I, then the long range field of the boundary will appear to be caused by an array of g.b.ds based on the reference structure composed of x_mA units and y_mB units, where $x_m/y_m = I$ (see also Read & Shockley 1950). If $x/y = I + \frac{1}{2}$ then the boundaries for which $x/y = I$ or $I+1$ are equally suitable reference structures for describing the long-range field of the boundary. This ambiguity is the same as that which arises in the most appropriate choice of reference structure for 1:1 non-favoured boundaries, where either of the corresponding favoured boundaries may be selected (see part I). For irrational values of x/y there exists a hierarchy of possible reference structures for describing the long-range field, in which the values of x/y for the reference structures are rational fractions such that $x+y$ decreases as one proceeds up the hierarchy. For example, for $x/y = \sqrt{3}$ one could choose $x/y = 173/100, 9/5, 2/1$. As one proceeds up such a hierarchy the corresponding g.b.d. spacings decrease and the Burgers vectors tend to increase. The limit of the hierarchy is always the integer nearest to x/y. Sutton *et al.* (1981) called a reference structure that is composed of a mixture of two different types of boundary unit a multiple unit reference structure (m.u.r.s.). G.b.ds based on a m.u.r.s. were similarly termed 'virtual'† because although they describe the long-range field of the boundary‡ they do not account for all the g.b.d. stress fields that are visible in the stress field map of the boundary.

Properties of the boundary that are dependent only on the long-range field are insensitive to whether the m.u.r.s. or favoured boundary reference structure is used. For example, it is well known that the strong beam image of a dislocation obtained in the transmission electron microscope by diffraction contrast is primarily caused by the scattering of electrons by the long-range field of the dislocation. It is therefore quite likely that a strong beam image of a boundary near to a m.u.r.s. will reveal the corresponding virtual s.g.b.d. network, provided there is sufficient scattering for any contrast to be formed at all. By using weaker beam conditions the electron scattering will occur in regions closer to the g.b.d. cores. Eventually, under very weak beam conditions, it may be possible to resolve the secondary g.b.ds based on the favoured boundary reference structure. It is clear, however, that the observation of intrinsic g.b.ds in a boundary

† This terminology is consistent with the definition of a 'virtual' g.b.d. provided by Hirth & Balluffi (1973).

‡ By the long-range field of the boundary we mean the field at distances comparable with the period of the boundary structure. The boundaries discussed in this section do not possess a field that extends infinitely far, in contrast to the field of a boundary containing imperfect steps as discussed in part II.

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does not necessarily imply that the underlying structure is a favoured boundary: it may be a m.u.r.s. If indeed a m.u.r.s. were interpreted as a favoured boundary it would imply that the m.u.r.s. occurs at a discontinuous change in boundary structure, which is not true in general.

4.2. *Extrinsic g.b.ds*

All g.b.ds discussed so far in this work have been an inseparable part of the equilibrium structure of the boundary, i.e. intrinsic g.b.ds. Extrinsic g.b.ds enter the boundary from the adjoining grains or they may be generated by Bardeen–Herring sources in the boundary. The distinction between intrinsic and extrinsic g.b.ds can be maintained only by reference to the equilibrium structure of the boundary before the extrinsic dislocations appeared. This distinction is redundant if the extrinsic g.b.ds become fully incorporated into the intrinsic g.b.d. array. Moreover, extrinsic g.b.ds may always be regarded as intrinsic g.b.ds of a boundary nearby in the misorientation/inclination range. Nevertheless, there are a number of expected differences between extrinsic and intrinsic g.b.ds, which indicate that extrinsic dislocations may be very important in some grain boundary processes whenever the distinction is meaningful.

First, as discussed in part I, §4.3 and part II, §4, intrinsic g.b.ds, which accommodate a misorientation from some reference structure, are rarely expected to be associated with steps in the boundary plane. It is only in very low Σ boundaries that it may be energetically favourable for non-primitive, stepless d.s.c. dislocations to dissociate into primitive d.s.c. dislocations, with associated steps. On the other hand a lattice dislocation entering a boundary must, in general, create a step in the boundary plane. Whatever the subsequent dissociation of this lattice dislocation into g.b.ds the total step height must be conserved. Thus extrinsic dislocations are sources of steps in the boundary plane.

Secondly, in high-angle tilt boundaries the Burgers vectors of such intrinsic g.b.ds are always perpendicular to the reference boundary plane (see part II, §3.2). Intrinsic dislocations in low-angle asymmetrical tilt boundaries are lattice dislocations and generally have Burgers vector components both parallel and perpendicular to the boundary plane. However, even in this case the net Burgers vector content parallel to the boundary plane is zero. In general the Burgers vectors of extrinsic g.b.ds have components both perpendicular and parallel to the boundary plane. Thus extrinsic g.b.ds are sources of Burgers vector components parallel to the boundary in high-angle pure tilt boundaries. As pointed out in part II a change in the mean boundary plane of a high-angle tilt boundary can be accomplished by an array of edge g.b.ds associated with steps and possessing Burgers vector components parallel to the reference boundary plane. Such a grain boundary has an elastic field that extends infinitely far and its occurrence may be stress-induced as in the formation of lenticular deformation twins. The structure of such a boundary is not the minimum boundary energy configuration because boundaries that appear in the equilibrium Wulff plot do not possess elastic fields of infinite range. The frequency of occurrence of these metastable interfaces presumably depends on the degree to which the specimen is equilibrated.

The third difference between extrinsic and intrinsic g.b.ds is that the atomic structure and stress field of an extrinsic g.b.d. can be entirely different from those of intrinsic g.b.ds associated with the localized, distinct, edge g.b.d. stress fields seen in the stress field maps of non-favoured tilt boundaries (see parts I and II). When a lattice dislocation enters the boundary it may dissociate into extrinsic g.b.ds based on a variety of possible reference structures. If the Burgers vectors of the dissociation products are not d.s.c. vectors of the coincidence system to which the

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non-favoured boundary belongs then the structure of the boundary will be changed far from their cores. However, it seems physically unreasonable that the dissociation products are governed by the boundary structure far away from their cores (say > 100 nm). On the contrary, one expects the boundary structure near the dislocations to govern their Burgers vectors and the atomic structure of their cores. In that case the local boundary structure is the reference structure for the dissociation products. It is, nevertheless, clear that whereas the choice of reference structure for describing the intrinsic g.b.d. content is arbitrary in that it does not influence the atomic structure of the boundary, the dissociation products of a lattice dislocation that entered the boundary are determined by the choice of reference structure. It is therefore possible for the dissociation products of a lattice dislocation to have Burgers vectors and atomic structures that are different from the intrinsic g.b.ds.

4.3. *Plane-matching g.b.ds*

The basic physical problem in understanding plane-matching dislocations (Pumphrey 1972) is why a one-dimensional matching of planes at a boundary should be so favourable that it is preserved by arrays of g.b.ds. As pointed out by Schindler *et al.* (1979) plane matching boundaries cannot be regarded as 'special' because they are far from any low-Σ orientation. Although no atomistic calculations of mixed tilt and twist boundary structures have been made the results presented in this work and by Sutton (1982) provide some clues as to what may be expected.

Any symmetrical tilt boundary may be regarded as a 180° twist boundary. Therefore, when the tilt angle of a symmetrical tilt boundary is varied from some favoured misorientation we may think of this as a tilt deviation applied to a twist boundary. The results presented in part I indicate that such tilt deviations are accommodated by intrinsic, secondary, edge g.b.ds that are always localized and distinct. These edge g.b.ds may be thought of as plane matching dislocations preserving the favoured symmetrical tilt (180° twist) boundary. Conversely, the result that the structures of non-favoured boundaries, at all tilt misorientations between any two favoured tilt boundaries, consist of specific sequences of only two fundamental structural elements, suggests that all tilt boundaries will resist a perturbation. In that case a twist deviation applied to any tilt boundary will result in the formation of networks of localized, distinct, screw dislocations. These screw dislocations will appear as plane matching dislocations preserving the orientation of planes perpendicular to the tilt axis of the original tilt boundary. These considerations imply that it is not one-dimensional lattice matching that is the reason *per se* for the existence of plane matching dislocations. It is rather that every tilt or twist boundary structure has a well defined structure and resists twist or tilt deviations respectively. However, atomistic calculations of mixed tilt and twist boundaries are required to substantiate this view further.

5. Implications for the properties of grain boundaries

5.1. *General classification of grain boundary properties*

To understand the relation between the structure and properties of grain boundaries it is convenient to distinguish between three classes of properties. The first is the class of properties that depend only on the structure of the core region of the boundary, i.e. up to about 5 Å (0.5 nm), say, on either side of the geometrical boundary plane. Examples of such properties are grain boundary diffusion, the effectiveness of boundaries to act as sources and sinks for vacancies and segregation effects. These properties govern such phenomena as the ability of a boundary to slide and migrate, boundary cavitation and embrittlement. The second is the class of properties

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that depends only on the long-range elastic field of the boundary, e.g. the long-range interaction of the boundary with crystal defects. The third is the class of properties that depend both on the structure of the core region and on the long-range elastic field of the boundary. Examples are the boundary energy and the rate at which boundaries are able to absorb impurity atoms.

When discussing the variation of some boundary property with misorientation it is important first to ascertain to which of the above three classes the property belongs. For example, let us assume that continuity of boundary structure exists throughout the misorientation range between two adjacent favoured boundaries. Hence the structure of the boundary core region changes continuously throughout this misorientation range. However, the long-range field of the boundary changes at m.u.r.s. orientations in the same way as it does at favoured boundary orientations. Therefore the first derivative of properties of the first class, with respect to boundary misorientation, is expected to be continuous throughout the misorientation range between the adjacent favoured boundary orientations. On the other hand a discontinuity is expected in the first derivative of properties of the second and third classes at m.u.r.s. orientations. If a discontinuous change in boundary structure occurs between the adjacent favoured boundaries then different boundary units appear in the non-favoured boundaries on either side of the misorientation, θ_t, at which the discontinuity occurs. If the property belongs to the first class, then both the property itself and its derivatives change discontinuously at θ_t. Furthermore, units introduced into boundaries on either side of a favoured boundary orientation are different. Hence, at misorientations near a favoured boundary, a property of the first class changes continuously but its first derivative does not. We may therefore conclude that only properties of the first class should be used to detect favoured boundaries. Favoured boundaries exist at those misorientations where the property itself is continuous but its first derivative, with respect to boundary misorientation, is not.

We turn now to the general differences expected for the properties of favoured and non-favoured boundaries. Non-favoured boundaries have longer-range elastic fields than favoured boundaries, enabling the former to interact with lattice defects that are further away from the boundary. Therefore properties of the second and third classes are expected to depend significantly on whether the boundary is favoured or non-favoured. The ability of a boundary to absorb or emit vacancies may be higher in non-favoured boundaries owing to the presence of terminating planes associated with secondary dislocation stress fields. In general, however, when we consider properties of the first class it is not obvious that large differences should occur for favoured and non-favoured boundaries. This is demonstrated below for grain boundary diffusion and has also been found in atomistic studies of the changes in boundary structure caused by segregation of impurities (Sutton & Vitek 1982).

5.2. *Grain boundary diffusion*

Grain boundary diffusion occurs in the core of grain boundaries (see, for example, Peterson 1980), and it is therefore a property of the first class. Perhaps the most widely accepted model of grain boundary diffusion is the so called 'pipe diffusion model', where rapid diffusion is envisaged along the cores of intrinsic g.b.ds. This model has been particularly successful in the low-angle régime where the intrinsic g.b.ds are lattice dislocations and semi-quantitative agreement with experiment has been obtained (Turnbull & Hoffman 1954). A non-favoured high-angle tilt boundary is composed of two species of fundamental structural elements. There is no *a priori* reason to expect one species of structural element to be an easier path for diffusion than another.

Therefore in principle the boundary regions between the centres of intrinsic secondary g.b.d. stress fields may be easier paths for diffusion. For example in part I, §4.2 the relaxed $\Sigma = 27\,(115)_1$ symmetrical $[1\bar{1}0]$ tilt boundary structure in aluminium was found to be favoured. Within each unit (see fig. 1*a* of part I) the irregular pentagon is seen to be an easy path for diffusion. On the other hand, the fundamental structural elements introduced at higher and lower angles of misorientation belong to more densely packed favoured boundaries, i.e. $\Sigma = 11\,(113)_1$ and the ideal crystal, respectively. Therefore the cores of $\pm\frac{2}{27}[115]$ d.s.c. dislocations, which preserve the $\Sigma = 27\,(115)_1$ favoured boundary structure and are located at all the centres of the secondary g.b.d. stress fields in the boundary, correspond to more densely packed regions of the non-favoured boundaries. We therefore expect the grain boundary diffusion coefficient to decrease as the deviation from the $\Sigma = 27\,(115)_1$ orientation increases. Herbeuval & Biscondi (1971) measured the penetration of zinc into $[1\bar{1}0]$ symmetrical tilt boundaries in aluminium. They found that the penetration parallel to the tilt axis was very low at both the $\Sigma = 11$ and ideal crystal orientations. The penetration increased uniformly to a pronounced maximum at about the $\Sigma = 27$ orientation. This is in complete agreement with the above considerations.

Rapid grain boundary diffusion along the cores of intrinsic secondary g.b.ds preserving a favoured boundary reference structure may be anticipated near the coherent twin ($\Sigma = 3\,(111)_1$, $109.47°/[1\bar{1}0]$) in f.c.c. crystals. The coherent twin is always favoured and densely packed. Hence if rapid diffusion occurs at all in nearby boundaries, it must be along the cores of the corresponding intrinsic secondary g.b.ds. However, the grain boundary diffusion coefficient is never expected to be the same in two tilt boundaries equally misoriented, but in opposite senses, from a favoured boundary orientation. This is because the core structures of corresponding intrinsic $\pm\,\boldsymbol{b}$ g.b.ds are never the same, except when the reference structure is the ideal lattice (see part I, §4.3). The measurements of Herbeuval & Biscondi (1971) show that the dependence of the penetration of zinc into $[1\bar{1}0]$ tilt boundaries in aluminium is asymmetrical with respect to the coherent twin orientation and there is a minimum at the coherent twin orientation.

5.3. *The energy against misorientation relation*

In this section we consider the variation of the boundary energy, γ, with the boundary misorientation, θ, assuming that the other four macroscopic degrees of freedom of the boundaries are fixed. Since the structures of twist boundaries may be classified in an analogous manner to those of tilt boundaries, in terms of favoured and non-favoured boundaries (Sutton 1982), the considerations of this section are equally applicable to twist boundaries. For tilt boundaries the tilt axis and ξ-system are assumed fixed, while for twist boundaries the twist axis and boundary plane are assumed fixed.

Since the stress fields of localized, distinct intrinsic g.b.ds are always associated with all fundamental structural elements introduced into boundaries, after a small misorientation from a favoured boundary orientation, there must always be cusps in $\gamma(\theta)$ at favoured boundary orientations. However, because favoured boundaries do not necessarily possess very low energies (see §3), it is possible that these cusps are shallow. At the same time cusps in $\gamma(\theta)$ also occur at m.u.r.s. orientations. However, the depth of such a cusp depends on the Burgers vector of the d.s.c. dislocations based on the m.u.r.s. Since a m.u.r.s. is frequently associated with a high value of Σ the depth of the corresponding cusps may be too small to be detected experimentally.

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5.4. *Grain boundary sliding and migration*

It has been suggested that grain boundary sliding is effected by the movement of intrinsic g.b.ds (see, for example, Kegg *et al.* 1973, Gates 1973). It is clear that for such a mechanism to operate there must be a net component of the Burgers vectors of the intrinsic dislocations parallel to the boundary plane. As pointed out in §4.2 a tilt boundary containing imperfect steps satisfies this condition. However, since an interface of this type may always be transformed into one that is free of imperfect steps by, for example, long-range diffusion, it is uncertain how significant this is for grain boundary sliding. If the tilt boundaries in a specimen are equilibrated they will contain only perfect steps and g.b.ds with Burgers vectors normal to the reference boundary planes. Sliding can then occur only if extrinsic dislocations are introduced into the boundary. This suggests an intimate relation between sliding of high-angle pure tilt boundaries and plastic deformation of the grain interiors. Experiments by Watanabe & Davies (1978) on the sliding of copper bicrystals demonstrate that the sliding rate is indeed closely related to the crystal deformation. They found that this relation is less pronounced when the boundaries had a twist component. The reason is that the sliding is then effected by both intrinsic screw g.b.d. glide and the glide/climb of extrinsic g.b.ds.

Smith & Rae (1979) proposed a model for grain boundary migration based on the movement of g.b.ds with steps associated with their cores. The local migration of the boundary plane when such a dislocation moves is equal to the height of the associated step. Since intrinsic g.b.ds accommodating a misorientation from some reference structure are not normally expected to be associated with steps they generally cannot be agents of grain boundary migration. At the same time it seems unlikely that a tilt boundary that is associated with a long-range stress field will not transform into one free of long-range stresses during recrystallization or grain growth. In that case only perfect steps would exist in the boundary. Therefore a dislocation mechanism of the migration of grain boundaries probably requires the presence of extrinsic g.b.ds possessing steps. Extrinsic dislocations are, of course, plentiful during the recrystallization of a deformed matrix. Recently, Balluffi & Cahn (1981) and Smith & King (1981) proposed a similar mechanism for diffusion-induced grain boundary migration. It appears that extrinsic g.b.ds may also be necessary in general for the operation of that mechanism.

6. Conclusions

1. The vectors characterizing the fundamental structural elements composing all boundaries in a certain misorientation range are the basis vectors of a two-dimensional lattice, called the decomposition lattice. Vectors characterizing the units of all the intervening boundaries are primitive lattice vectors of this decomposition lattice (p.d.l. vectors).

2. Conversely, the basis vectors of a decomposition lattice must be such that the vectors characterizing the units of all intervening boundaries are lattice vectors of this decomposition lattice. This is the governing condition on the basis vectors of a decomposition lattice. In the absence of discontinuous changes in boundary structure at non-favoured boundary orientations it follows from this governing condition that, in every ξ-system, at least one of every two adjacent favoured boundaries must be a centred boundary. Furthermore, for any two favoured boundaries in a ξ-system, of which at least one is centred, other favoured boundaries may have to exist in the misorientation range between them to satisfy the governing condition. The necessary condition

for the possible occurrence of a discontinuous change in boundary structure at a non-favoured boundary orientation was formulated. If this condition is satisfied, and it is energetically favourable for the discontinuity to occur, then two favoured boundaries may be adjacent and non-centred and/or an intervening boundary that was formerly required to be favoured is no longer favoured.

3. The observation of intrinsic g.b.ds in the transmission electron microscope does not imply that the corresponding reference structure is a favoured boundary: it may be a multiple unit reference structure (m.u.r.s.). This distinction is crucial for an understanding of the variation of the atomic structure and certain properties of boundaries in the misorientation range because discontinuous changes in boundary structure always occur at favoured boundary orientations but not, in general, at m.u.r.s. orientations.

4. Several important differences between intrinsic and extrinsic g.b.ds exist, whenever the distinction between these dislocations can be maintained. Extrinsic g.b.ds are generally associated with steps in the boundary plane, in contrast to secondary intrinsic g.b.ds accommodating a misorientation from some reference structure. In high-angle tilt boundaries the Burgers vectors of intrinsic g.b.ds accommodating a misorientation from some reference structure are always perpendicular to the reference boundary plane, whereas the Burgers vectors of extrinsic g.b.ds may point in any direction. The dissociation of an incoming lattice dislocation may produce extrinsic g.b.ds with no relation to the Burgers vectors or core structures of the underlying intrinsic g.b.ds based on the appropriate favoured boundary reference structure.

5. On the basis of the results for tilt boundaries, presented in parts I and II, and twist boundaries, discussed by Sutton (1982), it is suggested that all tilt or twist boundary structures are highly ordered. A tilt deviation applied to a twist boundary will therefore result in edge 'plane-matching dislocations' preserving the original twist boundary structure. Similarly, a twist deviation applied to a tilt boundary will result in screw 'plane-matching dislocations' preserving the original tilt boundary structure. Thus one-dimensional lattice matching is viewed as a consequence of, rather than a reason for, plane matching dislocations.

6. Grain boundary properties may be divided into three classes. Properties of the first and second classes depend only on the core structure and long-range field of the boundary respectively, whereas properties of the third class depend on both. Only properties of the first class should be used to detect favoured boundaries. Favoured boundaries exist at misorientations where a property of the first class is continuous, but its first derivative with respect to boundary misorientation is not. The grain boundary self-diffusion coefficient is a suitable property for determining which boundaries are favoured, but the grain boundary energy is not.

7. Rapid diffusion along the cores of intrinsic secondary g.b.ds, accommodating a misorientation from some favoured boundary reference structure, in high-angle tilt boundaries does not necessarily occur because those cores may be more densely packed than the boundary regions between them. However, if diffusion does occur predominantly along the cores of intrinsic g.b.ds in a high-angle tilt boundary, then the diffusion coefficients are not equal in boundaries equally misoriented from the favoured boundary orientation, but in opposite senses. This is because the core structures of $\pm \boldsymbol{b}$ intrinsic secondary edge g.b.ds in high-angle tilt boundaries are never identical.

8. Cusps in the energy against misorientation relation occur at both favoured boundary and m.u.r.s. orientations, and in each case the cusp depth depends on the Burgers vectors of the corresponding intrinsic g.b.ds. Most of these cusps are probably too shallow to be detected

experimentally. Furthermore, the cusp at a geometrically necessary favoured boundary orientation may be shallow because the energy of the favoured boundary can be relatively high.

9. The sliding rate of high-angle pure tilt boundaries will be, in general, closely coupled to the rate of bulk deformation. Lattice dislocations entering the boundary are usually the predominant source of g.b.ds with Burgers vectors components parallel to the boundary, and hence they become the agents of sliding.

10. Grain boundary migration by a dislocation mechanism at temperatures where long-range diffusion is possible generally requires the presence of extrinsic g.b.ds, to provide the necessary dislocations associated with steps.

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