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COMPUTER MODELING OF GRAIN BOUNDARIES IN CUBIC METALS

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Abstract - The current knowledge of grain boundary structure in cubic crystals modeled by computer simulation techniques is reviewed. The advantages and limitations of the methods and interatomic potentials employed are detailed and emphasized. Two different approaches are described: firstly, examples are given of individual special boundary structures that have matched well with particular experimental observations and, secondly, a series of more general boundary structures are illustrated which together form a structural unit model consistent with coincidence lattice theory and observations of secondary grain boundary dislocations. The information on computed grain boundary energies is also reviewed briefly and their importance and reliability discussed. The energy/misorientation relationship is discussed particularly in terms of the coincidence lattice model.

1. Introduction - It is now over a decade since the classical discrete lattice calculation was first applied to grain boundaries in cubic crystals. The pioneering work was performed by Weins, et al (1), Hasson, et al (2) and Dahl, et al (3) who presented results almost exclusively on short-period <100> and <110> symmetric tilt boundaries in an fcc crystal where the interatomic interactions were represented by Morse, Lennard-Jones and Johnson potentials. In recent years, the calculations have become more systematic and followed two approaches. Firstly, a series of longer period boundary structures have been computed with the aim of generalizing the structural unit model and relating structure to properties. Secondly, the structure of special, shorter period boundaries, have been determined and attempts made to correlate with specific experimental observations on the same system. Clearly, the first approach, which examines structural characteristics, should not rely much on the details of the relaxations whereas direct comparison with experimental data from a particular metal could be sensitive to the chosen potentials.

In this paper, a brief description is made of the calculations that have focussed in these two directions. Also, the information on computed grain boundary energies is summarized. A more extensive review of the early studies has been given by Harrison, et al (4) and a shorter update by Vitek, et al (5). To begin, however,
the framework within which the model functions is discussed by emphasizing some of the approximations that are imposed.

2. On the Methods and Potentials - The atomistic calculation using either static, dynamic or statistical techniques is extremely powerful for several reasons. Clearly, it has advantages over continuum elasticity since defect displacement fields can be computed that have no analytic solution. More importantly, it has predictive value since it can explore equilibrium atomic structures that may be only partially accessible to experimental observation. When thermal effects are introduced kinetic processes can also be simulated. However, the techniques have distinct limitations which need to be considered when analyzing the results. The difficulties inherent in the models have been discussed before (see e.g. (6)) but are important enough to be restated. For a more full description of the actual methods and construction of potentials see, e.g., Ref. (7).

a. In molecular statics thermal effects are excluded: lattice vibrations and configurational entropy are ignored and the simulation proceeds at absolute zero temperature. In addition, most static techniques are susceptible to the location of local equilibria or metastable states. Whilst these states can be of interest they are generally to be avoided. Tests can be made for local minima by using different initial configurations or occasionally restarting the simulation. Using molecular dynamics would be the best test for stability.

b. Unintended constraints imposed by the border conditions and model size should be avoided. Fixed borders will result in long range strain that will not only affect the defect structure but also its energy. Cyclic borders may impose an inappropriate symmetry and periodicity on the structure. Completely flexible borders would be preferred.

c. The interatomic potentials are not known exactly and are consequently constructed and employed using several approximations. This is probably the most serious deficiency in computer modeling of defects in metals. A common assumption is to use short-range, central pairwise forces for which there is no theoretical justification. Long-range oscillatory potentials, which have a sounder theoretical basis, have been employed but then summing the energy becomes a problem and cutoff radii have to be used. Due to the presence of the electron gas in metals volume dependent contributions to the total energy should be included but this has not always been the case. Equilibrium empirical potentials have been constructed to erroneously obey the Cauchy relations. Another important assumption is that the chosen potentials can be transferred to the defect region where, as is the case in grain boundaries, there can be a large redistribution of electrons. This transferability problem is unique to metals and does not exist, for example, in ionic crystal calculations.

Overall, it would appear that considerable care is needed in examining computer modeled results on grain boundaries in metals. This does not mean that useful results cannot be obtained especially if general trends in structure and energy are required rather than configurational details and absolute magnitudes.

3. Comparison with Experiment - A number of experimental observations of grain boundary structure have provided qualitative information that has been generally consistent with the calculated structures. Examples include the narrow cores of grain boundaries seen using the field ion microscope and the localized cores of grain boundary dislocations observed by transmission electron microscopy (TEM). Only a few experimental techniques at present can provide sufficient quantitative information to enable a direct correlation with computed results. In this section, three examples are given where satisfactory agreement was achieved between calculation and experiment using TEM, high resolution lattice imaging and x-ray diffraction. It should be remarked, however, that in some studies only limited correspondence between observation and calculation has been reported (see e.g. (8) or (9)). This has been attributed to the sensitivity of the structural details to the form of the chosen potential. This explanation and other oversimplifying factors in the
Comparisons are currently being investigated.

a. TEM - The existence of in-plane translations as predicted by computer modeling has been confirmed using TEM (10). Annealing twins in aluminum were observed using TEM and the relative translation between the adjacent crystals was deduced from the observation of interference fringes. The structures of the twin related boundaries were also simulated using molecular statics and a pseudopotential representing aluminum. Good agreement was achieved between the modeled and experimentally measured values of the translation vector for the (155) and (121) [011] boundaries. The relaxed structure of the latter boundary is shown in Fig. 1. It is of interest to note that this structure is very similar to that obtained from a hard-sphere model (11) and that this may, therefore, be indication of the "hardness" of the aluminum potential.

b. High Resolution Lattice Imaging - Recently, high resolution microscopy techniques have proved capable of providing information on tilt boundaries with resolution approaching atomic dimensions. Through careful optical processing and image simulation it is possible to obtain a two dimensional lattice image of atomic columns projected through the specimen thickness. An example is shown in Fig. 2 for a Σ=11 [110] tilt boundary in gold together with the structure calculated by quasi-molecular dynamics using a Morse potential (12). This structure is almost identical to that obtained by Pond, et al (13) using the aluminum pseudopotential. It is seen that the main features of the observed and calculated structure correlate reasonably well. However, in detail, the image appears to show a translation of about 0.1a at the boundary which is not present in the calculations. It is interesting to note that such a translation has been predicted in a hard-sphere model of this boundary (11).
c. X-ray Diffraction - It has been shown that x-ray diffraction from grain boundaries produces extra reflections in the diffraction pattern whose intensities can be related to the structure of the boundary. In recent work (14) diffraction from $22.6^\circ$ (Z=13) and $23.8^\circ$ [00\(\bar{1}\)] twist boundaries in gold was studied and the extra reflections, which form as relrods normal to the boundary plane, were measured. The Z=13 boundary was modeled using molecular statics with a number of empirical potentials representing fcc metals and the structure factors in reciprocal space calculated. It was found that most of the potentials could reproduce the correct characteristics of the strongest 'O' lattice reflections but that the weaker reflections were much more difficult to match. The structure which gave the best fit to the data is shown in Fig. 3. A striking feature of this boundary is the large displacement toward the boundary plane of the atoms nominally in "good" match.

Fig. 3: Perspective view of a Z=13 [00\(\bar{1}\)] twist boundary calculated using a spline potential representing gold.(from Ref. (14)). Two (00\(\bar{1}\)) planes below and above the midplane of the boundary region are shown, with each containing four CSL unit cells. Atom points are joined to form a contoured surface and, for clarity, the interplanar spacing has been increased by a factor of four.

From the previous examples it is seen that at present it is possible to make correlations between experiment and simulation and obtain encouraging results, but also that the matching is never complete. Consequently, it is considered that care is needed in interpreting the details of the modeled structures and that many more controlled experiments are needed so that the large volume of computed data can be calibrated.
A Structural Unit Model - One approach taken recently in computer modeling is to determine the structure of long period or 'general' grain boundaries. The purpose of this work is to answer the following questions: (a) is there a systematic relationship between the structure of long period boundaries and short period boundaries, and (b) can the structure of long period boundaries be related to the grain boundary dislocation model? Clearly, such an approach is aimed at determining how grain boundary structure can be characterized in a general way and places less emphasis on the details of the configurations which may vary from one potential to another.

A first attempt to answer these questions without using computer modeling was made by Bishop and Chalmers (15). Briefly, using a geometrical model, they showed that long period boundaries could be described as a sequence of structural ledges (units) which were characteristic of shorter period boundaries. They also showed that the perturbations in this sequence could be identified with the cores of grain boundary dislocations (GBDs). However, since they did not consider equilibrium configurations it was not possible to determine which structural units were physically significant and which actually correspond to the GBDs. Only relaxation using an interatomic potential along with a calculation of the stress fields near the boundary would resolve this. Such calculations have recently been performed by Sutton (16) and Sutton and Vitek (17) for several series of tilt boundaries which has confirmed the general applicability of the structural unit model especially in regimes far from short period boundaries. Only the basic concepts of their results are given here and are illustrated by reference to [001] symmetric tilt boundaries.

Sutton and Vitek calculated the core structure and associated hydrostatic stress field of several long and short period tilt boundaries in a particular series. They found that for some relatively low Σ boundaries the stress field was uniform, localized and planar whereas for all others the stress field was distinctly non-uniform. Examination of the core structures showed that those with a uniform stress field had a uniform structure which contained only one distinct structural unit (A structural unit was defined as a small group of atoms arranged in a characteristic configuration.) These boundaries they called "favored" and it was found that no two favored boundaries were composed of the same unit. The core structures of the other boundaries possessing a non-uniform stress field were found to contain more than one distinct structural unit and these they termed "non-favored." In addition, those non-favored boundaries which possessed misorientations which were intermediate between those of two favored boundaries had structures which were composed of mixtures of the units making up the two favored boundaries. In terms of dislocations Sutton and Vitek deduced that favored boundaries consisted of a contiguous sequence of primary (lattice) dislocations whose long-range stress fields almost cancel. Therefore, the non-uniformities in the stress fields of non-favored boundaries represented perturbations in the primary dislocation array which corresponded to the secondary grain boundary dislocation content. Hence, by comparing the core structures with the stress maps it was possible to determine which structural units were physically significant and actually corresponded to the GBDs.

Examples of favored boundaries calculated using a potential for copper are the Σ=5 (53.1°) [001] boundary which is composed of all type B units (Fig. 4(a)) and the Σ=1 (90°) "boundary" which is composed of all type A units (Fig. 4(d)). Two non-favored boundaries intermediate in the misorientation range are the Σ=17 (61.9°) boundary (Fig. 4(b)) and the Σ=37 (71.1°) boundary (Fig. 4(c)). The Σ=17 boundary is closer to the Σ=5 boundary in misorientation and is seen to consist of A units embedded in an array of a larger number of B units, i.e., ...ABABB..., while the Σ=37 boundary is closer to the Σ=1 boundary and consists of B units embedded in an array of a larger number of A units, i.e., ...AABABAABAB... The structures of all the other intermediate boundaries are derived from a simple rule of mixing of the A and B units. The duality between the structural unit description and the GBD description can be illustrated thus: each minority A unit in the Σ=17 boundary corresponds to the termination of two (120) planes and,
therefore, is the core a Σ=5 DSC-lattice GBD with Burgers vector \( b = \frac{1}{5} [2\bar{1}0] \). Also, each minority B unit in the Σ=37 boundary corresponds to the termination of two (110) planes, and therefore, is the core of a Σ=1 DSC-lattice GBD with Burgers vector \( b = \frac{1}{2} [1\bar{1}0] \). These latter GBDs are, of course, lattice dislocations, since the Σ=1 DSC-lattice is identical to the crystal lattice. The numbers of A and B units become equal in the Σ=13 \((67.4^\circ)\) boundary, and this boundary can, therefore, be described in terms of either Σ=5 or Σ=1 GBDs.

The origin of the structural units in the boundaries illustrated in Fig. 4 may be readily visualized by examining the structures produced by rigidly juxtaposing the two crystal lattices adjoining each boundary as illustrated in Fig. 5. Figure 5(a) shows the "dichromatic pattern" produced by juxtaposing the two crystal lattices in the Σ=5 orientation and allowing them to extend throughout all of space. For present purposes it is assumed that the lattice of filled triangles is located
a distance of $a/2$ below the lattice of open circles. It is readily seen that a row of incipient (but distorted) B units is present in the pattern along the direction MN. We can now construct the boundary illustrated in Fig. 4(a) by (1) removing the plane of filled triangles to the right of the core, rotating it by the angle $\theta$ and rejoining it appropriately to make up the final crystal lattice to the right of the core; (2) carrying out a similar operation for the plane of open circles to the left of the core; and (3) finally allowing the resulting bicrystal to relax to its equilibrium configuration, i.e., the configuration of Fig. 4(a). Similar rows of the incipient boundary core units may be seen along MN for the $\Sigma=17$ and $\Sigma=37$ boundaries in Figs. 5(b) and 5(c) respectively. These results show that the incipient basic structural units can be delineated in the rigid dichromatic pattern and that the final forms which they assume in the boundary core are dictated by the displacements which occur in the core when the bicrystal is allowed to relax. As emphasized earlier, the choice of units which are physically significant depends on the distribution of local stresses.

Sutton (18) has pointed out that the same general model might also apply to twist boundaries although the stress fields have yet to be determined. The relaxed structures of $\Sigma=5$ and 25 [001] twist boundaries (19) using the same potential for copper are shown in Fig. 6. It may be seen that the $\Sigma=5$ boundary consists of all one type of structural unit. On the other hand, the $\Sigma=25$ boundary consists of a mixture of: (1) the $\Sigma=5$ boundary units; (2) what are clearly $\Sigma=1$ boundary units; and (3) a "third type" of unit similar to the $\Sigma=5$ tilt boundary units. These same units are also clearly discernible in the rigid dichromatic patterns for these same boundaries illustrated in Fig. 7. It is also interesting to note that these same units (in different mixtures) appear in the dichromatic patterns for the $\Sigma=17$

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Fig. 6: Core structures of relaxed [001] twist boundaries calculated using a spline potential representing copper (from Ref. (19)). Shown are the first (002) planes of Crystal 1 and Crystal 2 adjoining the boundary viewed along twist axis.

Fig. 7: Dichromatic patterns formed by juxtaposing two rigid (002) planes of the fcc crystal lattice at $\Sigma=5$ and $\Sigma=25$ misorientations.
and $\Sigma$=37 boundaries illustrated in Fig. 5. These results indicate that the $\Sigma$=5 and $\Sigma$=1 twist boundaries may be favored and that intermediate boundaries may contain their units. The $\Sigma$=25 boundary is known to consist of a square grid of $\Sigma$=1 screw dislocations in a pattern corresponding to the square grid of $\Sigma$=5 units in Fig. 6(b). As pointed out by Sutton, this structure can, therefore, be interpreted on the following basis. The $\Sigma$=5 units are the intersections of a crossed grid of $\Sigma$=1 screw GBDs. The $\Sigma$=1 units comprise patches of perfect lattice preserved by the $\Sigma$=1 screw GBDs, and the units of the "third type" are the cores of the $\Sigma$=1 screw GBDs. It is seen that the structure of twist boundaries is inherently more complicated than tilt boundaries by the introduction of a third unit. Further work on these boundaries is in progress (20) in order to determine the local stress fields and GBD arrays which are physically present.

5. On Computed Grain Boundary Energies - It is generally recognized that grain boundary energies determined by computer modeling are much more sensitive to the form of potential than are the structures. One explanation (21) attributes this to the range of the potential: the structure being determined by near neighbor interactions while the energy depends on those of longer range. In view of this and the approximate nature of the potentials in general, it is not surprising that few studies place much confidence in the absolute magnitudes determined. In some cases, even relative magnitudes could be misleading unless tests are made to determine the constancy of a particular trend. In considering the energy/misorientation relationship it is relative magnitudes that are important since the presence or absence of cusps, as predicted by the CSL model and anticipated from various experimental observations, will establish the relative stability of boundaries. The evidence for cusps in the $E(\theta)$ curve, both the experimental and theoretical, has been reviewed recently by Balluffi, et al (22) and their main points are reiterated here with emphasis on the calculations. It should be remembered that the computed results represent an ideal situation never met in practice where there is only one macroscopic degree of freedom $\theta$, the temperature is OK and the impurity concentration is zero.

Numerous calculations of the $E(\theta)$ curve for [001] and [110] tilt boundaries in both fcc and bcc crystals exhibit non-monotonic behavior at relatively low $\Sigma$ values indicating the presence of cusps (23,2,24,16,25). However, the density of calculated points is never high enough to determine the shape of these cusps. Experimental measurements provide evidence for the existence of cusps on $E(\theta)$ curves for several [110] tilt/twin boundaries and at least one [001] tilt boundary (22). Only one calculated $E(\theta)$ curve for a [001] twist boundary in a metal is available (19) and this appears quite smooth with no cusps, although again the number of calculated points is small. More recent calculations have reproduced this smooth behavior but others have indicated that the effect could be dependent on the choice of potential (26). Direct experimental measurements are inconclusive on the question of cusps for [001] twist boundaries but indirect observations of GBDs near low $\Sigma$ misorientations infer cusp-like behavior should be present (22). Figure 8 shows an example of the apparent presence and absence of cusps in the $E(\theta)$ curve for [001] tilt and twist boundaries calculated using a potential representing copper (16, 19). Assuming the twist boundary result is a real effect then, for this potential, the difference between tilt and twist boundaries may be explained in one or more of the following ways:

1. The structure of [001] twist boundaries is inherently more complex than that of tilt boundaries. The structural unit arrays (compare Figs. 4 and 6) are two-dimensional rather than one-dimensional, and at least three types of units are required rather than two. In addition, it is known (19) that there are three different translational states for each [001] twist boundary in copper which may have almost the same energy, and that this introduces the possibility that partial GBDs may exist. Under these circumstances, a relatively large number of closely spaced favored boundaries may exist, leading to closely spaced weak cusps which have not yet been resolved in the calculated results.
2. The relaxations which occur in calculated twist boundaries may be less "complete" than those which occur in tilt boundaries, i.e., the structural units may be less relaxed and the GBDs, therefore, "weaker." This corresponds physically to less localized (more spread out) GBDs. In the extreme case, no appreciable secondary relaxations may occur of the type which produce physically real GBD structures and E(θ) cusps. According to the Brokman and Balluffi CSL model (27) this would be the case when the rigid boundary energy is independent of Σ.

3. The twist boundary core energy may vary with θ in such a way that the cusped elastic energy of the GBDs may be masked (see (22)).

4. Additional modes of relaxation beyond those considered to date, such as the removal of selected atoms in the core, (6, 26) or faceting, may be significant in [001] twist boundaries.

5. A relatively strong interaction may exist in twist boundaries between the GBDs and the core structure, and the core energy and elastic energy may not be easily separable (in, for example, the way proposed by Brokman and Balluffi (27)).

It is clear that if any further progress in understanding the energy/misorientation relationship is to be made from computer modeling then many more calculations are required to establish: a) which effects, if any, are artifacts of the potential; b) whether GBDs are actually present in the structures by calculation of the local stresses; and c) that the presence or absence of cusps is real by calculation of higher Σ boundaries in the immediate vicinity of the low Σ boundaries and thus determine the magnitude of the long range elastic energy.

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DISCUSSION

C.L. BRIANT: One of the problems mentioned throughout your paper is that the potentials are inadequate, and, indeed, in the few areas where experiments are available, the results suggest that they are inadequate. Does not this suggest that pair potentials are much too simple to ever explain grain boundaries in transition metals?

P.D. BRISTOWE: The difficulty in constructing reliable potentials for transition and noble metals is well known. The empirical pair potential approach is a first attempt at this problem and is not really intended to give information specific to these metals but rather to cubic crystals generally. Matching a potential to experimental data relevant to a particular metal may yield information on grain boundary structure pertinent to that metal but this is not guaranteed as appear to be the case in some recent comparisons with observations.

A. REVCOLEVSCHI: How do your (100) tilt boundary energy results compare with those proposed by Hasson of St-Etienne about ten years ago? Are your cusps located at the same \( \theta \) values?

P.D. BRISTOWE: The (100) tilt boundary energy results of Sutton (b) and of Hasson et al (2) are similar in that they indicate the presence of shallow cusps at relatively low values of \( \Sigma \), eg \( \Sigma = 5 \) (210) and (310).