In this chapter the results of the calculations on the Al(111)/Al₂O₃(0001)-interface are presented. In §4.2, the focus is on the determination of the values of the parameters used in the parameterized potentials. First, the parameters of the interactions in aluminum are determined followed by the parameters of the potentials across the interface. In §4.3 results are presented of the structure relaxations of this interface system. Besides the calculated energies and the crystallographic structures, values of the charges and dipole moments will be presented. The results are compared with results reported in literature in §4.4.

4.1 Introduction

Aluminum is commonly used in today’s materials technology. In particular, the interface between aluminum and alumina is crucial for various industrial applications. For instance, the low hardness and poor wear resistance are the principal reasons that limit the potential applications of aluminum alloys. Hardfacing on aluminum alloys, e.g. by electro-deposition and anodizing, may improve the hardness and wear resistance significantly. However, there are still major drawbacks. The bonding between these coatings and aluminum alloys is usually weak and may cause failure. The anodizing layer is brittle with a relatively low hardness (HVₓ 250 -500) to resist abrasive wear. For these reasons it would be of great practical importance to have a basic fundamental understanding of the bonding between dissimilar materials like aluminum and alumina.
In this chapter the crystallographic structure of the aluminum near the interface will be determined as well as the work of adhesion. The results will be compared with results of quantum mechanical calculations that are carried out on more simplified models of the interface system.

4.2 Determination of the interaction parameters

The parameters of the potentials needed for the calculations of the structure relaxations are determined with the help of the results of quantum mechanical calculations (see Chapter 2). The interactions that are needed are those in aluminum and the interactions across the interface, i.e. between the aluminum atoms and the oxide ions and between the aluminum atoms and the aluminum ions.

In the calculations of the relaxations, the ions in Al$_2$O$_3$ are kept at fixed positions and only the atoms in aluminum are relaxed. This is done so because the oxide is much more rigid than the metal and as a consequence the relaxations primarily occur in the metal.

4.2.1 Parameters of the aluminum interactions

To obtain the parameters of the interactions between the aluminum atoms the energy of a computational cell has been calculated for different values of the lattice parameter. In addition, various quantum mechanical calculations have been performed in which some of the aluminum atoms were not in their minimal energy position. These calculations are used to describe the force fields on the atoms. One of the structures used for the determination of the forces is the slab structure that is part of the computational cell in the quantum mechanical calculations for the interface system.

Each quantum mechanical calculation provides a value for the energy of a particular structure. For the same crystallographic structure, the energy has been calculated with parameterized potentials. For each set the relative deviation of the energy is calculated, i.e. the absolute value of the deviation divided by the absolute energy found in the quantum mechanical calculation.
For each atom, for which the force is calculated in the quantum mechanical calculations, the difference between the two calculated forces is determined. The absolute value is divided by the value of the force, calculated in the quantum mechanical calculations.

The combination of the mean relative spread in the calculated energies and in the calculated forces is minimized by varying the values of the parameters. The optimum set of parameters has been found by minimizing the differences between the energies and forces calculated with the quantum mechanical approach and the parameterized potentials. After fitting, the average of the relative spread in the calculated energy is equal to 3.5%, and the average spread in the calculated forces is 3.1%.

With the parameters obtained in this way, calculations have been performed on bulk aluminum to determine the material constants and to see how they compare to the experimental values. The lattice parameter for which the energy of the aluminum is lowest is found to be equal to 3.91Å, compared to 4.05Å in bulk aluminum\(^1\). The calculated optimum lattice parameter is 3.3% too small. This difference is caused by an underestimate of the lattice parameter in the quantum mechanical calculations. From theoretical calculations Siegel, Hector and Adams\(^10\) find two values for the lattice parameter of aluminum: a=4.039Å and a=3.971Å.

The following elastic constants are calculated by stretching the material in one direction and using the resulting deformation. The calculated values are given in the next table:

<table>
<thead>
<tr>
<th></th>
<th>Calculated (eV/Å(^3))</th>
<th>Reported (eV/Å(^3))</th>
<th>(GPa)</th>
<th>(GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_{11})</td>
<td>0.57</td>
<td>91.9</td>
<td>0.67</td>
<td>108(^2)</td>
</tr>
<tr>
<td>C(_{12})</td>
<td>0.43</td>
<td>68.9</td>
<td>0.38</td>
<td>62(^2)</td>
</tr>
<tr>
<td>C(_{44})</td>
<td>0.27</td>
<td>43.1</td>
<td>0.18</td>
<td>28(^2)</td>
</tr>
<tr>
<td>Bulk constant</td>
<td>0.48</td>
<td>76.6</td>
<td>0.48</td>
<td>73-85, 77(^2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>79.4, 82.0(^3,4,5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>73.5 (84.1)(^10)</td>
</tr>
</tbody>
</table>
From the results of the elastic constants, the Poisson’s ratio is found to be 0.31, while experimentally this value should be between 0.33 and 0.36.

The cohesive energy is calculated to be equal to 3.70 eV. This is about 10% larger than the experimental literature value of 3.39 eV. Another theoretical approach resulted in a calculated cohesive energy of 3.54 eV and 4.09 eV, depending on the theoretical approach that was followed.

4.2.2 Parameters of the interactions across the interface

Quantum mechanical calculations have been performed on computational cells displayed in Fig. 4-1. The results of these calculations are then employed to fit the parameters that determine the interactions across the Al/Al₂O₃-interface. In

![Fig. 4-1: Simplified model of the Al/Al₂O₃-interface for the quantum mechanical calculations (black=O²⁻-ions, top 2 layers of white=Al-atoms, remaining white=Al³⁺-ions).](image-url)
the calculations the distance between the metal and the ceramic slab and in the termination of the ceramic slab are varied.

For each set of calculations, i.e. one quantum mechanical and one with the parameterized potentials on the same computational cell, the energy difference is calculated. The absolute value of this difference was divided by the absolute value of the resulting energy of quantum mechanical calculation. For the forces the difference between the calculated forces has been taken relative to the absolute value of the average force. The combination of these two values is then minimized such that the corresponding parameters yield the best match between the results of the quantum mechanical calculations and those of the calculations using the parameterized potentials. With these parameters, the average error in the energy is 7.2% and the average error in the force is 35.5%.

4.3 Structural relaxation

The information extracted from the quantum mechanical calculations is used to perform structural relaxation calculations on the Al/Al$_2$O$_3$-interface system, where the Al$_2$O$_3$ is terminated with one layer of Al$^{3+}$-ions.

The computational cell, which is used in the relaxation calculations, is taken to be periodic in the two directions parallel to the interface, and along the direction perpendicular to the interface one computational cell is used.

Because of the periodicity, it is necessary that in the ceramic and the metal block the lattice spacing in the two directions parallel to the interface is the same. This is of course complicated by the fact that the two bulk materials have different lattice parameters. For calculations, which are quite time consuming even for small systems, this is solved by stretching or compressing one of the materials such that the periodicities match with a minimum number of atoms. Thus, one computational cell contains one unit cell of both materials or one unit cell of one material and two unit cells of the other material. This means that aluminum would have to be compressed in the in-plane directions. Since compression requires that work is exerted on the system, the calculation does not result in an absolute minimum energy configuration.

To get the atomic configuration with the lowest possible energy it is necessary to start with a configuration in which both materials do not experience stresses.
along the directions parallel to the interface. This results in computational cells that are infinitely large and therefore it is impossible to perform calculations on such a structure.

To overcome both problems, i.e. reducing the stress and dimensions of the computational cell, a trade off is made in which there are only a few unit cells in both in-plane directions of both materials, but such that the stresses in the materials are as small as possible. To build the interface system the lattice parameter of Al is reduced by 0.28% to 4.0382 Å, instead of 4.0495 Å. By doing this it is possible to fit three or six unit cells of Al₂O₃ to five unit cells of Al depending on the in-plane direction. In one direction this results in 6 times the [11-20]-direction of Al₂O₃, each 4.759 Å, resulting in a total length of 28.554 Å. This matches perfectly with 5 times the [01-1]-direction of Al, each 5.7108 Å. In the other direction 3 times the [1-100]-direction of Al₂O₃, 8.243 Å each, results in a total length of 24.729 Å. This is in perfect accordance with 5 times the [-211]-direction of Al, of 4.9458 Å each.

In the case of compressing Al, in such a way that one unit cell of the Al matches perfectly with one unit cell of the Al₂O₃, this would require a reduction of the lattice parameter by 4.0%, which is considerably larger than the 0.28% that is required in the configuration described above.

Experimental observations of this interface system are reported in the literature, but there is no preferred orientation relationship. Kaplan reports on this interface system where the aluminum is melt-infiltrated into polycrystalline Al₂O₃ and he finds that there is no detectable orientation relationship between aluminum and aluminum oxide. From observations of thin aluminum films deposited on Al₂O₃ it is concluded that the primary orientation is such that (0001) Al₂O₃ is parallel to (111) Al and (10-10) Al₂O₃ is parallel to (-110) Al. It means that the aluminum lattice is rotated over 30° with respect to aluminum. This orientation relationship requires a strain in aluminum of 4.3%. Two other orientations are observed, namely: the one that is used for the structure relaxations (with (10-10) Al₂O₃ parallel to (-12-1) Al) and one with 11° rotation with respect to the primary relationship (with (10-10) Al₂O₃ parallel to (5-4-1) Al). These observations have been made for thin films. The results might change for thicker layers due to the strain energy involved.

The result of the structure optimization is given in Fig. 4-2. Here, one computational cell is projected on to the paper along the [0-11] direction. In upper half of the figure, the atoms in the ceramic are drawn and the metal
Fig. 4-2: A view along the [0-11] of the computational cell with the relaxed atoms near the interface.

atoms are in the lower half. Along the [111]-direction, only the part of the computational cell is drawn in which the interface is situated. Along the [-211] direction a part of the atoms in the adjacent computational cells is drawn.

In the upper half of Fig. 4-2, it is clearly visible that the ceramic is built of one layer with only oxide ions and another one with only aluminum ions, which is situated between two oxide layers. The layers with only oxide ions consist of 108 ions per layer per computational cell, and the layers with aluminum ions
contain 36 ions per layer per computational cell. The ceramic block is terminated by one layer of aluminum ions, the distance between this layer and the next layer (a layer with only oxide ions) is smaller than in bulk Al\textsubscript{2}O\textsubscript{3}, as shown in the paper of Smith and Zhang\textsuperscript{9}. The distances between the remaining layers is the same as in bulk Al\textsubscript{2}O\textsubscript{3}. The other end of the ceramic is also terminated with one layer of aluminum ions. This is done such that there will be no dipole moment generated by the charges (this is done by starting and terminating the slab with an aluminum ion layer so that the layers are symmetric around the center) and that the total charge of the system is equal to zero.

In the lower half of Fig. 4-2 the positions of the aluminum atoms are drawn. The atoms near the bottom show the periodicity of bulk aluminum, while the atoms close to the interface are clearly displaced. The closer a layer of aluminum atoms is located to the interface the larger the structural distortions. The atoms located directly next to the interface even show the periodicity of the ceramic instead of the periodicity of the aluminum. This will be shown in greater detail later in this chapter; references will be made to the different layers near the interface, which are indicated in Fig. 4-2 by the markings 1a, 1b, 1c, 2, 3 and 4.

In Fig. 4-3, a distribution plot is given of the atoms near the interface. In the

![Distribution plot of the metal atoms and ceramic ions near the interface.](image-url)
figure the different layers are visible. On the left hand side the layers in the metal can be seen, they consist of 100 atoms. On the right hand side, the layers in the ceramic are visible. There are always two layers with 36 aluminum ions and a layer with 108 oxide ions.

On the left hand side of the zero, indicating the position of the interface, two distinct layers with 36 aluminum atoms are clearly seen. These two layers can also be distinguished in Fig. 4-2 as 1a and 1b. To the left of these two layers with 36 aluminum atoms a third layer with 36 atoms can be observed (layer 1c in Fig. 4-2). However, this layer is much less well organized than the other two layers, and therefore it is harder to distinguish this layer. The remaining atoms of the original top two layers of the aluminum block form a transition layer, which does not seem to have a clear crystallographic structure. More to the left, a relatively normal aluminum layer can be seen, which seems to be influenced only slightly by the interface.

So far, only the displacements perpendicular to the interface are used to analyze the behavior of the aluminum atoms near the interface. In the next section, the displacements along the interface are analyzed.

Fig. 4-4 shows the locations of the ions in the first two layers in the ceramic. They consist of a layer with only oxide ions and a layer with only metal ions. In Fig. 4-4, the border of the computational cell is drawn along with some of the

![Fig. 4-4: Locations of the ions in the two terminating layers of the Al₂O₃.](image-url)
ions in neighboring computational cells. With the thicker solid lines the periodicity of the two layers are indicated.

The aluminum ions can be found at three different locations with respect to the layer with only oxide ions. The configuration displayed in Fig. 4-4 represents only one possibility. The first of the other two locations can be achieved by shifting the layer with the aluminum ions one ninth of the periodicity of the computational cell along the horizontal direction. This is indicated by the dashed figure. The second one can be achieved by performing the same translation once more and it is indicated by the dotted line. In both cases, the aluminum ions are located at the corners and in the center of the dashed or dotted figure.

The next layer under investigation is the first layer from the interface of the aluminum. In Fig. 4-5, the first 108 atoms from the interface are depicted, although a normal aluminum layer in the computational cell contains 100 atoms. Actually, the layer is divided into 3 sub-layers (shown in Fig. 4.2 as 1a, 1b and 1c), of 36 atoms each. Each of these three sub layers follows the periodicity of the ceramic.

The brightness of the atoms indicates the distance of the atom to the interface and in this way information of all the three coordinates can be seen. The black atoms are the ones closest to the interface (sub layer 1a), while the brighter

**Fig. 4-5:** Locations of the atoms in the terminating layer of the aluminum.
atoms are farthest away from the first ceramic layer (sub layer 1c). Black indicates a distance of 0.7 Å between the atom and the first layer in the ceramic along the direction perpendicular to the interface and white indicates a distance of 2.8 Å to the first layer of the ceramic. It can be seen that the black and dark gray colored atoms show a periodic pattern, while the brighter atoms take almost random positions between the dark colored atoms.

Now it would be interesting to investigate how the periodicity of the atoms in the first layer of the metal and the periodicity of the atoms in the first layer of the ceramic compare to each other and to see if there is a relation between the

Fig. 4-6: On plane view of both the atoms in the first Al layer and the ions in the first two ceramic layers.
two systems. This can be seen in Fig. 4-6, where the atoms of both layers are shown simultaneously.

From Fig. 4-6 it can be seen that the black and dark gray colored atoms show the same periodicity as the oxide layer, and that they form hexagons around the metal ions, that are located between the oxide and metal layer. The brighter atoms show roughly the same periodicity as the metal ions, but they reveal large displacements along the interface.

It is possible to put the metal layer on top of the ceramic surface in three different ways, where each possibility results in a stable configuration from symmetry point of view. The various possibilities are summarized as follows:

The configuration displayed in Fig. 4-6, where all atoms are located in positions opposite to hollow sites (position between three atoms) in the oxide layer, and a part of the atoms are located directly opposite to the terminating ceramic layer with only metal ions.

Another option is the one where the atoms are translated from the positions shown in Fig. 4-6 such that all the atoms are located again directly opposite to a hollow site in the oxide layer, but the ions of the terminating layer are not located directly opposite to a metal atom.

![Fig. 4-7: Atoms in the second Al layer from the interface.](image)
A final possibility is the one where the atoms in the first metal layer are located directly opposite to the oxide ions.

From the result obtained for the structure relaxations, it can be concluded that the first option is energetically the most favorable one.

The remaining atoms in the second layer from the interface (layer 2 in Fig. 4-2) show no clear crystallographic structure. In Fig. 4-7 the 92 atoms of the second layer are shown that are located farthest away from the interface. However, it should be emphasized that there is no clear height differences between the atoms in the first layer that are located farthest away from the interface and the atoms in the second layer that are located the closest to the interface. This can also be seen from the graph in Fig. 4-3.

In general, the atoms in the third layer from the interface do not show large displacements, neither along the plane of the interface nor perpendicular to it. There are a few exceptions, as can be seen in Fig. 4-8, which shows some disturbances of the structure. However, in general the atoms are located as in the bulk structure of aluminum.

The atoms in the layers farther away from the interface are displaced over a smaller distance and are not displayed.

**Fig. 4-8:** Atoms in the third metal layer from the interface.
4.3.1 Charges of the atoms

In the calculations carried out for this interface system also the image charges are simulated. This is done by calculating a charge and a dipole moment for all the metal atoms. In this section, the results for the charges of the atoms will be presented.

In Fig. 4-9, the first two layers of the ceramic and the first layer of the metal are shown. In this figure, the gray scale does not indicate the height of the atoms in the first metal layer from the interface but it provides information about the charge calculated for that particular atom. In Fig. 4-9 black indicates that the

![Fig. 4-9: Charges formed on the atoms in the first Al layer.](image)
charge of the atom is equal to a charge of \(-3.0 \cdot 10^{-20}\) C which is equal to 0.19 times the charge of one electron. The white color indicates a charge of \(5.1 \cdot 10^{-20}\) C, and this is equal to 0.32 times the charge of one positron.

The atoms that follow the periodicity of the ceramic are now colored white (sublayer 1a) or light gray (sub layer 1b), while the atoms showing large displacements parallel to the interface are colored black or dark gray (sub layer 1c). The latter atoms are on locations directly opposite to the terminating Al\(^{3+}\)-layer of the ceramic and therefore they experience a potential, which causes the image charge to become negative. From the image it can be seen that the negative charge on these atoms depends on the displacement parallel to the interface. The charge is more negative when the displacement is smaller. The charge decreases to zero with increasing displacement.

The atoms that follow the periodicity of the last layer of O\(^{2-}\)-ions are all located in the hollow-positions directly opposite to the location right between three surrounding ions in the last layer of O\(^{2-}\)-ions. For each atom in one of these positions, the neighboring ions in the first two layers of the ceramic are the same. However, the charges of the atoms in these positions are not the same. The charge is either 0.3 times the charge of a positron or 0.07 times the charge of an electron.

The charges in the next layer of the metal show no clear pattern in relation to their locations parallel to the interface and neither the charges in the third metal layer show a clear pattern. Next, the charges in this last layer are so small that these are not of interest anymore in comparison to the charges in the first metal layer. Therefore, no analysis, with the aim of finding a relation between the location parallel to the interface and the charge of the atom, of these two layers is provided here.

In the graph shown in Fig. 4-10 the charge of the metal atoms as a function of the distance perpendicular to the first ceramic layer has been plotted. It can be seen quite clearly that there is a relation between the distance from the interface and the charge of the atom.

To the right in the graph are two sub-layers (1a and 1b) visible as two clusters of data points. The small cluster with charges around \(0.3 \cdot 1.6 \cdot 10^{-19}\) C represents the white colored atoms in the previous image, which are closest to the interface, and located opposite to the Al\(^{3+}\)-ions of the fourth ceramic layer. The other cluster is located around \(-0.07 \cdot 1.6 \cdot 10^{-19}\) C and it is associated with the atoms
located directly opposite to the ions in the third ceramic layer. These atoms are colored light gray in the previous image.

The remaining atoms of the first two metal layers are found at distances in the range from 2Å to 4Å from the interface. These are about 125 atoms for one computational cell. In the graph it can be clearly seen that there is a strong dependence: the farther the atoms away from the first layer of the ceramic the smaller the absolute value of the charge. Far to the left in the graph lie the atoms in the third metal layer. The atoms in this layer are located at distances between 5Å and 6Å from the interface. It can be seen that the charges of these atoms are quite small in comparison to those of the atoms in the first two layers of the metal. In addition, the spread in the distance to the interface is smaller than for the second metal layer. This can also be observed in Fig. 4-3.

\[ \text{Fig. 4-10: Charges induced in the metal as function of the distance from the ceramic.} \]

4.3.2 Dipole moments

So far, the distribution of the charges has been analyzed and the charges have been calculated to mimic the behavior of the image charges in the metal. The other quantities that have been calculated to mimic this behavior are the dipole moments of the atoms in the metal.
In the Fig. 4-11, the dipole moments of the atoms in the first metal layer are visualized. For each atom the size and direction of the dipole moment parallel to the interface is indicated by an arrow, and the size of the dipole moment perpendicular to the interface is indicated with the gray level of the atom. Like in Fig. 4-9, that shows the charges of the atoms in the first metal layer from the interface, the atoms, which are in the two sub-layers that are closest to the interface, are colored white (sub layer 1a) and light gray (sub layer 1b). The black and dark gray colored atoms are in the sub-layer (1c) located farthest away from the interface. These atoms are located directly opposite to the Al$^{3+}$-ions in the first layer of the ceramic.

**Fig. 4-11:** Dipole moments in the first Al layer.
As noted before the atoms in the first two sub-layers from the interface are located on positions directly between the three surrounding ions in the first layer in the ceramic with only oxide ions. The symmetry of the surrounding atoms is such that the potential for these atoms hardly changes upon small displacements parallel to the interface. Therefore, the atoms experience no or almost no electric field parallel to the interface. This results in a dipole moment of which the in-planar part is equal or almost equal to zero. Just as with the charges of the atoms, the dipole moments perpendicular to the interface depend on the locations of the ions in the third and fourth layer of the ceramic, both of these layers contain only Al$^{3+}$-ions. Atoms located on the same position as the ions in the fourth layer of the ceramic have a dipole moment of which the part perpendicular to the interface is $1.65 \times 10^{-30}$ Cm (white colored atoms). Atoms with the same position as the ions in the third ceramic layer have a dipole moment with almost no component perpendicular to the interface (these atoms are colored light gray).

The black and dark gray colored atoms have large in-plane displacements. In Fig. 4-11 it can be seen that the part of the dipole moment parallel to the interface is always pointing from the closest ion in the terminating layer of the ceramic. Not only this part of the dipole moment is pointing directly from the closest ion, but also the part perpendicular to the interface is pointing away from the closest ion. It can be seen that both the in-planar part as well as the part of the dipole moment perpendicular to the interface depend on the

![Fig. 4-12: Dipole moments as a function of the distance to the ceramic.](image-url)
displacement parallel to the interface, with respect to the closest ion in the ceramic.

In Fig. 4-12 the dependence of the part of the dipole moment perpendicular to the interface with the distance between the atom and the first layer of the ceramic is drawn. The behavior is quite similar to that of the graph showing the relation between the charge and the distance to the first ceramic layer, namely in Fig. 4-10.

To the right the two sub-layers can be distinguished with different values for the perpendicular part of the dipole moments. The remaining of the first two layers of the metal show a strong dependence of the perpendicular part of the dipole moment with the distance to the first ceramic layer. Like the charges in the third layer of the metal, which are found to be quite small in comparison to the charges in the first layer of the metal, the dipole moments perpendicular to the interface of the atoms in the third layer are quite small in comparison with the values of the atoms in the first metal layer.

The dependence of the charges on the distance to the first ceramic layer and the dependence of the part of the dipole moments perpendicular to the interface on the distance are quite similar. This similarity raises the question if there is a relation between the charge and the part of the dipole moment perpendicular to the interface for the atoms in the first layers of the metal. In Fig. 4-13 these two

![Graph](image)

**Fig. 4-13:** Relation between the charge and the dipole moments formed on Al atoms.
values are depicted together in one graph.

Clearly, for the atoms in the first three layers of the metal a relation exists between the charges and the part of the dipole moments perpendicular to the interface. The cluster of points in the right upper corner of the graph are the points associated with the atoms in the first sub-layer from the interface and the cluster of points left on the x-axis are the points associated with the atoms in the second sub-layer. The remaining atoms in the first three layers of the metal form a straight line towards the origin. This line also intersects the cluster of points of the first sub-layer.

In the discussion of the results, which focused on the charges and dipole moments, it was mentioned that the values for the atoms located directly opposite to the Al$^{3+}$-ions in the terminating ceramic layer depend on the displacement parallel to the interface. In the graph of Fig. 4-14 the relation between the charge, the part of the dipole moment parallel to the interface and perpendicular to the interface and the displacement parallel to interface is drawn. The displacement parallel to the interface is calculated with respect to the closest atom in the terminating ceramic layer.

In Fig. 4-14, it can be seen that the charges and the part of the dipole moments perpendicular to the interface decrease with increasing displacement parallel to

![Graph showing charge, dipole moment perpendicular and parallel to interface as function of in plane displacement.](image)

**Fig. 4-14:** Charge, dipole moment perpendicular and parallel to interface as function of in plane displacement.
the interface. While the part of the dipole moments parallel to the interface show a local maximum when the displacement is around 1Å, after which it decreases to zero.

### 4.3.3 Calculated energies

So far, the discussion has focused on the effects on the crystallographic structure, charges and dipole moments for atoms close to the interface. In this section, we concentrate on the calculated energies.

The cohesive energy is found to be equal to 3.70 eV. The calculated surface energy for the (111)-Al surface is equal to 1440 mJ/m². The surface energy is defined as the energy of a system with a free surface minus the energy if the same number of atoms is located in bulk aluminum.

Because no description is given for the interactions within the ceramic it is not possible to calculate the surface energy for the ceramic. Also for the calculation of the work of adhesion and the interface energy this generates some problems. To overcome these problems it is assumed that the energy associated with the interactions in the ceramic does not change under the influence of the presence or absence of the aluminum block.

The work of adhesion is defined as the energy needed to break the interactions across the interface divided by the surface area of the interface, see Eq. (1.4). Thus, the work of adhesion is equal to the sum of the total energy of the two systems with the free surface of aluminum and the ceramic minus the total energy of the interface system divided by the surface area. The work of adhesion that is calculated for the interface is found to be equal to 6.70 J/m². This is under the assumption that the energy of the ceramic does not change under the influence of the metal.

### 4.4 Comparison with literature

In literature two papers were found which focused on the same interface system but using different approximations.
Our calculated work of adhesion is considerably larger than the values reported for other theoretical calculations on this system and the experimental values reported in literature. However, it should be noted that both Smith and Zhang and Siegel, Hector and Adams find that the atop aluminum is energetically the most favorable just as was concluded near the end of paragraph 4.3.

It should be noted that all the calculated energies in these simulations are too large, i.e. for the calculated cohesive energy, the calculated surface energy of aluminum and finally for the work of adhesion.

Not only the energies but also the structure after relaxation should be compared with literature. A similarity between all the calculations is the splitting of the first aluminum layer from the interface. To investigate this further the calculated and reported distances between the layers and sub layers are given in table 4-3.

### Table 4-3: Spacing between the layers closest to the interface.

<table>
<thead>
<tr>
<th></th>
<th>Calculated (Å)</th>
<th>Smith and Zhang (Å)</th>
<th>Siegel, Hector and Adams (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2nd, 3rd Al layer</td>
<td>2.16</td>
<td>2.29</td>
<td></td>
</tr>
<tr>
<td>3rd sub layer, 2nd Al layer</td>
<td>0.84</td>
<td>2.11</td>
<td></td>
</tr>
<tr>
<td>2nd, 3rd Al sub layer</td>
<td>1.22</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>1st, 2nd Al sub layer</td>
<td>0.51</td>
<td>1.08</td>
<td></td>
</tr>
<tr>
<td>1st Al2O3 layer, 1st Al sub layer</td>
<td>0.77</td>
<td>1.26</td>
<td>0.70</td>
</tr>
</tbody>
</table>
The calculated distance between the first metal and the first ceramic layer is in good agreement with the values that are reported in the literature, which are obtained with different approaches. Further splitting of the first metal layer into three sub layers is more difficult to observe in the work of Smith and Zhang and of Siegel, Hector and Adams. But, it should be emphasized that these calculations were performed with another orientation relationship, for which the aluminum is stretched.

It is interesting to note that the distance between the first aluminum sub layer and the 4th layer of the ceramic (a layer with only $\text{Al}^{3+}$-ions), the distance between the second sub layer and the 3rd layer of the ceramic (also a layer with only $\text{Al}^{3+}$-ions) and the distance between the 3rd sub layer and the first ceramic layer are almost identical. The distances between these layers is 2.52Å, 2.52Å respectively 2.50Å. This is a good indication that the aluminum atoms follow the periodicity of the aluminum ions in aluminum oxide.

### 4.5 Conclusions

Although the energies, the cohesive energy, the surface energy of Al and the work of adhesion, are overestimated with our approach there is still a strong agreement between calculated and the reported structures. The cause of the overestimation of the work of adhesion may be due a too limited set of quantum mechanical calculations to determine the parameters of the interaction potentials.

Another reason may be that a large number of the quantum mechanical calculations were performed on an interface system in which the ceramic was terminated with a layer of oxide ions. In the paper by Siegel, Hector and Adams\textsuperscript{10} it is reported that this interface system has a much higher work of adhesion, around 10 J/m$^2$. This may have had a negative influence on the determination of the parameters.

### 4.6 References

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