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THE CALCULATED PROPERTIES OF GRAIN BOUNDARIES IN NICKEL OXIDE

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Résumé - Les calculs des propriétés des joints de coincidance en NiO faits par une simulation atomistique dans un réseau statique sont discutés. Les calculs considèrent les interfaces de torsion et de flexion, les interactions avec les défauts et les impuretés, les régions de charge spatiale et diffusion le long du joint.

Abstract - Atomistic static simulations of the properties of coincidence grain boundaries in NiO are discussed. The calculations include the structure of pure tilt and twist interfaces, the interactions with defects and impurities, space-charge regions and diffusion along the boundary.

1. Introduction.

Most oxide materials are polycrystalline and the grain boundaries may influence many important properties and processes. However, the structure and behaviour of boundaries in these materials are still poorly understood. Recent experiments and theoretical simulations are aimed at improving our knowledge of grain boundaries at a fundamental atomistic level. One area of particular interest is gaseous corrosion of metals where recent studies of the corrosion of nickel have shown that the rate at moderate temperatures is determined by the enhanced diffusion down the boundaries in the growing oxide scale /1,2/. Our calculations are directed to understanding this process and to interpreting the role of impurities in influencing the observed corrosion rate.

All the calculations described in this paper were carried out using a static lattice energy minimisation procedure that has been discussed in detail elsewhere /3,4/. The interactions between the ions consists of a Coulombic part, a short-range pair potential and the shell model /5/ is used to make the ions polarizable. An empirical potential which gives good agreement with the bulk elastic and dielectric properties of nickel oxide was used /6/. Two types of calculation are employed. First, relaxations maintaining the two-dimensional periodicity of the interface are used in the structure calculations. This method can also be used to study arrays of neutral defects in the interface such as might be appropriate for impurity segregation. However, defects and impurities in ionic materials carry charge in general and so this method cannot usually be employed. The second method of calculation has an inner region around the defect which is treated explicitly and matched to an outer region which polarizes as a dielectric continuum. The calculations have been done mainly for nickel oxide but most of the structural results would be similar for magnesium oxide and probably most other ionic materials with the rocksalt structure. The predominant defects depend also on the electronic structure of NiO and so would be very different for MgO.

The types of boundaries studied are so far limited to rather special cases because of the need to maintain a high degree of periodicity along the interface. Only high angle pure tilt or pure twist boundaries of high coincidence (i.e. high periodicity) have been considered. Although these are
Figure 1. Calculated structures of four typical coincidence tilt grain boundaries in NiO; (a) $\Sigma 5$, $36.9^\circ[001]$; (b) $\Sigma 25$, $73.7^\circ[001]$; (c) $\Sigma 11$, $129.5^\circ[011]$; (d) $\Sigma 19$, $26.5^\circ[011]$. 
of direct interest for comparison with experiments on bicrystals, in many applications more
general boundaries will predominate. For this reason a range of boundaries of different structure
have been studied with the aim of seeing how the properties vary with structure and if any general
features can be deduced.

In the following sections we consider the calculated structure of the boundaries, the formation
of defects and segregation of impurities, the asymmetric space-charge region generated by
dipolar boundaries and diffusion along the interface.

2. The Structure of Coincidence Boundaries.

The calculated structures of the tilt boundaries in NiO have been described elsewhere /7,8/ but
will be reviewed briefly here because they provide the basis for the later defect calculations. First,
the tilts about an [001] axis can be subdivided into two structural types. One series can be
analysed in terms of an array of [100] dislocations. The Σ5, 36.9° boundary is of this type and
illustrated in Figure 1(a). The other series resembles an array of [110] dislocations and an
example (Σ25, 73.7°) is shown in Figure 1(b). The energy of the [011] tilt boundaries as a function
of angle shows a deep cusp at the configuration of the (111) boundary which is a twin structure of
low interfacial energy. The boundaries on either side of this cusp again fall into different
structural groups. An example from both classes are shown in Figure 1. Thus, in this study of high
angle coincidence tilt boundaries, four different structural types have been identified. A member
from each class will be used in most of the following defect calculations so that common features
can be determined. Experimental studies on the energy and structure of well defined boundaries
/9,10/ are becoming available and will provide a useful validation of the theoretical models.

The [001] coincidence twist boundaries present a more complex picture. Wolf and Benedek
have considered simple twists in both the rocksalt structured oxides /11,12/ and the alkali halides
/13/. Despite the matching of oppositely charged ions in some places across the interface, the
Coulombic interaction across the boundary is repulsive. If the short-range pair potential has an
attractive tail this can compensate leaving a very weak binding and a large dilatation. However,
for NiO this binding is only around a hundredth of an eV per molecule unit. Thus for all practical
purposes the interface is unbound. Indeed, the large dilatation and low binding are related and so
a grain boundary with a large dilatation across the interface is not plausible in the pure material,
if the ionic model is believed. Nevertheless, we note that pure twist boundaries are observed
/14,15/.

The simple twist calculations are done with constraints which may not be physically realistic.
The number of ions in the boundary plane is conserved and the configurations searched in the
energy minimisation are limited. If the number of ions in the plane is reduced (while conserving the
total number of ions) a structure of lower total internal energy is found /16/. This is
restructured to produce a region of lattice rotated halfway between the upper and lower grain. It is
also possible to produce a strongly bound interface with a full density of ions but also with a
region of lattice rotated halfway between the upper and lower grains. The energy of this structure
is higher than for the simple twist and this interface is metastable with respect to dissociation into
free surfaces. Figure 2 shows the structure of the two types of bound interfaces for the Σ5, 36.9°
boundary. The calculations are summarized in Table 1.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Energy (Jm⁻²)</th>
<th>Binding (Jm⁻²)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>ideal</td>
<td>2.72</td>
<td>-0.02</td>
<td>unstable</td>
</tr>
<tr>
<td>restructured full density</td>
<td>3.54</td>
<td>+0.72</td>
<td>metastable</td>
</tr>
<tr>
<td>restructured reduced density</td>
<td>2.22</td>
<td>-0.50</td>
<td>stable</td>
</tr>
</tbody>
</table>

Table 1. Boundary and dissociation energies of calculated structures for Σ5 [001] twist boundaries
in NiO.
Figure 2. Structure of the boundary plane for a $\Sigma 5$, 36.9°[001] twist; (a) with a reduced density of ions and (b) with the full density of ions.

The structure of the other [001] twist boundaries can be deduced by analogy to the $\Sigma 5$ case /17/. The structures can be analysed in terms of a square array of screw dislocations leading to a maximum amount of undistorted lattice rotated halfway between the upper and lower grain. Frank's formula

$$d = (r \times l) 2\sin \theta / 2$$

enables the density of dislocations to be deduced. Here $d$ is the total Burgers vector cut by vector $r$ in the boundary plane, $l$ is the rotation axis and $\theta$ the angle. If the boundary is constructed from an array of primary $\langle 110 \rangle$ dislocations, they lie along the Coincidence Site Lattice (CSL) vectors for rotation angles $\theta < \pi/4$ and along the diagonals of the CSL for $\theta > \pi/4$. Figure 3 shows two examples of predicted boundary structures. Although it is possible to construct structures with a full density of ions, a lower energy is expected for boundary planes of reduced density. In some cases the reduction in density is greater than an ion pair in each CSL cell. The structures have been confirmed as stable bound interfaces by explicit atomistic simulation for the $\Sigma 5$, $\Sigma 13$, $\Sigma 17$ and $\Sigma 29$ boundaries. Although we cannot be certain that other lower energy structures do not exist, the calculations demonstrate that a very stable structure exists for all the [001] twist boundaries and this structure can be interpreted in terms of a square array of primary $\langle 110 \rangle$ screw dislocations.

Figure 3. Probable structures for the interface plane of [001] grain boundaries. (a) $\Sigma 65$, 30.5° and (b) $\Sigma 53$, 31.0°.
3. Defects and Impurities at Boundaries.

The interaction between a point defect (such as a vacancy) and the boundary is calculated from the difference in the formation energies at the bulk and near the interface. Nickel oxide is a non-stoichiometric material with a cation deficiency. The important defects are, therefore, cation vacancies and holes which are assumed to be localised on cations (i.e. as Ni$^{3+}$ ions). A complication with grain boundary studies is that while there may only be one possible defect site in the bulk or near a free surface, there are several inequivalent sites near a boundary. This leads to a range of interaction energies for each defect near any particular interface. The range of energies is shown in Table 2 for the cation vacancy along with the most bound energies for the anion vacancies and holes near the four typical tilt grain boundaries.

Table 2. Defect interaction energies with four typical grain boundaries in NiO /18/.

<table>
<thead>
<tr>
<th>Boundary</th>
<th>Cation Vac range(eV)</th>
<th>Anion Vac min(eV)</th>
<th>Hole(Ni$^{3+}$) min(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(310)[001]</td>
<td>-0.36 to +0.88</td>
<td>-0.30</td>
<td>-0.25</td>
</tr>
<tr>
<td>(320)[001]</td>
<td>-1.61 to +0.46</td>
<td>-1.25</td>
<td>-0.45</td>
</tr>
<tr>
<td>(211)[011]</td>
<td>-0.95 to +0.47</td>
<td>-0.98</td>
<td>-0.23</td>
</tr>
<tr>
<td>(122)[011]</td>
<td>-1.54 to +0.15</td>
<td>-1.56</td>
<td>-0.54</td>
</tr>
</tbody>
</table>

The results show that there is substantial variation in properties between different grain boundary structures. However, all boundaries have sites which are both more stable and less stable than in the bulk. Thus all defect concentrations are enhanced near the boundary. Since different sites are favourable for different defects the concentrations can be simultaneously enhanced for several defects without site competition. Other calculations have shown that both the Schottky and Frenkel energies are reduced near the (310) tilt boundary but as in the bulk, the Schottky energy remains the lower. The binding between holes and cation vacancies is substantially increased near the interface.

In NiO the binding of the cation vacancy to the each boundary is greater than that for the hole. Thus although both concentrations are enhanced the vacancy concentration should be greater leading to a negative boundary charge. The quantitative determination of defect concentrations requires minimisation of a free energy function of the form

\[
F=n_B^h F_B^h + n_B^v F_B^v + \int_{-L}^{L} dx (n^h(x) F^h + n^v(x) F^v + \rho(x) \phi(x) + T S_c(x)).
\]

In this approximate expression \( n \) is the density of defects, \( F \) the formation energy, the superscripts \( h \) and \( v \) refer to hole and vacancy defects and the subscript \( B \) refers to the boundary sites. \( S_c \) is the configurational entropy and \( \rho(x) \) is the charge density given by

\[
\rho(x)=q^h n^h(x) - q^v n^v(x),
\]

where \( q \) is the appropriate defect charge. The potential, \( \phi(x) \), is determined by Poisson's equation and the solution is analogous to that of Kliwer and Koehler /19/ for space-charge regions around free surfaces. The solution gives a negatively charged boundary screened by a space charge region with an enhanced hole concentration but a diminished cation vacancy concentration. However, for the (211)[011] boundary at 1000K the vacancy concentration averaged over the whole boundary region is calculated to be enhanced by approximately a factor of 40. The screening length is estimated to be only about 2nm.

Impurity segregation energies are calculated in the same way as the defect interaction energies. Table 3 summarizes the maximum segregation energies for three differently charged impurities in NiO. As for the intrinsic defects, there is substantial variation between the different grain
Table 3. Impurity segregation energies (eV) with four typical grain boundaries in NiO /18/.

<table>
<thead>
<tr>
<th>Boundary</th>
<th>Co$^{2+}$</th>
<th>Al$^{3+}$</th>
<th>Ce$^{4+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(310)/(001)</td>
<td>-0.09</td>
<td>-0.17</td>
<td>-1.15</td>
</tr>
<tr>
<td>(320)/(001)</td>
<td>-0.22</td>
<td>-0.39</td>
<td>-1.73</td>
</tr>
<tr>
<td>(211)/(011)</td>
<td>-0.12</td>
<td>-0.24</td>
<td>-0.41</td>
</tr>
<tr>
<td>(122)/(011)</td>
<td>-0.07</td>
<td>-0.53</td>
<td>-0.74</td>
</tr>
</tbody>
</table>

boundary structures. Nevertheless, some common trends are apparent. The segregation energies increase for the more highly charged ions at each boundary and there is always at least one site for which the segregation energy is negative. Therefore all impurities studied will segregate to all of the tilt grain boundaries. This result is likely to be true also for more general boundaries since it derives from the diversity of sites available at a boundary such that there is always a site that is favourable for any particular defect. Aliovalent impurities carry charge and so contribute to the space-charge region. The concentration near an interface must be calculated by a method analogous to that outlined for the defects. Isovalent impurities carry no charge and their concentrations can be estimated from a Langmuir isotherm. The segregation energies increase with ion size giving variations in the boundary concentrations from $3 \times 10^{-4}$ for Mg to full coverage (1.0) for Sr for the example of a (211) boundary at 1000K with a bulk impurity fraction of 100ppm. Full coverage, of course, does not imply that all cation sites are occupied with impurity, only that all the favourable sites are filled.

4. Dipolar space-charge regions.

The structural relaxations around a boundary or free surface can influence the space-charge region by generating a long-range potential that influences the defect formation and segregation energies. At the surface of an ionic crystal the different relaxations of the anions and cations and their polarization lead, in general, to a dipole layer. This introduces a potential into the bulk of the material which must be allowed for when calculating formation energies or discussing ionisation phenomena /20/. Similarly, the relaxations around a general grain boundary may lead to a dipole layer as can be seen by considering the boundary as two back to back surfaces. However, the symmetry of most coincidence boundaries means that no dipole is produced. Some coincidence boundaries lie along crystallographic directions in which the planar stacking sequence alternates between positively and negatively charged planes. This asymmetry gives rise to the same effect as may be expected in general unsymmetric boundaries. The dipole layer raises the electrostatic potential on one side of the interface and lowers it on the other side. This is shown schematically in Figure 4(a). The atomistic calculation of the (n11)/(011) boundaries confirms that such a potential is produced /21/.

The consequences of such an internal dipole potential is to increase the energy of one type of charged defect (e.g. cation vacancies) on one side of the crystal while lowering the energy of the compensating defect (e.g. holes). On the other side of the boundary the situation is reversed with the vacancies being more stable. This leads to an asymmetric defect distribution with an excess of vacancies on one side and an excess of holes on the other. This exactly screens the boundary potential leaving an asymmetric potential barrier at the interface shown in Figure 4(b). The screening space-charge region is asymmetric and contains increased defect concentrations. The resulting boundary potential is, at least for the (311) interface, an order of magnitude greater than the symmetric potentials induced by space-charge effects at the symmetric coincidence boundaries. Its asymmetry may lead to non-linear electrical effects.

5. Diffusion.

The grain boundaries presented here show, in many cases, an open structure. In particular, some of the tilt boundaries (e.g. the series (n10)/(001)) have open 'pipes' down the plane of the interface. This suggests possible pathways for enhanced but anisotropic diffusion. In this section,
we present some first results of calculations of the activation energy for diffusion. Figure 5 shows the results for cation vacancy diffusion down the $\Sigma 5, 36.9^\circ, (310)/[001]$ boundary which shows this 'pipe' structure. In Figure 5(b) a schematic diagram of unit cell of the boundary is shown. The lowest energy cation jump consists of a vacancy moving from a site above or below that marked 2 to the site marked 3 followed by the next jump back to an equivalent site, and so on down the boundary. On the left is the ionic path drawn on an expanded scale. The points 2 and 3 correspond to lattice sites as in the structure diagram and this plot shows that the motion carries the ion into the boundary as it follows the lowest energy path. In Figure 5(a) the energy as a function of distance is shown. The initial and final atomic sites are not equivalent so the barrier is not symmetrical. The rate determining jump from 2 to 3 has an activation barrier of 1.86eV but every alternate hop has a barrier of only 1.32eV. This activation energy is compared with that for the comparable process in the bulk and at a (001) surface in Table 4.

We see that the activation energy for cation diffusion down the open (310)/[001] boundary lies between that for the bulk and the surface. However, the more densely packed (211)/[011] boundary has a cation diffusion activation energy that is higher than for the bulk. Thus, again
Figure 5. (a) Activation energy barrier for cation vacancy diffusion down a (310)/[001] tilt boundary in NiO; (b) (i) ionic path between lattice sites 2 and 3; (ii) structure of boundary showing sites 2 and 3. Site 2 lies above or below the anion site shown.
Table 4. Activation energies (eV) for diffusion along tilt grain boundaries, at the surface and in the bulk of NiO.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk</td>
<td>2.39</td>
</tr>
<tr>
<td>surface</td>
<td>1.27</td>
</tr>
<tr>
<td>(310)/[001]</td>
<td>1.86</td>
</tr>
<tr>
<td>(211)/[011]</td>
<td>2.62</td>
</tr>
</tbody>
</table>

there is a wide variation with boundary structure with the possible result that some boundaries are fast diffusers while others are not. It should be stressed that these results are not a complete picture as other mechanisms have not been considered yet. In particular, these are doubly charged vacancies and interaction with the holes may be important.

6. Conclusions.

In this paper we have presented results for calculated grain boundary properties in nickel oxide. Stable, strongly bound structures have been found for all the coincidence tilt and twist boundaries studied. These often have a rather low density structure which suggests that they may provide pathways for enhanced diffusion. Since coincidence boundaries have especially high symmetry we have studied a range of structures to try to determine common features that will apply also to more general interfaces. We find that all intrinsic defect concentrations are enhanced near the boundaries but, for our examples, the net boundary charge is always negative. This is compensated by a space-charge region with an excess of holes. Similarly, we find that all impurities segregate to all the tilt grain boundaries. Thus, although there are substantial quantitative differences between different boundaries their qualitative behaviour is similar and likely to be the same for more general interfaces. The space-charge region around general boundaries and certain special coincidence boundaries will be affected by the planar dipole generated in the relaxed boundary structure. This leads to an asymmetric defect distribution and boundary potential barrier which may produce non-linear electrical characteristics. Finally, preliminary results for the activation energy for cation diffusion indicate a value between that for the surface and the bulk for one of the open structures but greater than the bulk for a more closely packed interface. This shows that very different diffusional behaviour may be expected in boundaries of different orientation.

Acknowledgement.

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References


**DISCUSSION**

**M. Schlüter:** Do we have a simple physical picture to explain why e.g. twist boundaries are rather anisotropic (i.e. flat) even in isotropic materials like NiO?

**P.W. Tasker:** The calculations permit relaxation over an extended region but do not allow gross rearrangements that, for example, remove the periodicity. However, experiments also seem to imply that the boundary region is very narrow. In an ionic material, distortion from the perfect lattice structure is particularly unfavourably energetically since it invariably decreases distances between like charged ions. Thus amorphous phases may have relatively higher energies than in more covalent materials. Perhaps this necessity to maintain as much perfect crystal as possible keeps the boundaries restructured but flat in the pure materials.

**M. Rühle:** 1) Can you please comment on the dependence of grain boundary energy as a function of misorientation. Do your calculations predict energy cusps? 2) How do segregated impurities influence the energy of different grain boundaries?

**P.W. Tasker:** 1) We have calculated the grain boundary energy as a function of misorientation for the <001> and <011> tilt axis. Apart from the obvious cusp at
the twin structure, the functions are smooth. However, we only have a limited number of fairly widely spaced points and we cannot say whether they may cusp points in the complete energy curve.

2) Segregation of impurities always lowers the energy of a boundary (but does not, of course, necessarily increase the binding). The effect depends on concentration and this is determined by the space-charge region for aliovalent impurities. This effect has not been calculated for the boundaries but our calculations on surfaces indicate that some dramatic effects can occur leading even to negative surface energies.

M. Schlüter: In semiconductors one knows the effect of enhanced diffusion due to carrier capture into bound states created by the diffusing atom. Do you know about such effects for diffusion in the space charge layers near boundaries?

P.W. Tasker: So far we have considered only the simple cation jumps and neglected, for example, the interaction with the holes. This may well be important particularly since the calculations indicate that the binding between vacancies and holes is enhanced in the boundary region. Other diffusion mechanisms including such effects will be considered in the future.

A. Atkinson: Are the activation energies for diffusion those for the vacancy jump or for atom diffusion i.e. do they include a contribution from the concentration of vacancies?

P.W. Tasker: The activation energies reported here are just for the cation vacancy jump. The vacancy concentration must also be included in assessing the diffusion but this is not included simply into the activation energy since it is related to the formation of the space-charge region.