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Grain Boundary Structures in f.c.c. and b.c.c. Metals and Sites for Segregated Impurities

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Abstract

The key features leading to low-energy grain boundaries in metals are discussed by reference to computer-simulated structures and geometrical analysis in terms of atom packing. Low energy is found to be associated with boundary structures consisting of relatively dense packing, and this can in turn be expressed in terms of the space-filling packing of coordination polyhedra. The geometrical method of analysis is shown to be well suited to the identification of interfacial sites for segregated impurities.

Introduction

The present authors have carried out an investigation of coincidence grain boundary structure by computer simulation; mainly $\langle 100\rangle$ and $\langle 110\rangle$ tilt boundaries in f.c.c. (Smith, Vitek & Pond, 1977; Pond & Vitek, 1977; Pond, Smith & Vitek, 1979) and b.c.c. metals (Vitek, Smith & Pond, 1979) have been studied. The procedure adopted for studying a chosen boundary was to create initially an unrelaxed model of that boundary and subsequently to allow relaxation to a minimum energy structure. The relaxation process allowed individual atoms to move away from their unrelaxed positions, and also rigid body displacement of one grain to occur relative to the other. In order to elucidate the characteristic features of fully relaxed boundary structures in f.c.c. metals the method, originally proposed by Frank & Kasper (1958) and developed by Bernal (1964), for analysing atomic packing in complex structures was used. This method of analysis showed that grain boundaries in f.c.c. metals contain structural elements similar to those found in close-packed crystals and other elements closely resembling configurations which occur in simple liquid metals. Atom-packing analysis has also been found useful in the study of simulated boundary structures in b.c.c. metals. Characteristic structural elements also exist in these boundaries but are distinct from those found in the boundaries of f.c.c. metals.

The purpose of the present work is to describe the method of atom-packing analysis, and to summarize the main conclusions reached by its application to simulated boundary structures. To illustrate the structural differences between boundaries in f.c.c. and b.c.c. metals, one simulated boundary in each type of metal is analysed in detail. The boundary structures chosen for presentation have identical relative orientations of the adjacent crystals, *viz* [110] 38·9°, and the plane of the boundary in both cases is $(1\bar{1}4)$, *i.e.* the two structures are $\Sigma = 9$ symmetrical tilt boundaries in f.c.c. and b.c.c. metals. In addition, preliminary results concerning the identification of sites for impurity atoms segregated to boundaries are presented.

Atom-packing analysis

Frank & Kasper (1958, 1959) developed an elegant geometrical procedure which they used to show that complex alloy structures can be represented as packings of spheres. This work inspired Bernal (1964) to consider the structure of simple liquids in terms of close-packing arrangements of identical spheres in which crystallization has been frustrated. The ideas contained in these works are especially appropriate for analysis of grain boundary structures in close-packed metals, and this has been recognized by the present authors and independently by Ashby, Spaepen & Williams (1978). In this section the basic geometrical definitions set out by Frank & Kasper (1958) are given,

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and the way in which the analysis may be extended to structures in b.c.c. metals is described.

It is more convenient to consider the arrangement and form of space-filling polyhedra representing close-packed spheres than to consider the spheres themselves. Three types of polyhedra are useful: (1) the *domain* of each atom, (2) the *coordination polyhedron* of each atom, and (3) the *coordination polyhedron* of voids at the interstices between spheres. Unambiguous definitions of these polyhedra require precise definition of *neighbouring spheres* (as opposed to nearest neighbours) and coordination number. Moreover, these definitions must remain valid when intersphere separations are distorted somewhat from equilibrium values as is likely to occur in interfacial structures. The domain of an atom is the space in which all points are nearer to the centre of that atom than that of any other. It is a polyhedron, each face of which is the plane equidistant between that atom and a neighbour. Consider all planes bisecting lines joining the central atom to all other atoms; the innermost polyhedron bounded by these planes is the domain of that central atom. Atoms which are neighbours must have one face of their domains in common. The number of neighbours is called the coordination number of the central atom, and the set of neighbours its coordination shell. The polyhedron whose edges are the lines joining the centres of all the atoms of the coordination shell which are also neighbours of each other is called its coordination polyhedron. A coordination polyhedron and domain have a dual relationship, each having a vertex corresponding to each face of the other. The edges of a void coordination polyhedron join the atoms in the coordination shell of a void as represented by a hypothetical sphere just filling that void.

In the analysis of grain boundary structures we have found the coordination polyhedra of atoms and voids to be particularly useful constructions, and have considered domains only in order to establish whether atoms are neighbours or not. We now consider the form of these polyhedra in f.c.c. and b.c.c. crystals. The domain of each atom in a f.c.c. crystal is a rhombic dodecahedron and the atomic coordination polyhedron is a cuboctahedron. There are two types of void coordination polyhedra, octahedra and tetrahedra; the centres of the octahedra are located at domain vertices where four edges meet, and the tetrahedra at vertices where three edges meet. All edges of both types of void coordination polyhedra are $\frac{1}{2}\langle 110\rangle$. Domains in b.c.c. crystals are truncated octahedra, and atomic coordination polyhedra are rhombic dodecahedra. There are two types of void coordination polyhedra, distorted octahedra (four $\langle 100\rangle$ and eight $\frac{1}{2}\langle 111\rangle$ edges) and distorted tetrahedra (two $\langle 100\rangle$ and four $\frac{1}{2}\langle 111\rangle$ edges). The distorted octahedra may be regarded as four distorted tetrahedra sharing a common $\langle 100\rangle$ edge.

We now consider the likely form of void coordination polyhedra in close-packed structures other than f.c.c. crystals. The densest arrangement of identical spheres in a plane is triangulated packing as in f.c.c. (111). It follows that we should expect coordination polyhedra with equilateral triangular faces to be ubiquitous in densely packed materials. Three of the five Platonic polyhedra (tetrahedra, octahedra and icosahedra) are of this type; the importance of the first two in f.c.c. crystals has been mentioned already, and the third is known to lead to local densities greater than that for f.c.c. crystals although such polyhedra alone cannot fill space (Wells, 1975). In an icosahedron formed by twelve identical spheres, a thirteenth sphere with 10% smaller diameter can be accommodated in the central void. Triangulated coordination polyhedra with coordination 14, 15 and 16 are also known to be important in complex alloy structures such as Laves phases (Frank & Kasper, 1959). If identical spheres are placed at the vertices of a symmetrical pentagonal bipyramid and the separation of the spheres along the axis is equal to the edge length in the pentagonal ring, the faces closely approach equilaterial triangles (Frank & Kasper, 1958). This figure is equivalent to five congruent tetrahedra with the bipyramid's axis as a common edge so that there is no central void unless some extension along the axis is present (M. F. Ashby, private communication). Further triangulated void coordination polyhedra were identified by Bernal (1964). In addition to tetrahedra and octahedra, Bernal found capped trigonal prisms, capped square antiprisms and tetragonal dodecahedra. He also identified uncapped trigonal prisms and square antiprisms; these latter polyhedra, having a mixture of square and equilaterial triangular faces, are examples of semiregular or Archimedean polyhedra.

The above discussion indicates that void coordination polyhedra in dense packings of identical spheres have triangulated or Archimedean form. The distinguishing features of these polyhedra are that all the edge lengths have magnitudes close to that of the sphere diameter, and that the central void is too small to accommodate a further sphere. It is reasonable to expect such void polyhedra to be prominent in f.c.c. metal grain boundary structures. The polyhedra in b.c.c. metal boundaries are likely to be similar to those in f.c.c. but, in general, distorted. It is reasonable to anticipate polyhedra having edge lengths with magnitudes equal to $\langle 100\rangle$ and $\frac{1}{2}\langle 111\rangle$ and values intermediate between these two.

Computer-simulated structures

We first consider the constraints on the formation of polyhedra at coincidence grain boundaries; there are two:

(*a*) the sequence of polyhedra forming the interface must be periodic due to the periodicity of the meeting grains;

(*b*) the interfacial polyhedra must be structurally complementary to those of the adjacent crystals.

In the computer-simulation work carried out so far, mainly $\langle 100\rangle$ and $\langle 110\rangle$ tilt boundaries have been considered. Therefore, because of constraint (*a*), only polyhedra consistent with ...*ababa*... stacking need be considered, *i.e.* the void polyhedra illustrated in Fig. 1 and the cube.

The general features of the structure of $\langle 100\rangle$ and $\langle 110\rangle$ tilt boundaries in Al have been reported (Smith, Vitek & Pond, 1977; Pond & Vitek, 1977; Pond, Smith & Vitek, 1979). Minimum-energy boundaries are generally narrow configurations characterized by relative displacements away from the coincidence position, and having somewhat lower density than perfect f.c.c. crystals. Tetrahedral, octahedral and/or trigonal prismatic void coordination polyhedra occur invariably, and often the square faces of trigonal prisms are capped by half octahedra. Fig. 2 shows the $\Sigma = 9$ $(1\bar{1}4)$ boundary in Al. The boundary may be regarded as a sequence of void polyhedra as shown in Fig. 2(*b*); tricapped trigonal prisms, *s* (shown hatched), are connected to bicapped trigonal prisms, *t*, by tetrahedra, *u*, all having edge magnitudes close to $a/\sqrt{2}$, where a is the lattice parameter. However, the restraining forces of the adjacent crystals do not allow all the interfacial material to form well-defined triangulated or Archimedean polyhedra; other irregular polyhedra, *r*, are also formed. The occurrence of isolated irregular polyhedra in this way is a general feature of the boundaries in f.c.c. metals studied so far, although exceptions do occur such as the very low energy $\Sigma = 11$ symmetrical (311) boundary which comprises entirely capped trigonal prisms (extended 5% in one dimension) and tetrahedra (Pond, Smith & Vitek, 1979).

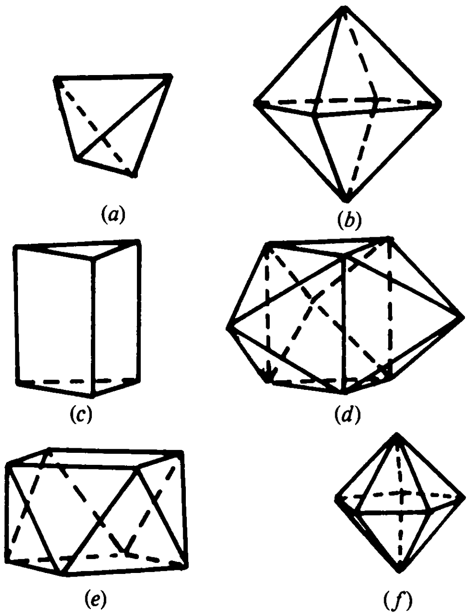
Fig. 1. Triangulated and Archimedean void coordination polyhedra consistent with ...*ababa*... stacking; (*a*) tetrahedron, (*b*) octahedron, (*c*) trigonal prism, (*d*) capped trigonal prism, (*e*) square antiprism, (*f*) pentagonal bipyramid. All edges have equal length.

An example of a minimum-energy boundary in b.c.c. Fe is shown in Fig. 3(*a*), and its analysis in terms of void coordination polyhedra in Fig. 3(*b*). The boundary has the same crystallographic form as that in Fig. 2(*a*), *i.e.* $\Sigma = 9$ symmetrical $(1\bar{1}4)$. Pentagonal biprisms *ecfhgde'* and *kilnmjk'* (where each letter represents a vertex atom and *e'* is $\langle 110\rangle$ perpendicularly below *e*, *etc.*) are connected to each other by face-sharing tetrahedra *eifh*, *eijh*, *ehjg* and *jhik'*. In this structure, microscopic mirror symmetry across the interface has been preserved and the atoms *b* and *h* occupy sites very close to coincidence sites; such configurations appear to be more common in boundaries of b.c.c. metals than of f.c.c. The coordination polyhedra of atoms *e* and *k* are pentagonal prisms, *e.g.* *cfhgdc'f'h'g'd'*, in which the edge magnitudes in the pentagonal rings are close to $a\sqrt{3}/2$ but the axes have a magnitude equal to $\sqrt{2}a$ [*c.f.* restriction (*a*)]. Atoms *e* and *k* do not occupy the centre of their respective prisms but have relaxed to the right

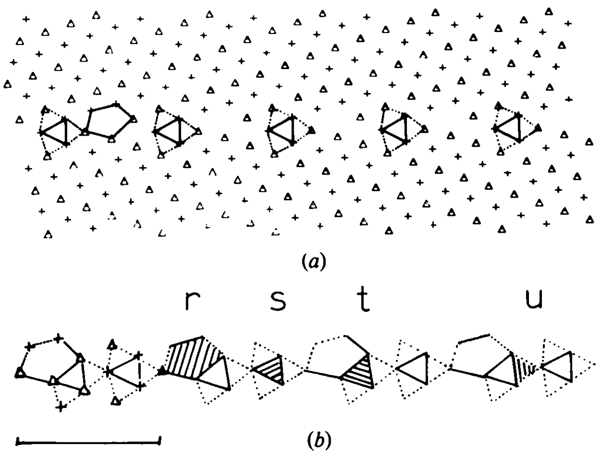

Fig. 2. (*a*) Low energy $\Sigma = 9$ symmetrical $(1\bar{1}4)$ boundary in Al. The tilt axis is $\langle 110\rangle$ and is perpendicular to the plane of the page; triangles and crosses represent ...*ababa*... stacking. (*b*) Schematic drawing of the sequence of void coordination polyhedra constituting the boundary in (*a*). The drawing has been constructed by tracing atomic positions in the interfacial region of (*a*), and joining these in order to show the edges of the void coordination polyhedra. Solid lines correspond to edges perpendicular to the tilt axis, and dotted lines correspond to inclined edges. The symbols *s*, *t* and *u* are located above examples of a tricapped trigonal prism (the trigonal prism is hatched), a bicapped trigonal prism and a tetrahedron, respectively. The symbol *r* corresponds to an irregular polyhedron which is not closely similar to any of the polyhedra in Fig. 1. The horizontal bar shows the length of the periodic boundary structure.

somewhat so as to be separated by approximately $a\sqrt{3}/2$ from the atoms *f,h,g* and *l,n,m*. A similar argument applies to *b* and *h* whose atomic coordination polyhedra are the trigonal prisms *abca'b'c'* and *eije'i'j'*. Thus, this particular boundary is comprised of triangulated void coordination polyhedra, although the axis length of the pentagonal bipyramids is $a\sqrt{2}$, *i.e.* not close-packed, and the triangulated faces are not equilateral. Finally, primitive cubic void coordination polyhedra have been found in some boundaries in Fe (Vitek, Smith & Pond, 1979).

Sites for segregated impurities

The two features most important in determining preferred interfacial sites for a segregant atom are its size and preferred coordination number. Impurity atoms may occupy interstitial sites, *i.e.* voids, or substitutional sites. Those occupying interstitial sites are likely to be smaller than solvent atoms; the sizes of inner spheres which can occupy the void coordination polyhedra illustrated in Fig. 1 are listed in Table 1. (Solvent atoms are assumed to have unit radius.) Irregular polyhedra in a given boundary structure, such as illustrated in Fig. 2, may provide additional interstitial sites with characteristic size and coordination number.

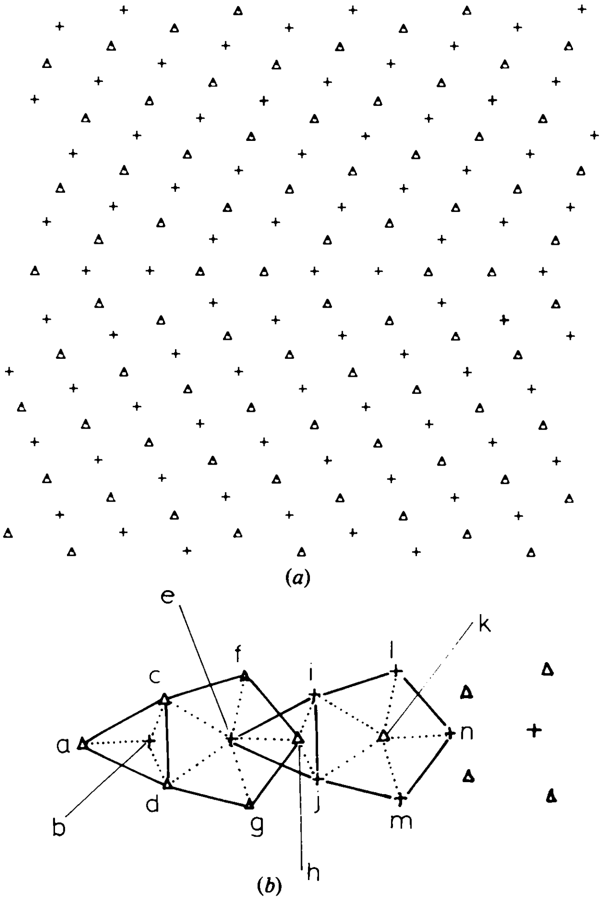

Fig. 3. (*a*) Low energy $\Sigma = 9$ symmetrical $(1\bar{1}4)$ boundary in Fe. Symbols as for 2(*a*). (*b*) Schematic drawing of the sequence of void coordination polyhedra.

Atoms rather larger than the solvent atoms may occupy substitutional sites; *e.g.* an atom with radius 25% larger than that of the solvent could replace atom *e* in Fig. 3. The coordination polyhedron of atom *b* is a trigonal prism, *acda'c'd'*, extended along its axis; it is noted that Sn, Sb and S are coordinated in a similar way in FeSn, FeSb and FeS which all have the NiAs structure. However, in these latter structures, the Fe atoms are not close-packed on the triangular faces of the prism but are parallel to the axis. Impurity atoms may also segregate to interstitial or substitutional sites which are associated in linear or planar arrays or finite clusters. A possible example of an isolated impurity cluster could be the formation of a tetrahedral arrangement of impurity atoms by substitution of a group of atoms such as *eifh* in Fig. 3. It is known that certain group V elements, P, Sb, As and Bi, form tetrahedral molecules in the vapour state and these molecules can be stable at relatively low temperatures (Bailar, Emeleus, Nyholm & Trotman-Dickenson, 1973). The As—As distance in As_4 is 2·43 compared with 2·56 Å for Fe—Fe in b.c.c. Fe, *i.e.* the strain of As—As bonds in substitutional tetrahedra would be of the order of 5%.

Discussion

Analysis of simulated grain boundary structures in terms of atom packing has been found to be very useful. The present authors believe that atom-packing analysis is most valuable as an analytical tool rather than as the basis for a model of grain boundary structure with predictive capability. As an analytical tool it has facilitated four major contributions to the

Table 1. *Void coordination polyhedra consistent with ...ababa... stacking*

Void coordination polyhedron	Inner sphere radius	Coordination number of interstitial impurity
Tetrahedron	0·225	4
Octahedron	0·414	6
Trigonal prism	0·732	6
Trigonal prism (capped)	0·732	9
Pentagonal bipyramid	*	7
Square antiprism	0·645	8

* 0·0 unless extended along axis.

understanding of computer-simulated grain boundary structures. It has:

(i) elucidated the nature of structural elements in minimum energy boundaries,

(ii) provided an appreciation of the reasons underlying the exceptionally low energy of certain boundaries such as the $\Sigma = 11$, (311) in Al,

(iii) clarified important structural differences between boundaries in Al and Fe,

(iv) provided a method for the identification of possible sites for impurities segregated to grain boundaries.

It was pointed out that the $\Sigma = 11$ symmetrical (311) boundary structure in Al has exceptionally low energy, *i.e.* of the order of that for the coherent twin, and comprises entirely capped trigonal prisms and tetrahedra with edge lengths distorted less than about 5% compared with the ideal value (this was the tolerance used by Bernal). In other words, the atoms constituting this boundary, as for the coherent (111) $\Sigma = 3$ twin boundary in f.c.c., are very efficiently packed without recourse to extensive local atomic relaxations. It is often helpful in this context to consider the two grains initially unrelaxed and separated at the interface. The grain surfaces, as represented by the outermost faces of the crystals' void coordination polyhedra, are nonplanar tessellations of equilateral triangles in f.c.c. material and isosceles triangles for b.c.c. Efficiently packed low-energy boundaries in f.c.c. metals appear to result if the two grains can be brought together in such a way that, with the aid of relative displacement and minimal local atomic relaxation, the interfacial configuration comprises predominantly triangulated and Archimedean void coordination polyhedra.

In the $\Sigma = 11$ (311) and $\Sigma = 3$ coherent (111) boundaries in Al, there is no relative displacement and atoms occupy coincidence sites. Expressed in atom-packing terms, the advantage of coincidence-site atoms is that they correspond to vertices common to the void coordination polyhedra of both grains. However, in general for boundaries in f.c.c. metals, relative displacement occurs in order to avoid overlap of atoms in the initial coincidence structure (Pond, Smith & Clark, 1974). Moreover, even with the aid of relative displacement and local atomic relaxation it is not generally possible for structures corresponding to sequences of triangulated and Archimedean polyhedra only to be attained. Boundary structures in b.c.c. Fe are somewhat different in the sense that structures containing coincident atoms are found to be stable more commonly than for f.c.c. This corresponds to the relatively greater importance of local relaxation in b.c.c. structures where void coordination polyhedral edge lengths can be in the range between the magnitudes of about $\langle 100 \rangle$ and $\frac{1}{2}\langle 111 \rangle$ compared with the f.c.c. case where edges must be about $\frac{1}{2}\langle 110 \rangle$ for close-packing.

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