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STRUCTURE AND PROPERTIES OF HIGH ANGLE GRAIN BOUNDARIES

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<u>Résumé</u> - Dans cet article de revue sont présentés la crystallographie des bicristaux, les conceptes de coincidence, les mécanismes de relaxation, les principes et résultats essentiels de modélisation sur ordinateur ainsi que la description des joints de grains à large angle de désorientation par des séries périodique de dislocations ou des séquences ordonnées de certains polyhèdres de coordination. Les relations de structure aux propriétés des joints de grains sont exposées à la lumière des modèles existants en insistant plus particulièrement sur la ségrégation d'impuretés au niveau des joints ainsi que ses effets sur leur structure comme observé dans les simulations sur ordinateur.

<u>Abstract</u> - This is a tutorial review covering the crystallography of bicrystals, coincidence concepts, relaxation mechanisms, principles and main results of computer modelling, and the description of high angle grain boundaries in terms of periodic arrays of either dislocations or ordered sequences of coordination polyhedra in the boundaries. Structure - property relations in grain boundaries are reviewed in the light of existing models, with special emphasis on the segregation of impurities at grain boundaries and its effects on boundary structure as indicated by computer modelling.

1. INTRODUCTION

With few exceptions, metals and ceramics are used in polycrystalline form. Boundaries between grains, or between different phases, often play a decisive role in determining the material's properties. For example, the toughness and strength of steels has been drastically improved since the 1950's by rigorous control of grain size, of the chemistry of grain boundaries and of nonmetallic inclusions in the metal.

HOMOPHASE BOUNDARIES are interfaces between regions of identical crystal structure; they include grain boundaries, twin boundaries, and domain boundaries. Stacking faults are commonly included in this category although they can be viewed as thin lamellae of a different (but related) crystal structure.

HETEROPHASE BOUNDARIES are interfaces between regions of different crystal structure which may, but need not, have different chemical

composition. Examples of the first kind would be boundaries between coexisting allotropic modifications, for instance between grains of the tetragonal and the monoclinic phase of $2rO_2$. Examples of the second kind are virtually omnipresent in technical alloys and ceramics, for instance the boundaries between austenite and ferrite in a 'duplex' stainless steel, or the surfaces of the non-metallic inclusions mentioned above. In both cases, with compositional difference and without, the regions adjoining the interface belong to different phases in the classical thermodynamic sense; therefore the simpler term PHASE BOUNDARIES is often used for them.

Control of grain boundary chemistry by doping, scavenging, selective precipitation or suppression of second phases has become standard practice, and so has the manipulation of grain boundary mobility and shape by pinning, or by directional solidification or annealing. A highly sophisticated practice of grain boundary engineering is in common use today for superalloys, certain high-technology ceramics, but also for such deceptively 'simple' materials as steels, whose design limits would be drastically lower without the benefit of boundary engineering. - Yet, only part of this engineering knowledge has a firm ground in science. In particular, understanding in terms of atomistic structure has lagged far behind the art of engineering manipulation for most types of internal boundaries.

For low-angle grain boundaries, a dislocation model was proposed by Taylor /1/ as early as 1934. Its verification by etch pit observations as well as the prediction of the influence of misorientation upon interfacial energy /2/ and boundary diffusivity /3/ were early triumphs of the evolving understanding of real crystal properties in terms of lattice dislocations.

For high-angle boundaries, the development of structural models has been slower and more tortuous. Theory and experimental techniques for constructing and testing detailed models have only recently become available, triggering a wave of exciting developments which are the main subject of this review.

Heterophase boundaries are more complicated still. Only quite recently have the first steps been taken towards an understanding of their structures, in particular for metal-ceramic boundaries. In contrast to grain boundaries, engineering control of phase boundaries has yet to be developed, and one could still hope that rapid progress might enable science to take the lead in this development.

The present paper will review the state of the subject with emphasis on recent ideas; experimental results and techniques will be discussed only in relation to theoretical concepts. For background, and for comprehensive summaries of experimental results, reviews and conference books are available /4-13/. The following section will introduce the special crystallographic nomenclature developed for boundaries, and discuss the geometry of unrelaxed bicrystals. Sections 3 and 4 deal with relaxation processes and their study by computer modelling, and section 5 reviews a priori ideas concerning the relation between the structure of grain boundaries and their properties. Finally, section 6 reviews computer modelling results concerning grain boundary segregation, where particularly detailed ideas have been developed very recently. No systematic treatment is attempted for heterophase boundaries, but important contributions to this subject are referenced.

2. CRYSTALLOGRAPHY OF RIGID BICRYSTALS

Since in a rigid bicrystal the atoms at the boundary occupy exact lattice positions belonging to both crystals, it is useful to consider two interpenetrating, infinite lattices (fig. 1). Pond and Bollmann /14/ introduced the concept of the DICHROMATIC PATTERN, which is the set of lattice points contributed by both lattices, but distinguished by different colours (fig. 2a). Given the symmetry groups and metrics of the 'black' and the 'white' lattice, seven additional parameters are required to fully define the dichromatic pattern: three for rotation, three for rigid body translation, and one describing the chirality (equal- or opposite-handedness) of the two lattices. In the following, the rotational displacement between the two lattices will be called MISORIENTATION, Θ .



1 Two inter-Fig. penetrating lattices with misorientation θ and boundary inclination Ψ . Shown here is the special case of a tilt boundary (asymmetric); in the general case, the axes of θ and Ψ would not be coincident.

An elegant framework for the description of dichromatic patterns /15-17/ is provided by the COLOURED SYMMETRY GROUPS introduced by Shubnikov /18, 19/. For two identical lattices coloured 'black' and 'white', the coloured space group comprises a set of 'white' operations between points of the white lattice, an analogous set of 'black' operations (these two sets are the classical symmetry groups of the constituent lattices), and in addition, a set of 'coloured' operations relating points of different colour to each other. The coloured group completely defines the symmetry of the dichromatic pattern as a function of the "generating operation" (defined by its rotational and translational components, R and τ) /20/ and of the symmetry groups of the two crystals. It may contain symmetry elements higher than those occurring in the classical crystallographic point groups, e.g., 8- or 12-fold axes /16/). To ensure uniqueness of crystallographic description, the coordinate system must be suitably chosen with respect to the symmetry elements of the bicrystal /15, 21-23/.

As originally presented, the dichromatic pattern concept holds for lattices with atoms in special positions (e.g., corners) of the unit cell. It has recently been extended /15, 21/ to the case of atoms in general positions. The operation of all the symmetry elements of the point group multiplies such atoms to give a lattice complex, and the interpenetration of two such lattices is called a DICHROMATIC COMPLEX. Dichromatic patterns formed by two identical lattices are called HOMOGENEOUS. They lend themselves to the description of grain boundaries, twin boundaries and stacking faults. The interpenetration of two dissimilar lattices, which is of interest for the description of heterophase boundaries, gives rise to a HETEROGENEOUS DICHROMATIC PATTERN whose symmetry can contain no coloured operations pertaining to all points. Their properties and construction /15, 21, 24/ will not be discussed further in this review.



Fig. 2 - (a) Dichromatic pattern, $\Theta = 36.9^{\circ} / [001]$; (b) Boundary $(130)_1$, $(130)_2$, generated from the dichromatic pattern in (a).



Fig. 3 - (a) Coincidence site lattice in the dichromatic pattern of fig. 2a (Σ = 5); (b) O-lattice (=CSL plus dashed lines)

TO CONSTRUCT A GRAIN BOUNDARY, a plane of desired orientation is passed through the dichromatic pattern, and black atoms are discarded

on the one side, white atoms on the other (fig. 2b). Obviously, the atomic arrangement in the boundary plane, and its planar symmetry, will vary with its orientation within the given dichromatic pattern. The orientation of the boundary plane is referred to as its INCLINATION, (fig. 1). Ten parameters are required for the description of an unrelaxed boundary: seven for the dichromatic pattern, and three for the boundary inclination.

When the two component lattices of the dichromatic pattern are brought to coincide in one of their lattice points, other coincidences will be found in periodic repetition (fig. 3a). The periodicity will vary sharply and discontinuously with the misorientation. The set of the coincident (two-colour) lattice points is called the COINCIDENCE SITE LATTICE ("CSL"). Its unit cell volume is a multiple Σ of that of the original lattice: out of Σ white atoms, and out of Σ black atoms, one is both white and black. The density of coincidence sites in a grain boundary plane, Γ , depends on the inclination within the given CSL /26/. SPECIAL GRAIN BOUNDARIES are characterized by high values of Γ and low values of Σ . Intuitively, one would expect them to have specially low specific interfacial energies, corresponding to cusps in the Wulff plot * , and perhaps other property extrema.

The coincidence site lattice can be represented /15-17/ as the intersection of the translational symmetry elements of the white and black crystals in the given misorientation,

 $CSL = T_{W} \cap (R|\tau) T_{R} (R|\tau)^{-1}$

The coincidence site concept dates back to a suggestion by Friedel in 1926 /25/; it was applied to the description of high angle grain boundaries in the 1960's /27-30/.

In the nomenclature for grain boundaries, it is customary to state both Σ and the angle and axis of misorientation, e.g. $\Sigma = 5$, 36.9° /[001] for the pattern in fig. 2a. The inclination is specified by the Miller indices of the boundary plane in both lattices, (hkl), /(hkl)₂. For symmetric tilt boundaries, the indices in the second lattice are some permutation of those in the first, and can be omitted, e.g. $\Sigma = 5$ (130) 36.9° /[001] for the boundary shown in fig. 2b. For a pure twist boundary, the plane identifies the axis; $\Sigma = 5$ (001) suffices to designate a twist boundary corresponding to the plane of the paper in fig. 2a. There are cases of multiplicity (several misorientations giving the same Σ). These are sometimes distinguished by suffixes, e.g. $\Sigma = 17a$ for $\Theta = 28.1^{\circ}$ /[001] and Σ = 17b for $\Theta = 61.9^{\circ}$ /[221].

Beside the CSL, two other types of periodicity can be discerned in the dichromatic pattern: the O-Lattice (Bollmann, /31/), and the DSC-Lattice /29/.

The O-lattice can be defined as the point set of all possible origins for rotational transformations between the black and the white lattice of a dichromatic pattern or complex. Such points need not be lattice points of the constituent lattices, as seen in fig. 3b. The physical significance of the O-lattice lies in the fact that it identifies

^{*)} A polar plot of interfacial energy per unit area vs. either inclination or misorientation. The distinction is frequently neglected, although the two kinds of Wulff plot are relevant to different phenomena. For instance, in the coupled growth of two solid phases from the melt, $E(\Theta)$ will determine their mutual orientation, $E(\Psi)$ their shapes.

regions of "near-coincidence", or potential good registry when relaxation is allowed. Its periodicity varies continuously with the misorientation, like that of a Moiré pattern /32/.



The DSC Lattice is made up of the sum (or difference) of all vectors linking lattice points of different colour in the dichromatic pattern (fig. 4a). It has the important property that a translation of one lattice against the other by any DSC vector restores the dichromatic pattern, albeit with shifted coincidence sites (fig. 4b). This property has given rise to its name (Displacement Shift Complete). It is useful for describing intrinsic grain boundary dislocations: when perfect, their Burgers vectors must be taken from the set of the DSC vectors /22/. The periodicity of the DSC-lattice is reciprocally related to that of the CSL /26/. The DSC can be represented /15-17/ as the union of the translational subgroups of the two misoriented crystals:

DSC =
$$T_W \cup (R|\tau) T_B (R|\tau)^{-1}$$

Misorientations producing high coincidence site densities (low Σ), and special boundaries with high Γ , as well as search routines for these, have been tabulated for cubic /29,33/ and noncubic (so far mainly hexagonal /34,35/) lattices. In the case of non-cubic lattices, and for heterophase boundaries between dissimilar lattices /24,36,37/, one looks for "near coincidences" within an imposed tolerance limit. (Anisotropic expansion will disturb such coincidences.) "Near-coincident" lattices are described by a double set of DSC-lattices /37/.

3. RELAXATION

Apart from twin boundaries, coincidence boundaries in a rigid bicrystal contain only few coincidence sites, and many sites with quite abnormal interatomic distances. Relaxation is necessary to make such boundaries energetically viable, and in this regard, the coincidence concepts should be viewed as heuristic tools to identify suitable starting situations for the relaxation process.

Another tool for this purpose, similarly serviceable, is provided by the "hard sphere models" proposed by Ashby and Spaepen /38-40/. Here the boundary is constructed by mechanically nesting two half-crystals together so that they form three contacts in each period of the boundary. Among the various arrangements which may satisfy this condition, the one with the highest density of atomic packing (the least excess volume) is selected.

Of the ten parameters which define a boundary, nine are, in principle, available for relaxation. Only the chirality parameter cannot be relaxed. Several relaxation mechanisms can be envisaged /21/:

(i) Removal of atoms from misfit regions, creating "structural vacancies" /41,21/.

(ii) Rigid body translation of the component lattices away from the coincidence position. The translation vector may have components both in the plane of the boundary and perpendicular to it; the latter will give rise to excess volume. As discussed by Pond /42/, certain constraints must be imposed on the translations to ensure compatibility of facets at triple lines. Experimentally, translations can be measured by Moiré fringe offsets /43/, or by displacement fringes /43,44/ in TEM, or by high resolution electron microscopy /45,46/. Often the rigid body translation accounts for the major part of the relaxation energy /47,48/, and in most of the structures analyzed so far, no boundary atoms are actually left in coincidence positions /49/.

(iii) Individual displacements of atoms, This will be discussed in detail below.

(iv) Incorporation of impurity atoms in boundary positions /50/ as "constitutional impurities". Both the hard sphere models and other analyses of relaxed boundary structures indicate the occurrence of holes suitable for interstitial atoms (greater than 0.6 of the diameter of the lattice atom) and for substitutional atoms in almost all boundaries /39, 50/. An important case of constitutional impurities is the incorporation of differently charged atoms in the boundaries of ionic crystals in order to alleviate the Coulomb repulsion of ions of equal sign facing each other across a boundary /51/.

(v) The misfit can be accommodated by normal lattice dislocations, as in low angle grain boundaries ("primary relaxation"). The spacing of such dislocations will be that of the O-lattice /52/.

(vi) The misfit can be accommodated by dislocations with DSC Burgers vectors ("secondary relaxation", /52/].

(vii) Faceting, or the decomposition of a boundary into two types of boundary with lower total energy.

Individual motion of atoms, which has been found to give the second largest energy contribution in the relaxation process (after translation), is studied by computer modelling of the energy of various boundary configurations. This is the subject of the next chapter.

4. COMPUTER MODELLING OF GRAIN BOUNDARY STRUCTURES

Despite the many-body nature of the cohesive force system in solids, models based on central pair forces have been successfully applied to the computation of minimum energy configurations for various lattice defects and even for liquids /53, 54, 55/. Morse potentials, pseudopotentials and spline - fitted empirical potentials are used, with constants adjusted so as to reproduce elastic constants, lattice energies, phonon dispersion data, stacking faults and sometimes point defect energies /53, 56, 49, 47/. The use of point defect energies for fitting potentials has been criticized /57, 58/. A point of debate is how the volume dependence of the cohesive forces can best be taken into account in models based on pair potentials /47, 49, 59/. Another problem is presented by the Friedel-oscillations of real potentials, which slow down convergence. For tractability, the potentials are either damped artificially /60/ or truncated after the second neighbour (in bcc crystals), or after the third (in fcc); these are the shortest interaction distances required to make the lattices stable.

STATIC CALCULATIONS simulate only the situation at 0 K, neglecting the effects of vibrational and configurational entropy. Starting from an assumed configuration, e.g. a rigid bicrystal coincidence boundary with protruding atoms removed, the energy is minimized by moving all atoms incrementally and iteratively in the direction of the steepest local energy gradient. One important problem here is to avoid secondary energy minima (metastable configurations), another is the choice of suitable boundary conditions to avoid undue restrictions on the structures resulting from the relaxation process.

MOLECULAR DYNAMICS /61/ allow the simulation of finite temperature situations and of kinetic effects - e.g., diffusional processes /62, 63, 64, 65/, grain boundary migration and sliding /61/. Again one starts from a plausible configuration (often the result of a static relaxation procedure). The atoms are assigned Maxwell-Boltzmann-distributed velocities with random directions, and their positions are calculated for many successive time increments. The midpoints of the vibrations of the atoms form a model of the time-averaged structure, at the temperature defined by the velocity input.

Molecular dynamics models are less prone to becoming trapped in metastable configurations, and more tolerant with respect to starting geometries. One of the first molecular dynamics calculation of a grain boundary structure /66/ started with a layer of "liquid" between two crystalline grains and let the atoms successively become attached to either grain. Although its results were reported as momentary snap-shots of the vibrating ensemble rather than in the currently preferred form of a time-averaged structure, they show suggestive similarities with recent molecular dynamics results obtained by relaxation of rigid bicrystal models /61/. As an alternative to truly dynamic modelling, Monte Carlo calculations have been used for a qualitative study of segregation sites for Bi in copper grain boundaries /67/.

Early attempts to achieve agreement between diffraction experiments and statically relaxed grain boundary configurations were only partially successful, and it was feared that the relaxation results might be hypercritically sensitive to the type of potential chosen. Recently, Wolf /47, 68/ has demonstrated that distinctly different structures are formed by relaxation of the same starting structure when a "hard" potential (Al) is used, and with "soft" ones (Cu, Ag, ionic crystals). The same conclusion was reached by Sutton and Vitek /69/ when comparing results for copper and aluminium /70/. However, in the group of "soft" potentials, Wolf's results indicate little sensitivity of the relaxed structures to the potential in three cases out of four; the fourth case concerns an extremely shallow spline potential. Wolf's values for the energies of relaxed structures in copper are in excellent quantitative agreement with results obtained by Bristowe and Crocker /71/ using different relaxation techniques. Similarity of calculated energies, with respect to specially low values for certain low Σ misorientations, was found for four different pair potentials studied by Brokman and Balluffi /52/, and further cases of agreement, in spite of different potentials being used, have been reported /59, 72, 69, 73/.

In summary, it seems that computer modelling of grain boundary structures has matured to a state where meaningful results can be obtained with careful technique. Such results are suitable for the study of trends, or for combination with empirical data from high resolution imaging or from diffraction results. Doubtless the increased use of molecular dynamics will soon bring further advances in the reliability of model structures.

As an example of the power of molecular dynamics modelling, fig. 5 shows jump paths and jump frequencies for vacancy migration in bcc iron, computed by Kwok et al. /62, 64/. The calculations confirmed that, as had been long expected from isotope effects and activation volumes, the activation energies for the formation and migration of vacancies are much lower in the grain boundary than in the lattice (for the preferred B-sites, $E_{\rm F}$ = 0.94 eV, $E_{\rm M}$ = 0.51 eV). (For fcc-iron, a much wider range of $E_{\rm F}$, with 0.1 eV for one particularly favoured site, and other values as high as 1.4 eV, was reported as a result of calculations for asymmetrical tilt boundaries by Dahl et al. /74/).



Fig. 5 - Diffusion paths and relative jump frequencies of vacancies into various sites of a Σ = 5/ [001] symmetric tilt boundary in bcc iron, calculated by molecular dynamics for T = 1300 K /64/

Number of vacancy jumps into each of the sites during a typical run: A 3, B 126, C 20, D 32, E 7, F 6, G 1 The calculations for bcc-iron indicate that in the boundary, just as in the lattice, the energies of formation for interstitials are much greater than for vacancies, so that diffusion is concluded to proceed by a vacancy mechanism. (A ring exchange, involving the formation and annihilation of a vacancy-interstitial pair and the net movement of a vacancy was also observed in the molecular dynamics simulation, cf. fig. 5). A strong preference for B-B'-jumps makes the well-established anisotropy of grain boundary diffusion understandable; the model also gives tangible meaning to the otherwise somewhat nebulous concept of "width" for a boundary serving as a diffusion path. Similar results have been obtained for preferred jump paths in fcc materials /65/.

5. STRUCTURAL UNITS AND GRAIN BOUNDARY DISLOCATIONS

Sutton and Vitek made a series of comprehensive studies on the structures of symmetric /69/ and asymmetric /75/ tilt boundaries, and of twist boundaries /76/, in fcc crystals. They used static calculations with potentials for both aluminium and copper. Misorientations up to $\Sigma = 411$ were analyzed for symmetric tilt boundaries.

Some tilt boundaries were found to consist of one single type of recurrent atomic arrangement, or STRUCTURAL UNIT, and all other boundaries were found to be made up of mixtures of these (fig. 6b, e). Boundaries containing only one type of structural unit have stress fields which are essentially limited to the core zone; their long range stress fields are very weak. These boundaries are termed FAVOURED BOUNDARIES. (Note that this does not imply particularly low energy: the core units may harbour enough strain to make the boundary energy high despite a weak long range stress field.) - The range of



Fig. 6 - Core structures of symmetrical [001] tilt boundaries in an fcc lattice. Static calculation with a pair potential for copper, showing regular sequences of "structural units" (o marks atoms at z=0, \triangleleft at z=1/2), (a) unrelaxed, (b)-(e) relaxed /69, 63, 73/.

C4-12

all possible misorientations can be viewed as divided into sectors, each delimited by two favoured boundaries. In each sector, the intermediate (non-favoured) boundaries consist of structural units taken from the delimiting favoured ones, arranged in ordered sequence, and in proportions given by a linear mixture rule (fig. 6c, d).

Inspection of fig. 6c will show that each A-unit in the $\Sigma = 17$ boundary corresponds to the termination of two symmetrical (120) planes. Thus, each A-unit in this boundary represents a dislocation with b = (1/5) [210]. This is a DSC lattice vector of the $\Sigma = 5$ coincidence lattice. The B-units are elements of a 90°-"boundary" in the undisturbed lattice (fig. 6e), for which $\Sigma = 1$ and the unit cells of the DSC and the crystal lattice are identical. Where such units occur as a minority component among the A-units in the $\Sigma = 37$ boundary shown in fig. 6d, they mark the termination of two (110) planes, or an ordinary lattice dislocation with b = (1/2)[110] in each crystal. The stress fields surrounding the relaxed boundaries agree with the presence of these dislocations /69/.

Thus we note that the "primary" and "secondary" dislocation mechanisms of relaxation mentioned above give the same results as when each atom individually seeks its optimum position. Both descriptions are compatible with TEM observations. The equivalence of models based on periodic arrays of either grain boundary dislocations or structural units in the boundaries was recognized as early as 1968 by Bishop and Chalmers /28/, and further evolved by Brokman and Balluffi /52/.



Fig. 7 - Polyhedra occurring as structural units in grain boundaries /49/

It has been pointed out that the structural units formed by the relaxation process can already be identified, with distorted shape, in the unrelaxed boundary structure (fig. 6a).

It is significant that the structural units formed by computed relaxation movements in CSL-boundaries /50/ correspond to the polyhedra found in the hard sphere models of Ashby, Spaepen and al.

/38, 40/, and also to the "random close packed polyhedra" identified by Bernal /77/ as the building blocks of monatomic amorphous solids (fig. 7). The polyhedra which form the structural units of grain boundaries in bcc metals are not truly close packed, but they show nearest and second-nearest neighbour distances very similar to those in the undisturbed crystal /50,49/. Twist boundaries, too, are found to consist of such polyhedra /78, 79, 76/, cf. fig. 8.



Fig. 8 - Structure of a $\Sigma = 13$ (001) twist boundary in silver, from diffraction experiments and static modelling /78/

At present, computer modelling has advanced a considerable way beyond experiment. The experimental elucidation of grain boundary structures is laborious and hampered by methodical restrictions. Most of the information comes from X-ray and electron diffraction, and recently, from high resolution electron microscopy. The state of the art has been reviewed in the literature /63, 78, 80, 81, 42, 82, 83, 45/ and will be discussed further at this conference. In summary, one can say that there is qualitative agreement between experiment and computer modelling, so that the characteristic atomic arrangements described in this section appear fairly secure. There seems to be a wide-spread feeling that the structures derived from computer modelling by energy minimization are safer than the absolute values of the energies.

6. STRUCTURE - PROPERTY RELATIONS IN GRAIN BOUNDARIES

A large volume of experimental evidence /84/ demonstrates that the properties of grain boundaries vary with their crystallographic nature, and thus with their structure. Frequent observations of grain boundary faceting (reviewed in /85, 84/) prove that there are boundaries whose energy is so much lower than that of others that moreboundary area may be expended if an unfavourable boundary can thereby be replaced by facets of lower energy. Boundaries formed by "natural selection", as in aggregates of smoke particles /86/ or in certain sintering experiments /87, 88/, are restricted to a few discrete types which thus reveal themselves as energetically favoured, and which also distinguish themselves from "random" boundaries with regard to other properties, e.g., lower rates of intercrystalline corrosion. Experimental results have been reviewed generally /4, 89, 90/ and with regard to special properties such as boundary energy /84/, diffusivity /91, 92, 63, 93/, segregation /85/, mechanical /94, 95/, electrical

/96/ and corrosion properties /97/, and with regard to the interaction between boundaries and point defects which manifests itself in the boundaries' capacity to act as sources or sinks for point defects, for instance in the phenomena of creep, sintering, grain boundary migration etc. /4, 98, 99, 100/.

low- angle boundaries, the Read-Shockley model /2/ had very early For brought about a satisfactory, structure-related understanding of the wav in which the properties of a boundary vary with its misorientation. Attempts to develop a similar understanding for high-angle boundaries, based on the density of coincidence sites in the boundary plane, or on similar descriptors within the framework of CSL and O-Lattice formalism, produced partially encouraging the complete success. Faceting was found to produce both results but no and high- Σ boundaries /84/; grain boundary diffusivity was found low to be low for some low- Σ boundaries, but not for all; sintering experiments /87/ revealed that in copper, some boundaries with high Σ , 11, were energetically favoured over $low-\Sigma$ boundaries such e.q. Σ = $\Sigma = 5$. In particular, the intense search for "cusps" in the Wulff as plot proved disappointing. Such cusps were expected for boundaries with a high planar density of coincidence sites, Γ *. An example from



Fig. 9 - Calculated (left) and measured (right) grain boundary energies for [110]tilt boundaries in aluminium. Hasson and Goux /101/

^{*)}When only certain families of boundaries are considered, e.g., all symmetrical tilt boundaries around a given axis, low Σ is equivalent to high Γ .

the pioneer work of Hasson and Goux /101/ is shown in fig. 9. In the case of [011] tilt boundaries, the experiments did confirm the expected energy minima for $\Sigma = 3$ (trivial, since this is the first order twin orientation) and $\Sigma = 11$, but in the family of [001] tilt boundaries the expected, shallow cusps for $\Sigma = 5$ and $\Sigma = 13$ were indiscernible against the experimental scatter. (There is agreement now that deep cusps occur only in the [011] family of tilt boundaries, not in the [001] tilt family, and neither in twist boundaries in metals.) However, later experiments and computations with more refined relaxation methods also failed to conclusively confirm a simple, general relation between grain boundary energy and coincidence site density. In particular, boundaries of higher Σ were sometimes found to have lower energy than low- Σ boundaries. Several plausible excuses have been suggested for this:

(i) grain boundary energies can only be measured at high temperature, while all systematic energy calculations for boundary families so far are for 0 K, being based on static calculations /63/. If, as both theory /102, 101, 103/ and experiment /104a/ suggest, grain boundaries may undergo phase transformations below the melting temperature, considerable differences in energy could arise.

(ii) In most cases measurements and calculations alike are too widely spaced to reveal really narrow cusps, and expected cusps may be masked by impurity effects.

(iii) Wolf /47/ has emphasized that relaxation calculations which do not correctly allow for the volume expansion of the boundary core may suppress translational components of the relaxation, and that this might in fact cause larger errors for $low-\Sigma$ than for high- Σ -boundaries.

While these legitimate arguments help to lessen the weight of the inconsistencies, they do not lend positive support to the expected singularity of special, or high- Γ (= low- Σ) boundaries, and we are left on ground which is too shaky for comfort.

A turning point was reached with the realization /105/ that the composition of a boundary in terms of either one single structural unit or a mixture of units might be more important for its properties than the coincidence site density.

Sutton and Vitek /105/ make a distinction between properties which are determined by the core structure (and thus the short range stress field), and properties which are influenced partly or exclusively by the long range stress field. Diffusivity is a property of the first kind. Between any two consecutive favoured boundaries, it is expected to vary smoothly with the mixing ratio of the structural units. Abrupt changes (discontinuities in the first derivative of properties vs. misorientation) are expected /105, 63/ at those delimiting boundaries where one type of structural unit in a binary mixture gives way to another type (AB \rightarrow B \rightarrow BC), or at boundaries representing special mixtures, e.g., ABABAB... (cf. fig. 10).

Grain boundary energy is a property determined by both short and long range stress fields. For families of symmetric tilt boundaries, it is argued /105, 52/ that in principle, energy cusps are to be expected for all favoured boundaries, because at both sides of the favoured misorientations, an increasing density of grain boundary dislocations builds up increasing long range stress fields. The main point,

C4-16

however, is that such cusps may be quite shallow if the structural units in the core of the favoured boundary are high-energy configurations themselves. - As a rule, such cusps will be asymmetric, because a "pure B" boundary will have on its one side mixtures of B with A, on the other B with C.



Fig. 10 - Sequence of structural units in symmetrical [001] tilt boundaries (static calculation for Cu /69/), and the expected variation of grain boundary diffusivity /63/

7. GRAIN BOUNDARY SEGREGATION

Segregation of impurities to grain boundaries can cause catastrophic embrittlement of materials, and can drastically affect creep corrosion sensitivity, and other properties. ductility, stress Consequently, it has been the subject of intensive research, especially since the advent of surface analytical methods like AES and SIMS. As a result, the "microchemistry" of grain boundaries is now well known /106/. This includes comprehensive empirical data for the segregation propensity of various impurities in technically important metals, prime representatives being P, As, Sn in steels, and Bi in Cu. Theoretical models for the time and temperature dependence of /107, 108, 67/, and engineering models for embrittlement segregation and its prevention /109, 110/ have been developed. The phenomenology and the chemistry of grain boundary segregation have been amply reviewed /9, 106, 111, 109, 13, 112/.

Here, we will consider only the relation between grain boundary structure and segregation. That such an interaction exists is indicated by the observation of segregation-induced faceting of boundaries /113, 114, 115/, and by some AES work /116, 117/.

As early as 1972, Dahl et al. /74/ computed the behaviour of carbon atoms in grain boundaries of bcc iron by molecular dynamics. In the

vicinity of the C atoms, the boundary structure changed towards more close packed configurations. Recent calculations by Nichols /118/ indicate the same behaviour.

Sutton and Vitek /59/ have studied the behaviour of Bi (a strong segregant and embrittler) and of Ag (a weak segregant) in copper and gold by static calculations. To deal with foreign atoms at a grain boundary, concentration and density dependent pair potentials /119/ and a revised relaxation procedure /59/ had to be developed. Symmetric $\Sigma = 5$ (210) and $\Sigma = 17$ (530)/[001] tilt boundaries were studied, the former being a favoured boundary and the latter a non-favoured one which contains structural elements of the (210) boundary (B) together with elements of the undisturbed crystal (A) (cf. fig. 6e); later the study was extended /120/ to variants of these boundaries containing another type of (210)-element, B'. The energies of segregation at various sites in a given boundary were found to differ widely. For a given structural unit, the segregation energy also varied considerably with its surroundings in the boundary (i.e. the boundary type). The large Bi atoms go into those sites which are surrounded by a tensile stress field in the uncontaminated boundary - in "hard sphere" terms, the segregant chooses the most spacious sites (fig. 11). This confirms the expectation that segregation should be selective with respect to both site and boundary type. The latter selectivity has been elegantly demonstrated by Roy, Erb and Gleiter /121/ who studied the fracture of Bi-embrittled sintered joints between Cu spheres and a Cu plate under ultrasonic loading. The boundaries with the least impurity content, which were the last to break, were all "low energy boundaries", corresponding to preferred orientations which in previous experiments /87, 88/ had formed by rotation of spheres during long-time sintering, and were presumed to contain no intrinsic dislocations.



Fig. 11 - Segregation enthalpies for Bi atoms in copper tilt boundaries (a) Σ = 5, (b) Σ = 17; static calculation /59/

The computer simulations by Vitek et al. /59, 120/ indicate that the incorporation of Bi atoms in Cu boundaries is accompanied by an expansion perpendicular to the boundary, which could be interpreted as a weakening of boundary cohesion (embrittlement).

The depth of boundary trap sites for large impurities is changed when adjacent trap sites are filled, even though they are separated by intervening host atom sites. Filling all deep trap sites in a $\Sigma = 17$ boundary brought about a strong rigid body translation in the boundary plane as well as an increased expansion perpendicular to the boundary. The relative energies of the three stable types of $\Sigma = 17$ (530) boundaries were made more unequal by incorporation of Bi atoms. Such an effect could be responsible for the segregation-induced faceting which has been observed in Bi-doped copper /122/.

The site selectivity of segregation could explain the observation that grain boundary diffusivity can be affected by segregation /92/, and the site competition between two simultaneously segregating species which has been conclusively demonstrated in the case of C and P in Fe /123/.

Segregation of phosphorus and boron to grain boundaries in bcc iron has recently been studied by Hashimoto, Ishida, Yamamoto and Doyama /124/. Using molecular dynamics with a Morse potential which had been amorphous Fe-B and Fe-P alloys, they successfully applied to identified the sites at which impurity atoms introduced close to the boundary came to rest. The boundaries studied were symmetrical $\Sigma = 5$ (013) and $\Sigma = 9$ (114) tilt boundaries. Boron, an interstitial solute, goes to the centres of the compact polyhedra of which the boundaries are made up, without seriously affecting the structure of the grain boundary. Phosphorus is normally a substitutional impurity in iron, but when it segregates, it too goes to the interstitial sites at the centres of the grain boundary polyhedra. At the same time, strong short-range faceting occurs in certain types of the simulated boundary structures. Both impurities form clusters $Fe_s X$ in the $\Sigma = 5$ boundary, and Fe₇X in Σ = 9, corresponding to the polyhedra occurring in these boundaries. The FeeP cluster occurs "naturally" in the compound FeeP, and also in amorphous Fe-P-alloys.

The bonding of host atoms and impurities in these boundaries was investigated by calculation of the local densities of electron energy states /125/, of vibrational states /126/, and experimentally, after opening the boundary by fracture, by XPS /127/. All the evidence points to strong bonds being formed between P and the Fe atoms in a cluster, while the bonds from the cluster to the surrounding iron atoms are weakened. This would explain the embrittling effect of phosphorus segregation, supporting earlier hypotheses derived from grain boundary microchemistry /128/. Boron, on the other hand, is found to strengthen the Fe-Fe-bonding across the grain boundary, in keeping with its known anti-embrittling effect. Shortening of Fe-Fe-bonds across the boundary was also found when the segregant was C, another known anti-embrittling agent /118/.

Bonding in metal-impurity clusters has also been studied by Briant and Messmer /129, 130, 131/. They looked at Bernal polyhedra of a few types which occur in boundaries, though not actually taken from a relaxed boundary model. Energy levels and valence electron density distributions were calculated by a molecular orbital method for clusters of types M_4X , M_8X , M_9X and $M_{10}X$, with M = Fe, Ni, Mn and Cr and X = P, S, C and B. Throughout, the embrittling impurity elements (P and S) were found to draw electrons towards metal-impurity bonds, weakening the metal-metal bonding. The anti-embrittling ("cohesion enhancing") elements B and C do not drain electrons from the metal-metal bonds; their bonding with the host atoms is thought to add to the cohesion across the boundary. An open question is the influence of impurity concentration on grain boundary structure. Only a few levels have been probed so far. Vitek's calculations were restricted to concentrations below 10 % of the grain boundary sites; Hashimoto et al. filled all available interstitial sites in their iron grain boundaries. No modelling has been undertaken to see whether such boundaries are capable of taking up further impurities, which could lead to reconstruction and to the formation of direct X-X-bonds. Some authors have argued that X-X interactions are important in embrittlement /132, 133/.

An interesting and technically important question concerns the interaction of two or more kinds of foreign atoms at grain boundaries. In steels, there is evidence that substitutional alloying elements such as Mn, Cr, Ni and the impurity elements mutually enhance each others' segregation; Guttmann /134, 135, 136/ has shown that such co-segregation is thermodynamically plausible. On the other hand, in highly pure iron, carbon has been shown to displace phosphorus from grain boundary sites /123/. The cluster calculations of Briant and Messmer /129/ indicate that the concentration of bonding electrons to the internal cluster orbitals and away from the matrix bonds is stronger for Cr - P and Mn-P than for Fe-P, which would be in accord with Guttmann's cosegregation model /135/.

8. CONCLUSION AND OUTLOOK

At the moment, computer modelling has forged far ahead of the experimental data base. There is an urgent need of molecular dynamics work to confirm and improve the static results, which seem to have arrived at a point where further refinement is no longer meaningful in view of the neglected entropy effects. Also, quantum mechanical methods not dependent on the pair interaction approximation could now be brought to bear: the simpler methods have reached a convergence of results which would seem to justify the greater effort.

There is a gap between experiment and computation: 'substances' for computer modelling have generally been chosen because good pair potentials happened to be available, without much regard to experimental background. On the other hand, most of the measurements of grain boundary energies, diffusivities, and segregation were made before models could tell the experimenters where interesting effects might be looked for. It is to be hoped that experimentalists will now take up the challenge of the many plausible, but still hypothetical prediction's derived from computer modelling, and that the range of experimental methods might be widened. For instance, the applicability of local probes such as Mössbauer atoms, positron annihilation, or EXAFS to problems of grain boundary structure seems to be largely untried.

An important experimental problem seems to be the purity of the grain boundaries studied. In view of the sometimes drastic effects of segregants on grain boundary structure, improved documentation of the chemical state of the boundaries studied seems mandatory, and the preparation of highly pure boundaries would be worth a strong effort.

At the present state of the art, it might be worth while to apply a semi-empirical approach to the elucidation of boundary structures, combining data from X-ray diffraction and high resolution electron microscopy with advanced computer modelling to provide sets of reliable atomic coordinates for a few model boundaries which could then become the object of deeper study by quantum mechanical methods.

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C4-22

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