Geometrical model for the energy of semicoherent interphase interfaces

(O-lattice/orientation relationship/habit plane/primary intrinsic dislocations)

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ABSTRACT The basis for the considerations given in this paper is the O-lattice description of crystalline interfaces of Bollmann. In the development of his approach presented here, all possible interfacial planes between two crystal phases having a defined orientation relationship are considered. The energies of these interfaces are then computed in terms of the energies of the primary intrinsic dislocations. A number of modeling interactions are incorporated into this approach, and a better agreement with experimental data is thus obtained.

The O-lattice theory of crystal interfaces of Bollmann (1) is the most general geometrical treatment to have been developed. A natural extension of the Coincidence Site Lattice approach to the structure of homophase boundaries, it may also be used to consider the structure of interphase interfaces. However, because coincidence site lattices are not necessarily generated in the two-phase case, the O-lattice theory is at present basically restricted to the consideration of semicoherent (2) interphase interfaces, described in terms of the primary O-lattice. These interfaces are of considerable importance.

Bollmann has suggested a geometrical parameter (1) that varies monotonically with the energy of such semicoherent interfaces. His parameter, \( P \), has been used to compute the relative favorabilities of the three special interfacial planes that may occur between two crystal phases in a particular orientation relationship (O.R.). This particular O.R. defines the O-lattice cell, and it is the faces of this cell that are taken to be the three special interfacial planes. The present study extends these arguments such that the assumption that one of these special interfacial planes has lowest energy is not made. Rather, the modeling has been performed in such a way as to include the possibility of computing the energy of any interfacial plane between two phases having a defined O.R. We show that this extension to the Bollmann approach removes some of the difficulties in his predictions and produces results that more closely match experimental observations.

The O-lattice method

The O-lattice is formed from the interpenetration, with the relevant O.R., of the two crystal lattices. The coincidences of equivalent interstitial points (rather than only lattice points as in the coincidence site lattice approach) are designated O lattice points. The O-points constitute regions of good geometrical fit between the two crystal lattices. The misfit between O-points is considered to be localized into cell walls, which form dislocations when sectioned by the interfacial plane.

Mathematically, the O-lattice is produced as follows. Let the transformation between the crystal lattices 1 and 2 be the matrix \( A \) so that \( x_2 = Ax_1 \). If the transformed point \( x_2 \) is of the same coordinates as \( x_1 \) or separated from such a point by a lattice translation vector \( t \), then \( x_2 \) is an O-point, \( x_o \). Thus, \( x_2 = Ax_1 + t \).

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FIG. 1. Construction showing the intersection of a pair of cell walls by an interface plane at an arbitrary inclination. The intersections form the array of dislocations on the interface plane.

\[ x_1 + t = x_o \text{ and } (I - A^{-1})x_o = T x_o = t \] (I is the identity matrix). Now the vectors \( t \) represent the discontinuities in the match between the interpenetrating crystal lattices, and it is therefore at this juncture that the Burgers vectors have to be chosen. The determinant of the matrix, \( T \), may be used as a measure of the overall match between the crystals—the smaller the value of the determinant, the larger the volume of the O-lattice cell. The latter cell, for the interphase case, is a parallelepiped.

The geometrical parameter \( P \)

Bollman’s suggestion is that the relative energies of interfacial planes may be considered by using a purely geometrical approach. Because the energy of semicoherent interphase interfaces increases with increasing dislocation density, a parameter such as \( P = \Sigma (b_i^2/d_i^2) \), in which \( b_i \) are the Burgers vectors of the interfacial dislocations and \( d_i \) the perpendicular spacings between their lines, may be assumed to “vary monotonically with the energy in the range of interest” (1). However, it is also assumed that the optimal boundary will lie parallel to one of the surfaces of the O-lattice unit cell; hence, there are only three \( P \) values to compute to determine the optimal interface.

The possible interfacial planes are automatic products of the O-lattice calculation and, hence, of the O.R. obtaining between the two crystal phases. Therefore it is a straightforward task notionally to vary the O.R. (by varying the transformation matrix \( A \)) and to find the overall optimal O.R./interfacial plane. This approach was used successfully by Bollmann and Nissen (4) to account for the observed O.R./interface plane in the orthoclase/low albite case. In addition, Perio et al. (5) have used the method to find optimal O.R./interfaces in the copper/chromium (fcc/bcc) system. At each of these minima in \( P \), the determinant of the matrix \( T \) was equal to zero.

Extension to a general interface

During the above discussion, we have emphasized that the initial approach to a geometrical $P$ parameter has been limited to the consideration of three interfaces per O.R. However, during our work we considered that the rate of change of interfacial energy with interfacial plane would repay examination, rendering it necessary to consider interfaces other than those parallel to O-lattice unit cell surfaces.

If $a^{(0)}$, $b^{(0)}$, and $c^{(0)}$ are the O-lattice unit vectors, then the perpendicular distance between parallel surfaces of the cell is $d'_3 = |(a^{(0)} \cdot b^{(0)}) \cdot c^{(0)}|/|(a^{(0)} \cdot b^{(0)})|$ for example. If the cells of misfit are taken as being of the same shape as the O-lattice unit cell, $d'_3$ is also the perpendicular distance between adjacent members of one array of parallel cell walls. When the interface plane sections that array, dislocations are produced. Because the dislocation lines always lie within the plane of the cell walls, the perpendicular spacing between the lines is simply: $d_3 = d'_3/\sin \phi_3$, in which $\phi$ is the angle between the interface normal and the normal to the cell walls (Fig. 1). Hence, the geometrical parameter $P$ is simply extended to any interface plane.

Preliminary consideration of an fcc/bcc system

The calculation of the O-lattice for $\alpha$ and $\beta$ brass in a Nishi-yma–Wasserman (6, 7) (N–W) orientation relationship has been used by Bollmann as an example of the use of the theory (8). Fig. 2 is a corresponding computed stereographic contour plot of the $P$ parameter in this orientation. The plot was formed by taking a regular $(r, \theta)$ coordinate array on the stereogram, converting $(r, \theta)$ into plane indices $(hkl)$ by treating each position as a stereographic pole, sectioning the O-lattice unit cell on $(hkl)$ to calculate $d_1$, $d_2$, and $d_3$, calculating $P$, and finally normalizing and contouring. The contour plot displays monoclinic symmetry (point group $2/m$), which represents the intersection of the point groups of the fcc and bcc structures taken in the N–W orientation relationship; $2/m$ is also the point group of the O-lattice.

The minimum in this contour plot is very broad and occurs at an interface plane that is not parallel to any of the surfaces of the O-lattice unit cell (marked on Fig. 2). Instead, it is centered roughly equidistant from all three, at a pole of indices approximately $(223)_m$. Because this is not reported as a commonly observed fcc/bcc habit plane, the nature of the geometrical parameter $P$ must be further examined.

Modification of the geometrical parameter

The interface considered in this section is in fact the homophase boundary between MoO$_3$ smoke crystals, treated both theoretically (9) and experimentally by Matthews (10). The orthorhombic smoke crystals from boundaries parallel to (010), and the observed frequency distribution of angular misorientations, $\psi$, close to $\pi/2$ around [010] is shown in his figure 4 (10). It is apparent that $\psi = \pi/2 \pm f$, in which $f = 2(a-c)/(a+c)$ is an energetically favorable misorientation. Matthews interprets this in terms of the energy of the dislocation structure of the interface. At $\psi = \pi/2$, the structure will consist of two arrays of edge dislocations, with Burgers vectors [000] and [00c], accommo-

Fig. 2. Stereographic contour plot of the $P$ parameter for interface planes between $\alpha_{bc}$ and $\beta_{bc}$ brass in the N–W orientation relationship. On this and all succeeding stereograms the poles are indexed with respect to the fcc phase, and the open circles mark the poles of the surfaces of the O-lattice unit cell. Furthermore, all the plots contain contours from 1.1 to 3.0 inclusive, in steps of 0.1, and from 3.25 to the maximal value in steps of 0.25. All the poles are normalized to the minimal value, which in every case occurs near the center of the stereogram.

Fig. 3. (After Matthews, refs. 9 and 10.) The energy ($E$) plotted against misorientation around [010] for [010] grain boundaries between MoO$_3$ smoke crystals. The edge curve corresponds to the Frank and van der Merwe equation (11) for edge dislocation interfaces, the screw curve to Matthews’ own equation for arrays of screw dislocations. The latter curve has cusped minima at $\psi = \pi/2 \pm f$.

Fig. 4. Plots of the parameter $P$ against misorientation $\psi$ around [010] for [010] boundaries between MoO$_3$ smoke crystals.

Fig. 5. Plot of determinant $T$, where $T$ is the matrix $(I - A^{-1})$, against misorientation around [010] for MoO$_3$ smoke crystals.
Fig. 6. Plots of the parameter $Q$ against misorientation around [010] for (010) grain boundaries between MoO$_3$ smoke crystals.

dating the mismatch between c and a. At $\psi = \pi/2 \pm f$, the [101] direction matches exactly with [101] in the other crystal, and a single array of $\frac{1}{2}[001]$ screw dislocations accommodates the misorientation between the other pair of (101) directions. By using the Frank and van der Merwe (11) equation for the energy of the edge arrays and his own equation for the energy of screw arrays, Matthews produced the graph shown in Fig. 3. The work of Matthews on MoO$_3$ smoke crystals thus represents a useful test for the purely geometrical approach. However, $P$ is only useful as a comparative measure of interfacial energy for similar dislocation structures and will not provide a quantitative prediction of which type of interface will be observed.

Fig. 4 shows the computed graphs of the variation in the $P$ value for the (010) interface with misorientation around [010] for both the edge and screw dislocation cases. Whereas $P_{\text{edge}}$ is of a shape similar to that of the Frank and van der Merwe graph (Fig. 3), the $P_{\text{screw}}$ also decreases smoothly to a minimum at the $\pi/2$ position, thus suggesting that the parameter is, in this case, of rather limited predictive use. Fig. 5 shows a plot of the determinant of $T$ against misorientation. (Because the [010] direction is irrelevant to the present analysis, the b lattice parameters in the two crystals were assigned arbitrary, different values, to ensure that the O-lattice unit cell remained a parallelepiped.) Determinant $T$ shows minima at the $\psi = \pi/2 \pm f$ positions, where the match along one direction is essentially perfect (i.e., along (101)), so that the curve is of a shape similar to that of the Matthews screw energy plot. It is therefore clear that the determinant $T = 0$ criterion of Perio et al. (5) for an optimal boundary is only applicable here when the interfacial dislocations have screw character. The reasons for this are involved both with the shape of the O-lattice unit cell and with the nature of the parameter $P$.

The physical meaning of determinant $T = 0$ is that the volume of the O-lattice cell is infinite, which is precisely the situation when the match between the crystals in any direction is perfect. A minimum in $P$ is achieved, however, not when one $d_i$ becomes infinite, but when neither $d_i$ is small, because small $d$ will always dominate $P$ due to the inverse square relation. The sizes of the $d_i$ are determined by the shape of the O-lattice unit cell and not its volume.

The difference between the O-lattices for edge and screw dislocations means that in the former case there are always two arrays of identical spacings, whereas it is only at the $\pi/2$ position that the two screw arrays are equally spaced. At the $\pi/2 \pm f$ position, there is only one screw array. Hence, it is apparent that

Fig. 7. Plots of the parameter $R$ against misorientation around [010] for (010) grain boundaries between MoO$_3$ smoke crystals. These plots enable qualitative predictions to be made which are in accord with the quantitative calculations of Fig. 3.

Fig. 8. Stereographic contour plot of the parameter $Q$ for interfaces between $\alpha$ and $\beta$ brass in the N-W orientation relationship.

Fig. 9. Stereographic contour plot of the parameter $P$ for interfaces between $\alpha$ and $\beta$ brass in the K-S orientation relationship.
FIG. 10. Stereographic contour plots of the parameter $R$ for interfaces between $\alpha$ and $\beta$ brass in various orientation relationships: (a) K-S; (b) $\beta$ rotated around (111)$_\alpha$ by 5.25° relative to $\alpha$ (N-W); (c) $\beta$ rotated around (111)$_\alpha$ by 10.5° relative to $\alpha$ (K-S); (d) half way between $\alpha$ and $\beta$; (e) half way between $\beta$ and c. (f) Stereogram showing the loci of the minima in the $R$ parameter generated by O.R. variation. K, L, M, N, and O are the points corresponding to the minima in a–e. The other points, A–J, arise from other variants of the same O.R.s, all with (111)$_\alpha$//(110)$_\beta$ in common. Thus C, H, and M are minima generated in N-W orientations; A, E, F, J, K, and O arise from K-S orientations.
the number of dislocation intersections varies with orientation like \( P \) for the edge case and like \( T \) for the screw case.

It is therefore suggested that the dislocation intersections should be included in the geometrical model, so that the plots of the geometrical parameter against crystal orientation should assume shapes more similar to the Matthews energy plots. Algebraically, the intersections are to be described by terms such as \((b_1b_2/d_1d_2)\); physically, it is clearly reasonable to expect the energy of the interactions between the dislocation arrays to play a large part in determining relative interfacial energies.

Fig. 6 shows graphs of \( Q = \sum \Sigma (b_i/b_j/d_i/d_j) \) against orientation. The edge plot is substantially similar to that of Fig. 5, but the \( Q_{\text{screw}} \) clearly shows a broader minimum, with a tendency to the formation of “shoulders” on the curve in the vicinity of \( \psi = \pi/2 \pm f \). \( Q_{\text{screw}} \) still does not show cusps at the \( \pi/2 \pm f \) positions, however, suggesting that the inverse square relationship is still producing an excessive contribution from finely spaced arrays (i.e., there is no discontinuity at the orientations where the interface contains only one set of dislocations). Fig. 7 shows plots of \( R = \sum \Sigma (b_i/b_j/d_i/d_j)^{1/2} \); again, the edge plot shows a parabolic minimum at \( \pi/2 \), whereas distinct cusps have appeared on \( R_{\text{screw}} \). It is therefore suggested that a new parameter, \( R \), which is still purely geometrical and simple to compute, represents a more useful measure of relative interfacial favorabilities than Bollmann’s \( P \).

**Test of new geometrical parameters in other two-phase systems**

The contour plots of Figs. 8 and 10b are the plots of \( Q \) and \( R \) corresponding to the N–W oriented \( \alpha/\beta \) brass for which Fig. 2 is the \( P \) plot. As the dislocation interactions are incorporated (Fig. 8), the minimum stretches toward the surfaces of the O-lattice unit cell; when the inverse square relationship is abandoned in favor of a simple inverse (Fig. 10b), the minimum actually decomposes into three, centered on the O-lattice cell faces. It is thus clear that only by the use of the \( R \) parameter can the geometrical prediction of the widely observed (111)\( _{\alpha} \)//(110)\( _{\beta} \) habit plane be made. In addition, the model predicts that (0.74 0.10 0.66), and (0.10 0.74 0.66), should be slightly more favorable habit planes even than (111)\( _{\alpha} \). However, the geometrical models all assume a structureless interfacial plane in terms of atomic positions. The calculated parameters are considered only as interactions between dislocations, so that the high atomic density on the interfacial plane will almost certainly cause (111)\( _{\alpha} \)//(110)\( _{\beta} \) to be, in practice, the most favorable habit. A broad maximum is observed centered near (111)\( _{\alpha} \), in which region the normal to high energy segments of interface (e.g., growth steps) should lie.

Figs. 9 and 10c display the same effect of plotting \( P \) and \( R \) for \( \alpha/\beta \) brass related by the Kurdjumov–Sachs (12) (K–S) orientation relationship. Again, using the \( R \) parameter causes the broad minimum in \( P \) to decompose onto the three O-lattice unit cell surfaces. In this case the contour plot and the O-lattice have triclinic symmetry; the lowest minimum here occurs on (0.12 0.87 0.47)\( _{\alpha} \) and the maximum is centered near (112)\( _{\alpha} \).

Fig. 10 a–c shows plots of \( R \) for various \( \alpha/\beta \) O.R.S with (111)\( _{\alpha} \)//(110)\( _{\beta} \) in common, ranging between two K–S variants 10.5° apart, via an N–W orientation in between, and two intermediate positions. Because there are three distinct N–W variants (and thus six K–S) with (111)\( _{\alpha} \)//(110)\( _{\beta} \) in common, it is possible to plot the loci of the poles of the most favorable interfacial planes on a stereogram such as Fig. 10f. It is apparent that there is thus a region 15–20° away from (111)\( _{\alpha} \) in which there is predicted to be a high probability of finding an \( \alpha/\beta \) interface and which is relatively insensitive to small changes in O.R.

**Conclusions**

The geometrical parameter, \( P \), suggested by Bollmann, has been used to compute the relative favorability of all possible interface planes between two phases in a given O.R. It has been found that the minimum in \( P \) did not occur for the interfaces previously assumed to have the lowest energy (i.e., those parallel to the surfaces of the O-lattice unit cell) and thus containing two rather than three dislocation arrays. In addition, the work of Matthews on MoO\(_3\) smoke crystals has been used as a test for this geometrical parameter. The \( P \) parameter produces a minimum only at a misorientation of \( \pi/2 \) for both edge and screw dislocations for two reasons. First, no cross terms (corresponding to dislocation line intersections) are included in the calculation of \( P \); hence, a new parameter \( Q \) was computed and compared with experiment. Second, the inverse square relationship (\( P \) and \( Q \) are constant) causes the parameter to be dominated by finely spaced dislocation arrays. A parameter \( R = \sum \Sigma (b_i/b_j/d_i/d_j)^{1/2} \) has therefore been suggested which has been shown to make qualitative predictions of relative boundary favorability that are consistent with the experimental results of Matthews.

The parameter \( R \) has also been applied to the fcc/bcc case, and it has been shown that only by using this parameter is (111)\( _{\alpha} \)//(110)\( _{\beta} \) predicted to be a low energy habit plane. In addition, other minima in the value of the parameter occur for interfaces parallel to the surfaces of the O-lattice unit cell. The result of this is that a large number of favorable \( \alpha/\beta \) interfacial planes are generated, each corresponding to a particular O.R. close to N–W. The interface plane (111)\( _{\alpha} \)//(110)\( _{\beta} \) is expected to be of a low energy for all these O.R.S, and the other favorable minima all lie 15–20° away from (111)\( _{\alpha} \).

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