Energy ordering of grain boundaries in Cr$_2$O$_3$: insights from theory

A G Van Der Geest$^{1,2}$, M M Islam$^{1,3}$, T Couvant$^4$ and B Diawara$^1$

1 Laboratoire de Physico-Chimie des Surfaces, CNRS-ENSCP (UMR7045), Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, F-75005 Paris, France
2 Department of Physics, Applied Physics, and Astronomy, University of Binghamton, State University of New York, PO Box 6000, Binghamton, NY 13902-6000, USA
3 Mulliken Center for Theoretical Chemistry, Institut für Physikalische und Theoretische Chemie, Universität Bonn, Beringstrasse 4, D-53115 Bonn, Germany
4 EDF R&D, Centre des Renardières, Route de Sens 77818, Moret-sur-Loing, France

E-mail: bob-diawara@chimie-paristech.fr

Received 1 July 2013, in final form 6 September 2013
Published 7 November 2013
Online at stacks.iop.org/JPhysCM/25/485005

Abstract

The grain boundaries (GBs) of corundum Cr$_2$O$_3$ are known to play an important role in the diffusion of ions within the oxide, which is an important phenomenon for the corrosion of stainless steels. The extent of the growth of oxide layers in stainless steel depends upon which interfaces are preferred within Cr$_2$O$_3$. Therefore, we have constructed four different grain boundary planes (rhombohedral, basal, prismatic and pyramidal) and their various associated interface symmetries known in literature for corundum Al$_2$O$_3$. Their structural, electronic, and energetic properties are investigated theoretically with periodic boundary conditions using the DFT + $U$ approach. We find that the prismatic screw GB with a Cr–O plane interface is the energetically preferred GB with the rhombohedral GB with screw symmetry and Cr vacancy termination being the second energetically preferred GB. The increase of the number of in-plane Cr atoms at the interface of prismatic GB enhances the stability, which is also evident in the electronic density of states.

(Some figures may appear in colour only in the online journal)

1. Introduction

In many applications, the ability of Cr$_2$O$_3$ thin films to prevent corrosion is used to improve the corrosion resistance of metallic structures. This involves the inclusion of Cr in stainless steels and other metal alloys with the intent of the Cr forming Cr$_2$O$_3$ scale at interfaces with oxygen or water. In particular, austenitic alloys (austenitic stainless steels and nickel-based alloys) are used in the nuclear industry as components in pressurized water reactors (PWRs). On these alloys, the native Cr$_2$O$_3$ films inhibit the diffusion of ions of the underlying material and oxygen from the environment, thus preventing oxidation.

Understanding the real mechanisms involved in the growth of the protective oxide layer is an important issue. Based on the identified mechanisms, modeling and computer simulation of the growth of oxide layers allow the long term prediction of the mechanical and chemical behavior of metallic materials in corrosive environments. Among the various approaches, atomistic modeling is particularly interesting, providing access to the effect of the local chemistry and structure of the film, while also allowing for a fine-tuning of the interplay of the elementary processes involved during oxidation [1]. Such atomistic models need local values of the diffusion coefficient to account for the local chemical and topological environments. Some attempts have been made to calculate the diffusion coefficients by ab initio calculations of both Cr$_2$O$_3$ and at the interfaces in a complex Cr/Cr$_2$O$_3$/Cr(OH)$_3$ system [2]. In all these works, the oxide scale is considered as uniform, while numerous studies have shown that the presence of grain boundaries (GBs) in the oxide affects ion diffusion in the oxide. As is shown by Tsai et al [3], Cr and O diffusing through GBs have different diffusion rates compared to bulk Cr$_2$O$_3$. Therefore to appropriately study diffusion in Cr$_2$O$_3$, GBs must be considered.

It is important to understand the structure of the GB interfaces that exist within the oxide to study diffusion at
GBs using ab initio models. However, there are relatively few studies of these structures for Cr$_2$O$_3$. Fang et al [4] have used ab initio techniques to study temperature dependent energies of a prismatic interface and two separate Basal interfaces along with the segregation energies of several dopants at these interfaces. Catlow et al [5] used empirical potentials to study several twin boundary conditions. While Cr$_2$O$_3$ grain boundary structures have not been heavily discussed within ab initio literature, alumina, which also possesses the corundum structure, has been intensively studied. Specifically, several grain boundary orientations within Al$_2$O$_3$ have been determined within a density functional theory, DFT, approach combined with experimental results. Marinopoulos et al have studied the rhombohedral [6] and basal [7] plane GBs with their common symmetries, while Fabris et al have studied the prismatic [8] and pyramidal [9] planes and symmetries.

In the present study, we have considered various possible twin interfacial structures at Cr$_2$O$_3$ GBs using 4 GB planes with several associated symmetries for a total of 10 interface systems as determined in Al$_2$O$_3$ literature. We have calculated the structural, energetic and electronic properties of Cr$_2$O$_3$ GBs and evaluated the relative stability for the first time.

2. Computational method

The calculations to investigate the atomic structures and system energies of the grain boundaries were performed using DFT + U as implemented within the VASP [10, 11] software package. A spin polarized GGA-PW91 functional [12] within a projector augmented-wave framework [13, 14] was used with an energy cutoff of 520 eV as optimized for the bulk properties of Cr$_2$O$_3$ in the present study. It should be noted that the GGA-PW91 is known to overestimate binding energy with the addition of $U$ and may lead to negative phonon frequencies. To test the PW91 functional the bulk material and prismatic interfaces were calculated for GGA-PBE and the results show negligible differences in structure and energetics. Monkhorst–Pack [15] $\mathbf{k}$ point grids of $4 \times 4 \times 4$ for the bulk Cr$_2$O$_3$ and $4 \times 4 \times 1$ for the grain boundaries were used. For Cr, a $+U$ correction was applied for the strongly localized correlated d electrons based upon the approach of Dudarev et al [16] with an effective on-site coulomb interaction parameter of 5 eV as defined in [17]. Geometry optimizations were performed with the conjugate gradient algorithm within an energy difference of $10^{-4}$ eV (which is converged when compared to $10^{-5}$ eV).

The atomic positions (unless otherwise stated) and all three lattice vectors were optimized for bulk Cr$_2$O$_3$, while for each of the interface systems the atomic positions and the cell direction perpendicular to the GB were optimized. The lattice vectors parallel to the GBs were considered as fixed because it was felt that the bulk of the grains only allows negligible changes to the lattice constants parallel to the GB.

The interfacial energies for a specific grain boundary were calculated by

$$E_{\text{int}} = \frac{(E_{\text{GB}} - nE_{\text{bulk}})}{2A},$$

(1)

Here $E_{\text{GB}}$ is the total energy of the interface, $E_{\text{bulk}}$ is the energy of a single formula unit of Cr$_2$O$_3$ in the bulk, $n$ is the number of formula units in the GB, and A is the area of the interface plane in the supercell. Effectively, this compares the GB to an infinitely large bulk system that is the most stable isomorph of Cr$_2$O$_3$. This reduces the inherent difficulty of comparing energies between different interfaces by comparing their differences from the bulk state. The lower the interface energy the more energetically stable the GB is. In this way, the energetic stability among the various GBs can be compared, as was performed for Al$_2$O$_3$ systems [6–9] and prismatic and basal interfaces in Cr$_2$O$_3$ [4].

3. Construction of grain boundary models

Using the planes and symmetries determined within Al$_2$O$_3$ it is possible to sample realistic planes and symmetries for Cr$_2$O$_3$. Thus these structures were constructed for Cr$_2$O$_3$. All of the grain boundaries considered here were constructed by first optimizing the bulk corundum structure (the structural parameters are in table 1), then by creating a cell structure periodic in all three directions which includes two grain boundaries perpendicular to the $\mathbf{c}$ axis. While this arrangement has the possibility of the two grain boundaries interacting, the size of the grains (the grain size is discussed below in this section) was chosen to minimize this interaction by reducing the number of atoms per cell. However, slight variation is seen in the density of states (DOS), which is due to this assumption.

---

Table 1. The Bulk Cr$_2$O$_3$ lattice parameters, atomic positions, and magnetic moments for PW91 and PBE functionals compared to experiment. Bulk Cr$_2$O$_3$ has a space group of 167 with a Pearson symbol of hR30. The Cr atoms are represented by Wyckoff position 12c and the O represented by Wyckoff position 18e. Cr$_2$O$_3$ is antiferromagnetic, therefore the magnetization shown is the absolute value of a single Cr atom.

| Parameter | PW91 + $U$ | PBE + $U$ | PBE+$U$ [18] |
|-----------|------------|-----------|-------------|
| $a$ (Å)   | 4.9507(4)  | 5.07292   | 5.0572      | 5.052       |
| $c$ (Å)   | 13.5656(7) | 13.83012  | 13.84018    | 13.8531     |
| $c/a$     | 2.74       | 2.73      | 2.73        | 2.74        |
| Cr (frac.)| (0, 0, 0.35)| (0, 0, 0.34845) | (0, 0, 0.34849) | —          |
| O (frac.) | (0.31, 0, $\frac{1}{2}$) | (0.30282, 0, $\frac{1}{2}$) | (0.30302, 0, $\frac{1}{2}$) | —          |
| $\mu$ ($\mu_B$) | 3.8$^a$ | 3.02 | 2.97 | 2.9 |
It is worth noting that all of the grain boundaries studied are of the form where the two grains have the same interfacial planes represented as (abcd) || (abed) where (abcd) is the interface plane of a given grain. For each of the systems constructed, we took the original bulk corundum structure and created a mirror grain across a GB interface plane (a list of GBs are in table 2 and shown in figure 1), then applied shifts to the new mirrored grain parallel to the interface plane to create the symmetry groups. Here this was done within supercells with lattice vectors $\vec{e}_1$, $\vec{e}_2$, and $\vec{e}_3$ as defined for each of the rhombohedral, basal, prismatic and pyramidal interfaces in table 2. The vectors $\vec{e}_1$ and $\vec{e}_2$ are parallel to the interface plane, while $\vec{e}_3$ is perpendicular to the interface. The in-plane shifts were applied by pre-factors $T_1$ and $T_2$ (also in table 2) in the $\vec{e}_1$ and $\vec{e}_2$ directions, while $T_3$ was applied for alternately terminated interfaces. The mirror symmetry is obtained when $T_1 = T_2 = 0$, while the vector pre-factors for the rotational, glide, and screw symmetries vary with surface direction. The rhombohedral systems consist of 5 Cr layers per grain for the vacancy terminated system (4 for the O terminated), while the pyramidal system has 3 Cr layers for the Cr terminated and 6 for the O terminated system. The basal and prismatic GBs both have 6 layers (Cr for basal and Cr–O for prismatic).

Every rectangular cell is constructed to contain two interfaces due to the periodic symmetry of the cells. It is worth noting that both the [5052] and [5054] directions for the rhombohedral and pyramidal directions respectively require more than 20 atomic planes to be periodic in the bulk system. However, the cell size can be reduced due to the two sides of the grain boundary having the same angle between $\vec{e}_1$ and a bulk Cr$_2$O$_3$ lattice vector. All the GB interfaces are illustrated in figures 2 (rhombohedral), 3 (basal), 4 (prismatic) and 5 (pyramidal).

The major distinction between the Al$_2$O$_3$ GBs and the Cr$_2$O$_3$ GBs is the consideration of spin at the interface for Cr$_2$O$_3$. Alumina is non-magnetic while chromia is antiferromagnetic. The most favorable spin orientation in the bulk that accounts for the chromia antiferromagnetism is with alternating spins within each Cr layer (defined parallel to the (0001) plane) with the atom with a lower $z$ coordinate being spin up and the atom with a higher $z$ coordinate being spin down [17] as shown in figure 1. The combination of grain boundaries of different planes through this bulk spin structure can make predicting the preferred spin state difficult.

Table 2. Each grain boundary type considered shown with its interface plane and the Miller indices of the vectors used to construct the cell. The symmetries for each grain boundary type are then given along with the relative shifts in each direction and with the interfacial energy $E_{\text{int}}$. The parenthesis represents the surface termination of the symmetry. $V$ stands for Cr vacancy termination, O stands for O termination, Cr is Cr termination, and a lack of parenthesis is a Cr–O plane.

| Grain boundary Symmetry | Label | $\vec{e}_1$ | $\vec{e}_2$ | $\vec{e}_3$ | $E_{\text{int}}$ (Cr$_2$O$_3$) (J m$^{-2}$) | $E_{\text{int}}$ (Al$_2$O$_3$) (J m$^{-2}$) |
|------------------------|------|------------|------------|------------|--------------------------------|--------------------------------|
Figure 2. The three rhombohedral grain boundary planes: (a) Glide (G) with vacancy termination, (b) Glide (G) with oxygen termination, and (c) Screw (S) with vacancy termination. Here red represents O, blue is spin up Cr, and white is spin down Cr. All three GBs are viewed along the [1210] direction.

Figure 3. The three basal grain boundary planes: (a) Rotational (R) symmetry with Cr termination, (b) Mirror (M) symmetry with O termination, and (c) Glide (G) symmetry with O termination. Here red represents O, blue is spin up Cr, and white is spin down Cr. The rotational GB is viewed along the [1210] direction, while the glide and mirror GBs are viewed from the [1010] direction to show the shift in the vertical arrangement of Cr atoms between the two GBs as described in the text.

Therefore, several spin states were tried for each interface and the most energetically preferred spin state was used for the grain boundary.

All the spin states used can be arranged into three groups. In the first group, the spin structures are aligned as if they were within a continuous bulk structure. Two examples of this are seen for the prismatic GB with screw symmetry in figure 4(b) and the Cr terminated pyramidal GB with glide symmetry shown in figure 5(a). However, due to the symmetry of the interfaces, this is often not a reasonable spin configuration. This leads to the second type of spin state where the spins at the interface are the inverse of spins expected...
Figure 4. The two prismatic grain boundary planes: (a) Screw (S) symmetry and (b) Glide (G) symmetry. Here red represents O, blue is spin up Cr, and white is spin down Cr. All three GBs are viewed along the \([\bar{1}2\bar{1}0]\) direction.

Figure 5. The two pyramidal grain boundary planes: (a) Glide (G) symmetry with Cr termination symmetry, and (b) Glide (G) symmetry with O termination. Here red represents O, green represents spin up Cr, and blue is spin down Cr.

in the next row of a single grain. This will be referred to as the two grains being anti-aligned with each other. The rhombohedral GB with vacancy terminated screw symmetry is an example of anti-aligned spin states as seen in figure 2(c). The final spin state is shown in figure 3(a), where the basal GB with rotational symmetry has a horizontally shifted spin state between the two grains that is neither aligned nor anti-aligned. It can be seen that the spin orientation for the basal GB has been shifted by one Cr atom in the \([\bar{1}0\bar{1}0]\) direction in relation to what would exist for a spin aligned system like that seen for the prismatic screw GB.

4. Results and discussion

To aid in the understanding of the energy ordering among the various GB planes, we first discuss the structural details, the
changes in the electronic density of states, DOS, of all the GB interfaces of Cr$_2$O$_3$, and compare the energetic stability among them.

### 4.1. Rhombohedral grain boundaries

For the rhombohedral systems the energy ordering of the three symmetry systems can be described based upon an analysis of the bond distances between the Cr–O bonds, Cr–Cr spacing, and O–O spacing in the first layers from the interface. This is because all three of the systems considered for the rhombohedral GB (the O terminated interface with glide symmetry rG(O), the Cr vacancy terminated interface with glide symmetry rG(V), and the Cr vacancy terminated screw symmetry rS(V)) have anti-aligned spins at the interface. This causes the magnetic effects to only amplify the energy ordering resulting from the strained bond distances. Starting with the least energetically favorable rhombohedral interface, rG(V), two features of the interfacial structure can be seen that affect the interfacial energy of the system. First, the spacing between O atoms on either side of the interface is 2.24 Å, which is ~0.4 Å shorter than the smallest spacing seen in the bulk (2.66 Å). This is after an expansion of around 2% in the first couple of atomic layers of the interface. Each Cr at the interface has 2/3 of its bonds strained by between 0.1 and 0.2 Å, which corresponds to a 5–10% strain in the bond. Finally, the most energetically favorable rhombohedral system is the rS(V) system, which contains reasonable O–O separation, but has a large strain in the Cr–O bonds in the first couple of atomic layers of the interface. Each Cr at the interface has 2/3 of its bonds strained by between 0.1 and 0.2 Å, which corresponds to a 5–10% strain in the bond. This is followed energetically by the rG(O) rhombohedral system, which contains reasonable O–O separation, but has a large strain in the Cr–O bonds in the first couple of atomic layers of the interface. Each Cr at the interface has 2/3 of its bonds strained by between 0.1 and 0.2 Å, which corresponds to a 5–10% strain in the bond.

### 4.2. Basal grain boundaries

The basal GB plane is particularly interesting because of the close structural relationship between the mirror, bM(O), and glide-mirror, bG(O), systems. It is important to note that the bG(O) system during unconstrained optimization shifted to the bM(O) symmetry. However, we felt that the bulk portion of each grain would prevent this shift in physical systems. Therefore, several layers in the ‘bulk’ of each grain were constrained to the locations of the idealized symmetrical grain boundary. This resulted in a gradual shift in atomic position between the two bulk regions with the atoms at the interface resembling the bM(O) interface as shown in figures 3(b) and (c). Since the bG(O) and the bM(O) interfaces are similar, it is the constraint of fixing the bulk regions of the bG(O) that shifts this system to slightly higher energies. The difference in energy between the bM(O) interface and the br(Cr) interface can be explained by the same structuring as seen by the Al$_2$O$_3$ basal interface [7]. The bulk corundum structure as shown in figure 1 has a stacking of cations parallel to the [0001] direction of the form void–Cr↑–Cr↑–void (two vertical sets offset by a single step) with a spacing of 2.72 Å between Cr sites. However, for the basal GBs this stacking is changed. In the bR(Cr) interface shown in figure 3(a) the two stacks change to one stack being void–Cr↑–void with the other becoming void–Cr↑–Cr↑–void–Cr↑–void with spacing between Cr of 2.58 and 2.63 Å (between similar spins). For the bM(O) interface shown in figure 3(b) the first stack stays the same i.e. void–Cr↑–Cr↑–void with Cr spacing of 2.75 Å, while the second stack becomes void–Cr↑–Cr↑–Cr↑–Cr↑–void with Cr spacing of 2.63, 2.46, and 2.63 Å. When the difference between the Cr spacing in each stack is compared we see that the bond distances are similar except for the addition of the 2.46 Å for the bM(O) interface. This compression of 0.15 Å (effectively doubling the other distances) is expected to be the cause of the increase in $E_{mag}$ for bM(O) in comparison to the bR(Cr) even with the two same spin neighbors in the bR(Cr) system. The DOS of the basal plane GBs for figures 6(d)–(f) supports this analysis with the bands beneath the Fermi energies of the bM(O) and bG(O) systems shifting position by around an eV while the bR(Cr) system shifts band shape with a slight increase in energy with the band just below the Fermi energy being spin polarized. This large shift in the band positions with respect to the bR(Cr) corresponds to the higher energy of the bM(O) and bG(O) systems.

### 4.3. Prismatic grain boundaries

Both prismatic GB planes are terminated in Cr–O planes. For the glide plane interface, prG, the interface plane is in between two Cr–O planes parallel to the [0001] direction, while for the screw plane interface, prS, the interface is at a Cr–O plane. The biggest difference between the bulk and either the prG or the prS interfaces is the distribution of the Cr atoms within the O anion lattice. In the bulk the Cr cations are distributed in a single plane in the (1010) direction in pairs of the form void–Cr↑–Cr↓–void with each plane offset by one plane (i.e. the next plane has the distribution of Cr↑–Cr↓–void–Cr↑). The intra-Cr spacing distance for the bulk is 2.959 Å with the two Cr offset slightly in the (0001) direction. For both the prG and the prS GBs, aside from minor changes in the O positions due to geometry optimization, the interface occurs where this distribution of Cr atoms has changed as shown in figure 4. In the prG system the ABC plane distribution of the Cr atoms at the interface has planes of A = (void–void), B = (void–Cr↑–Cr↓–void),
Figure 6. The density of states, DOS, of the GB interfaces. The Fermi energy is at 0 eV. The black curves correspond to the DOS of the bulk like regions of the interface, while the red curves are the DOS of the interface regions. Solid lines represent spin up and dashed lines are spin down. The GBs represented here are the (a) rhombohedral Glide (V), (b) rhombohedral Glide (O), (c) rhombohedral Screw (V), (d) basal Glide-Mirror (O), and (e) basal Glide (O), (f) basal Rotational (Cr), (g) prismatic Screw, (h) prismatic Glide (Cr), (i) pyramidal Glide (Cr), and (j) pyramidal Glide (O) interfaces. Color online. The projected DOS of the s, p, and d states are not shown to allow for comparison between the bulk and interface states. However, the deep energy states at around 17.5 eV are dominated by O s states and the states near the Fermi energy are predominately O p and Cr d states (Cr s states exist in this region as well, but the d states dominate). Note: slight variations in the bulk like regions are due to the two GBs interacting slightly.

and C = (void–Cr(↑)–Cr(↓)–Cr(↑)–Cr(↓)–void). It is worth noting that the middle two Cr atoms in both the B and C planes are not shifted in the (0001) direction. This also increases the number of neighboring in-plane Cr atoms from 1 (for bulk) to 2 and 3 for the C plane interface cations. Both of these effects are expected to raise the energy of the interface. The prS interface also has an ABC plane distribution. However, for prS the values are A = (void–Cr(↑)–void), B = (void–Cr(↑)–Cr(↓)–Cr(↑)–void), and C = (void). For the B plane the middle Cr atom has 2 in-plane Cr neighbors, which causes a smaller increase in the interface energy than for the prG interface. Therefore, the prS interface is the most energetically preferred prismatic twin grain boundary. This agrees with the Al2O3 prismatic GBs as described by Fabris et al [8]. The DOS in figures 6(g) and (h) for these two systems show a large deviation from the bulk regions of each interface.
with new states generated above both the s and p/d clusters of states. These are due to the additional Cr neighbors due to the modified stacking order.

4.4. Pyramidal grain boundaries

Like the other GB planes the pyramidal GB planes were selected from those considered in the Al2O3 literature [9]. This resulted in two glide symmetry systems, one with Cr termination, pyG(Cr), and one with O termination, pyG(O). However, when these two structures were constructed for Cr2O3 the pyG(O) system shifted the first atomic layers upon optimization to become the pyG(Cr) interface. It can therefore be concluded that unlike the Al2O3 structure pyG(O) is not stable in Cr2O3. During the optimization of the pyG(O) system a quasi-stable system arose that resembled the Al2O3 pyG(O) system. This Cr2O3 system has a spacing of 2.51 Å between interfacial Cr, compared to the 2.72 Å in bulk, and an inter-O spacing of 2.02 Å compared to the 2.66 Å minimum distance between O atoms in the bulk. This highly strained inter-Cr and inter-O spacing is the cause of the pyG(O) interface shifting to the pyG(Cr) interface. However, this is not strongly portrayed in the DOS as shown in figures 6(i) and (j) where the DOS do not significantly change in relation to the bulk structures.

4.5. Magnetic moments at grain boundaries

The absolute value of the magnetic moments of the Cr atoms, |µ|, at each of the GBs were seen to vary by no more than 0.1 µB. These shifts in the |µ| are all smaller than the change in |µ| between the different functionalized shown in table 1. However, while this shift is bordering on negligible it is interesting to note that the GB, prS, with the smallest shift in |µ| (by 0.02 µB) has the lowest interface energy and the systems with higher |µ| tend to have higher energies (the rG(V) and bM(O) having the largest changes in |µ| of 0.09 µB and 0.08 µB respectively). This reflects the effect of the magnetic moment on the structural optimizations of higher energy interfaces.

4.6. Energy ordering of grain boundaries

Using (1) to calculate the interfacial energy allows for comparison among the interfaces. In particular, it allows for the comparison of the energies of the surface bonding and interface splitting that would be major determining factors in which interfaces exist at grain boundaries. As can be seen in table 2 the six most energetically favorable interfaces are the prS < rS(V) < prG < bR(Cr) < rG(O) < pyG(Cr). This is consistent with the calculations of Fang et al [4], which have the prismatic interface energy being at lower energy than either the Cr or O terminated basal interfaces. For the Cr2O3 GBs two of the first three most favorable systems are the prismatic symmetries considered because the O lattice is effectively unchanged for the prismatic systems and only the Cr ion stacking (in the [1010] direction) is changed as discussed above. This effectively changes the bonding structure of the Cr without changing the O lattice. Conversely, the rhombohedral system, which is the second most favorable system, is characterized by moderate strain at the interface demonstrated by the single strained Cr–O bond for the interfacial Cr and the O, which does not significantly modify the DOS. This results in an energetically stable structure between the two prismatic systems. The energetically favorable basal plane system follows the prismatic and rhombohedral interfaces because the rotational symmetry system combines the strained interface with a Cr ordering change (this time in the [0001] direction). Finally, the single stable pyramidal plane interface is of the highest energy of the four planes considered because of the high number of strained atomic planes as discussed above with both the Cr–Cr interfacial plane distance and the O–O interfacial plane distance compressed between 0.2 and 0.4 Å.

5. Conclusion

In conclusion, we have studied twin grain boundaries with multiple symmetries for each of the rhombohedral, basal, prismatic, and pyramidal planes based upon the structures from the literature for Al2O3, which has the same corundum structure, followed by a DOS analysis. From this we see that the prismatic screw with a Cr–O plane interface is energetically the most preferred system. The rhombohedral screw symmetry interface with vacancy termination, the prismatic glide symmetry interface and the basal rotational symmetry interface are the second, third and fourth energetically preferred systems respectively, with a range of ~0.4 J m⁻² among them. The remaining interfaces then start with at least this much higher energy than the basal rotational system. This suggests that other systems are significantly less probable than these four preferred systems, which therefore means that these four interfaces will be the most common twin grain boundaries found in poly-crystalline Cr2O3. Furthermore the DOS reveal that the prismatic systems have higher polarized defect states than the rhombohedral screw interface.

Acknowledgments

Post-doctoral grants of the Electricite de France (EDF) for the support of A G Van Der Geest and M M Islam are acknowledged.

References

[1] Diawara B, Beh Y A and Marcus P 2010 Nucleation and growth of oxide layers on stainless steels (FeCr) using a virtual oxide layer model J. Phys. Chem. C 114 19299–307
[2] Yu H, Chen C, Jiang R, Qiu P and Li Y 2012 Migration of ion vacancy in hydroxylated oxide film formed on Cr: a density functional theory investigation J. Phys. Chem. C 116 25478–85
[3] Tsai S C, Huntz A M and Dolin C 1996 Growth mechanism of Cr2O3 scales: oxygen and chromium diffusion, oxidation kinetics and effect of yttrium Mater. Sci. Eng. A 212 6–13
[4] Fang H Z, Wang Y, Shang S L, Jablonski P D and Liu Z K 2012 First-principles calculations of interfacial and segregation energies in $\alpha$-Cr$_2$O$_3$ J. Phys.: Condens. Matter 24 225001

[5] Catlow C R A, Parker S C and Allen M P 1989 Computer Modelling of Fluids, Polymers and Solids (Dordrecht: Kluwer)

[6] Marinopoulos A G and Elsässer C 2000 Microscopic structure and bonding at the rhombohedral twin interface in $\alpha$-Al$_2$O$_3$ Acta Mater. 48 4375–86

[7] Marinopoulos A G, Nufer S and Elsässer C 2001 Interfacial structures and energetics of basal twins in $\alpha$-Al$_2$O$_3$: first-principles density-functional and empirical calculations Phys. Rev. B 63 165112

[8] Fabris S, Nufer S, Elsässer C and Gemming T 2002 Prismatic $\sigma 3$(1010) twin boundary in $\alpha$-Al$_2$O$_3$ investigated by density functional theory and transmission electron microscopy Phys. Rev. B 66 155415

[9] Fabris S and Elsässer C 2001 $\sigma 13$(1014) twin in $\alpha$-Al$_2$O$_3$: a model for a general grain boundary Phys. Rev. B 64 245117

[10] Kresse G and Furthmüller J 1996 Efficiency of $ab$ initio total energy calculations for metals and semiconductors using a plane-wave basis set Comput. Mater. Sci. 6 15–50

[11] Kresse G and Furthmüller J 1996 Efficient iterative schemes for $ab$ initio total-energy calculations using a plane-wave basis set Phys. Rev. B 54 11169–86

[12] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J and Fiolhais C 1993 Erratum: Atoms, molecules, solids, and surfaces: applications of the generalized gradient approximation for exchange and correlation Phys. Rev. B 48 6978

[13] Blöchl P E 1994 Projector augmented-wave method Phys. Rev. B 50 17953–79

[14] Kresse G and Joubert D 1999 From ultrasoft pseudopotentials to the projector augmented-wave method Phys. Rev. B 59 1758–75

[15] Monkhorst H J and Pack J D 1976 Special points for Brillouin-zone integrations Phys. Rev. B 13 5188–92

[16] Dudarev S L, Botton G A, Savrasov S Y, Humphreys C J and Sutton A P 1998 Electron-energy-loss spectra and the structural stability of nickel oxide: an LSDA + U study Phys. Rev. B 57 1505–9

[17] Rohrbach A, Hafner J and Kresse G 2004 $Ab$ initio study of the (0001) surfaces of hematite and chromia: influence of strong electronic correlations Phys. Rev. B 70 125426

[18] Mosey N J, Liao P and Carter E A 2008 Rotationally invariant $ab$ initio evaluation of Coulomb and exchange parameters for DFT + $U$ calculations J. Chem. Phys. 129 014103

[19] Finger L W and Hazen R M 1980 Crystal structure and isothermal compression of Fe$_2$O$_3$, Cr$_2$O$_3$, and V$_2$O$_3$ to 50 kbars J. Appl. Phys. 51 5362–7