THEORETICAL MODELING OF (001) α–ALUMINA SURFACE

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The structure of (001) surface of α–alumina was modeled using empirical pair–wise 6–12 type potential. The surface energy, the quality of the top atomic plane, the statical relaxation of ten top atomic planes and the computational conditions needed for correct modeling of this type of surface were determined.

INTRODUCTION

An extraordinary interest in understanding of the structure of alumina surface is caused by wide application of Al_2O_3, ranging from construction ceramics to catalysis and microelectronics.

Reliable models of the surface should provide information important for improvement of existing technological processes and the development of new ones. Whether a series of subsequent steps of surface processes on solid – gas interface results in chemical transformation or not, the first step of any surface process is the physical adsorption. The detailed knowledge of atomic structure and energetics of the surface is needed for the understanding of this process, and even more for the understanding and eventually forecasting of a subsequent chemical events.

Two principal aspects of surface modeling have to be considered. First, the choice of suitable two-dimensionally periodic slab of finite thickness, representing the considered surface. The interface solid phase - fluid phase (or vacuum) is represented by the upper atomic plane of the slab while the effect of the bulk should be included using sufficiently thick slab with the structure of its lower part fully compatible with those of the bulk material.

The questions of the number of atoms of different kinds included into the slab, the slab stoichiometry, the slab polarity and its symmetry are to be accounted in this connection.

Secondly, the method of the slab energy calculation must be chosen. This is responsible for the optimisation of geometry of the upper part of the slab which is done *via* the total energy minimisation with respect to defined set of atomic coordinates. Moreover, the method of energy calculation consistently define the potential above the surface, thus determining the kinetics and equilibrium of subsequent physical adsorption processes. The possibilities of using *ab initio* or semiempirical crystal orbital methods versus methods based on empirical pair-wise potentials are to be carefully considered.

α–alumina plays a dominant role in the modeling of Al_2O_3 surfaces. Despite of its own technological importance, this is caused by the fact that α–Al_2O_3 has well-determined structure.

The goal of the present paper is to propose the method suitable for the study of static relaxation of Al_2O_3 surfaces and to compare the results obtained for the (001) surface of α–Al_2O_3 with results provided by other methods.

METHOD

Figure 1 shows the arrangement of atomic (001)-planes schematically projected on the *c*-axis. The symbol OOO means that all three oxygen atoms have the same *c*-coordinate; their displacements in a, b directions are different. Analogically, displayed Al atoms are not aligned in the *c*-direction, i.e. their a, b coordinates vary. The identity period in the *c*-direction is 18 atomic planes.

The symbols A, B and C denote all three topologically non-equivalent choices of two-dimensional representation of the solid phase - fluid phase interface. A', B' and C' are possible bottom cuts of the slab, forming thus nine possibilities of slab construction in combination with the top planes. However, only the top atomic planes are important for our purposes, the bottom ones represent only the semi-infinite bulk, which is not fully included into simulation. Having X and X' chosen (X stays for any of A, B or C), the thickness of the slab is defined by the number of atomic planes between these cuts. The slab has to be thick

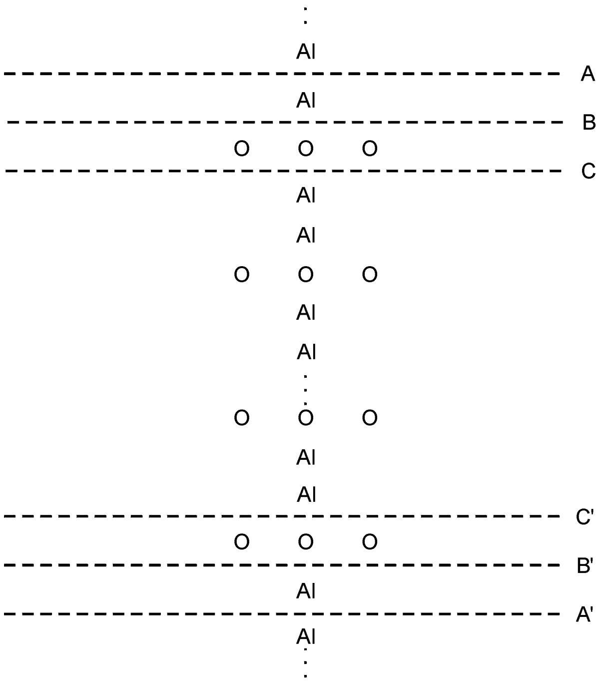

Figure 1. Arrangement of atomic (001)–planes schematically projected on the *c*–axis.

enough that the interaction of atoms in the top and bottom planes is negligible. In other words, the results of top surface should not be influenced by the choice of A', B' or C' ending of the slab. For convenience, such bottom cut was chosen which provide stoichiometry closest to formula unit. Taking into account the above considerations, three types of slabs (AA', BB' and CB') resulted for our calculations. The AA' and BB' types are non-polar slabs; AA' and CB' types have exactly the Al_2O_3 stoichiometry. The CB'- type slabs do not fulfill the condition according to Tasker [1] (the dipole moment through the slab is in this case non-zero) and in case of summation of electrostatic energy the slab energy will diverge. The actual slab is defined by its type and the number of atomic planes. Throughout this paper we use the following notation for actual slabs: the symbol of the slab type followed by the number of atomic planes in parentheses, e.g. AA'(9) means the slab :

Al - OOO- Al - Al - OOO - Al - Al - OOO - Al

Quantum-chemical methods are rigorous means for calculation of the slab energy. However, with growing complexity of the object under the study (e.g. more thick slab or more complex basic unit) various approximative quantum–chemical methods are used. Slabs of α–Al_2O_3, corresponding to various crystal surfaces, were studied using quantum-chemical methods of various level of accuracy, varying from semi-empirical level [2], through *ab initio* Hartree-Fock level [3] to *ab initio* density-functional level [4, 5]. Because of enormous computing demands of these calculations, only slabs of very limited thickness were studied by quantum-chemical methods. There is questionable, whether the thickness of slabs studied by these methods is sufficient to emulate the effect of semi-infinite bulk - we stated that the top and bottom atomic planes should have such distance that there is no interaction of these planes. On the other hand, some detailed information concerning the electron structure, charge distribution, density of states and the role of individual atomic orbitals in individual energy bands can be provided only by the quantum-chemical calculation. Depending on the nature of the problem studied, there are situations when the slab energy is the most important information desired and the accuracy of the structure model is more important than the accuracy of the energy calculation, e.g. in case of the study of static or dynamic surface relaxation. In such cases, the use of relatively thick slabs in combination with empirical potentials can be preferable.

Empirical potential functions of 12-6 type, without Coulomb terms, were adopted for calculation of energies of individual slabs [3]. Generally, potential functions which include Coulomb terms are used for computations of energies of ionic or polar covalent materials [6 - 10]. It is obvious that the atomic charges in the boundary atomic planes (planes close to the cut) differ from those in the bulk. Moreover when the surface atomic planes are allowed to relax, e.g. to change their c-coordinates, the interatomic distances and consequently the charges are changed. Therefore, the use of constant atomic charges does not guarantee a correct prediction of the surface microstructure. On the other hand, the proper parametrisation of empirical potentials may result in effective inclusion of electrostatic interactions. Such potentials, having electrostatic interactions included implicitely, seem to be suitable for the study of surface relaxations, while more complicated potential functions with explicit inclusion of the electrostatic part will be more suitable for the study of properties of inner part of bulk and for properties which depend on the derivatives of the energy with respect to atomic coordinates, e.g. vibration frequencies or elastic moduli.

The most general change of the atomic structure of the surface layers is called reconstruction. This phenomenon includes all possible changes of the atomic coordinates and it can result into surface which is not planar. Theoretical study (and forecasting) of reconstruction in the most general form is practically impossible. All studies of surface reconstruction assume some two-dimensional periodicity of the surface reconstruction. Also with this approximation the theoretical study of surface reconstruction is an extraordinary hard task and there are only few papers dealing with this phenomenon. Usually, a more approximative concept called surface relaxation is used. In case of relaxation, there are not allowed fully independent movements of individual surface (or near surface) atoms. All atoms in certain atomic plane change their coordinate in direction perpendicular to the surface simultaneously. The planarity of the surface is conserved in this case. Two levels of approximation are distinguished in the case of relaxation: dynamic relaxation when individual movements of atoms in the plane are allowed (with superimposed two-dimensional periodicity) and more approximative statical relaxation, when only the change of the coordinate perpendicular to the surface is allowed simultaneously for all atoms of the considered plane.

The potential, used in the present work, was 12-6 type potential used in the form:

$$U(r) = \varepsilon_0[\ (\sigma_0 / r)^{12} - 2\ (\sigma_0 / r)^6\ ] \tag{1}$$

where r is interatomic distance, ε_0 and σ_0 are empirical constants which depend on the quality of the atom pair considered. The values of empirical parameters $\varepsilon_0(\mathrm{Al, Al}) = 4.527$ kcal mol^{-1}, $\sigma_0(\mathrm{Al, Al}) = 0.3001$ nm, $\varepsilon_0(\mathrm{Al, O}) = 21.322$ kcal mol^{-1}, $\sigma_0(\mathrm{Al, O}) = 0.1875$ nm, $\varepsilon_0(\mathrm{O, O}) = 1.859$ kcal mol^{-1}, $\sigma_0(\mathrm{O, O}) = 0.2902$ nm were taken from paper [3], where these values were obtained in such way, that the energy of formation of α–alumina was reproduced and simultaneously the norm of gradient of energy with respect to lattice parameters and atomic coordinates was minimal (for experimental values of lattice parameters and atomic coordinates). The program WMIN [11] was used for calculation of slab energies. The surface calculations were performed in slab geometry, using periodic boundary conditions, so that the system treated consists of an array of slabs, separated by vacuum layers. Each slab has infinite extent in the plane parallel to the surface. This geometry was used for computational convenience, because the program used is designed for three-dimensional periodic calculations. This arrangement causes the need for answering one additional question: what is sufficient thickness of the vacuum layer to avoid artefacts arising from the used geometry. The use of effective, implicit inclusion of the electrostatic energy *via* empirically parametrised 12-6 potential is also motivated by the geometry arrangement used: the explicit expression of the Coulomb energy decreases proportionally to r^{-1} what causes (in straightforward, naive implementation of computation) numerical difficulties. Also in case of more sophisticated computational scheme, the Coulomb interaction of charges will decrease proportionally to zero-order polygamma function, causing this way interaction of neighboring slabs at relatively high distance. In the case of use of the 12-6 type potential one would expect quick decreasing of the potential in the vacuum region and consequently relatively small spacing of slabs could be expected as sufficient. However, the decrease of potential energy will be slower as expected form the first insight; as showed by Steele [12], the summation of a 12-6 potential over all atoms in an infinite plane gives 10-4 behaviour of the potential function and after summation over planes one has the potential energy decrease slower than d^{-4}, where d is the distance from the surface atomic plane. In case of infinite number of atomic planes, the potential energy behaves as trigamma function and for finite number of planes the decreasing of potential energy approaches the behaviour of x^{-4} function with decreasing number of atomic planes in the slab. This is reason for testing of influence of the thickness of the vacuum layer on the calculated results despite of the fact that the interaction of neighboring slabs decreases more quickly than in the case of explicit inclusion of charge-charge Coulombic terms; because of various number of atomic planes simultaneously with various quality of atomic planes, the numerical testing using modern computers is more efficient than analytical derivation of the potential behaviour for all individual cases. Anyway, the effect of slab spacing must be taken into account and such spacing has to be chosen for the final computation, which does not influence the results obtained.

The influence of three factors on the results was investigated: influence of the slab thickness, influence of the thickness of the vacuum layer and the type of the top surface atomic plane of the slab. The investigated properties are the surface energy and the amount of relaxation of the surface planes.

Let the slab has n atomic planes which corresponds to summary formula $a(Al_2O_3)$ (note that for some slab types a does not need to be an integer number). The calculation provides the enthalpy of formation for 1 mole of such $a(Al_2O_3)$ units, so our reference enthalpy of formation for three-dimensionally infinite crystal is a-times the enthalpy of formation for 1 mole of the bulk Al_2O_3 (one does not take the experimental value but the value provided by calculation for crystal in fixed experimental geometry using the actual potential function - due to non perfect reproduction of the experimental enthalpy of formation and due to truncation errors this value can be slightly different from the experimental one). The difference of the obtained enthalpy of formation of the slab and the reference enthalpy of formation of the crystal is the surface energy of two moles of two-dimensional basic units (note that the slab has two surfaces per one $a(Al_2O_3)$ unit). Knowing the area of two-dimensional basic unit, one can obtain the surface energy per 1 m^2. Computing the surface energy first for the unrelaxed symmetric slabs (i.e. AA', BB', CC') one can proceed the relaxation of only one surface for both, symmetric and non-symmetric slabs.

The relaxation of the surface plane is expressed in percents of the interplane distance corresponding to crystal geometry. The positive relaxation corresponds to decrease of the interplane distance. Zero value means the non-relaxed plane and 100% means that the interplane distance is zero (in the case of planes with low reticular density an extremal statical relaxation can lead to merging of neighboring planes). The gradient optimalisation method (implemented in the WMIN program) was used for relaxing of the positions of the atomar planes considered. The statical relaxation was examined up to twelve surface planes.

RESULTS

Figure 2 shows the dependence of total energy of unrelaxed slabs on the identity period *c*. The corresponding width of the vacuum space between layers (what is the difference of *c*-value and the width of the slab) thus vary from 2 nm to 70 nm. The dependencies are shown for two layers: AA'(54) and AA'(162). The figure clearly demonstrates the independence of the total slab energy of unrelaxed surface on the width of the vacuum space between layers for the widths of the vacuum gaps over 2 nm. This condition was fulfilled for all the computations presented in this paper.

Figure 3 shows the surface energy of unrelaxed surface of AA'(n) - type slabs as function of the number of atomic planes in the slab. The dependencies are shown for two values of the identity period in the *c*-direction: $c = 4$ nm and $c = 80$ nm, respectively. The curves for $c = 4$ and $c = 80$ are identical, demonstrating again the independence of the surface energy of unrelaxed surface on the width of the vacuum space between layers for the widths of the vacuum gaps over 2 nm. Much more important information showed by figure 3 is the number of atomic planes when the interaction of X and Y' surfaces losses its influence on the value of the surface energy. For AA'(*n*) and BB'(*n*) slabs this is for $n > 24$ and for CB' this occurs for $n > 27$.

The value of surface energy reaches a limit value for number of atomic planes sufficiently large, when the distance of the top and the bottom atomic planes provides only negligible interaction of these planes.

For all slab types studied, the number of atomic planes needed for correct simulation of the surface of bulk material exceeds 24. The use of lower number of atomic planes therefore corresponds to simulation of ultra-thin layers - there is well known that such layers have special properties, which differ from properties of ordinary surface. The needed layer thickness for the simulation of the surface of bulk material does not represent any problem when using empirical potentials for computations; on the other hand, in case of quantum-chemical calculations this slab thickness means high requirements of computational resources because the two-dimensional computational cell contains 30 atoms already in this relative simple case. Several papers dealing with α–alumina surfaces use slab thickness less than limit obtained (e.g. [3, 5, 14]); some conclusions of such works have to be treated with caution.

Figure 3 shows oscillations of the surface energy in the region where the surface energy does not depend on the slab thickness. These oscillations are random errors caused by round-off errors, because the surface energy is obtained as a difference of two big numbers.

Figure 4 shows the surface energy of relaxed surface of the AA'(162) slab as function of the number of relaxed top atomic planes. This is a typical example of the course of the dependence of surface energy on the number of relaxed planes. Figure 4 demonstrates that relaxation of twelve top planes is sufficient to obtain reliable surface energy and structure of AA'-type slab of (001) surface of $\alpha\text{–}Al_2O_3$. Similar results were obtained for other examined slabs. The derivative of the curve obtained shows the relative importance of relaxation of individual atomic planes.

Figure 5 shows the dependence of the surface energy of the relaxed surface of AA'(*n*) slabs on the number of atomic planes in the slab (*n*). The number of relaxed top planes (Npl) is the parameter of the curves shown. This figure demonstrates that 24 atomic planes and relaxation of 10 top planes provides sufficiently

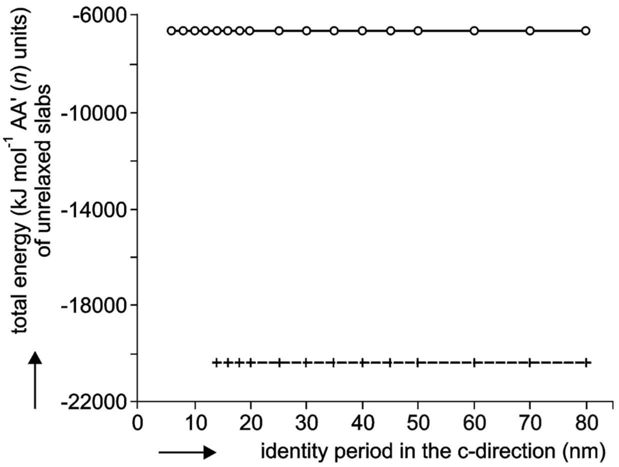

Figure 2. Dependence of total energy (kJ mol^{-1} AA'(*n*) units) of unrelaxed slabs on the identity period *c*.
○ - AA'(54), + - AA'(162).

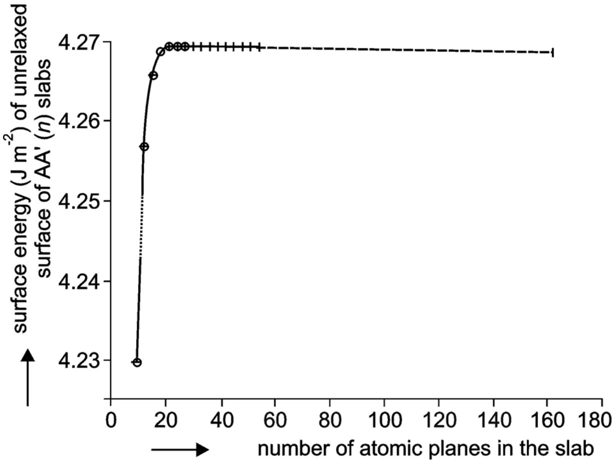

Figure 3. Dependence of surface energy (J m^{-2}) of unrelaxed surface of AA'(*n*) - type slabs on the number of atomic planes in the slab.
○ - $c = 4$, + - $c = 80$

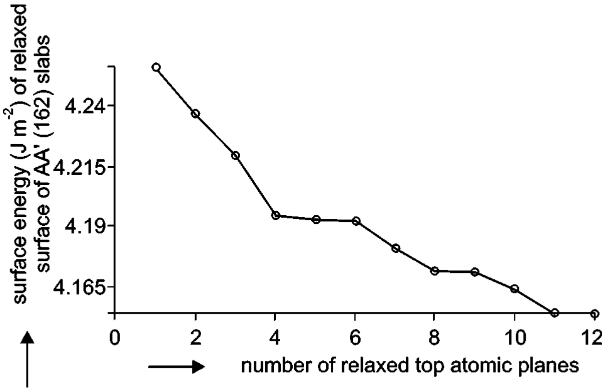

Figure 4. Dependence of the surface energy (J m^{-2}) of relaxed surface of the AA'(162) slabs on the number of relaxed top atomic planes.

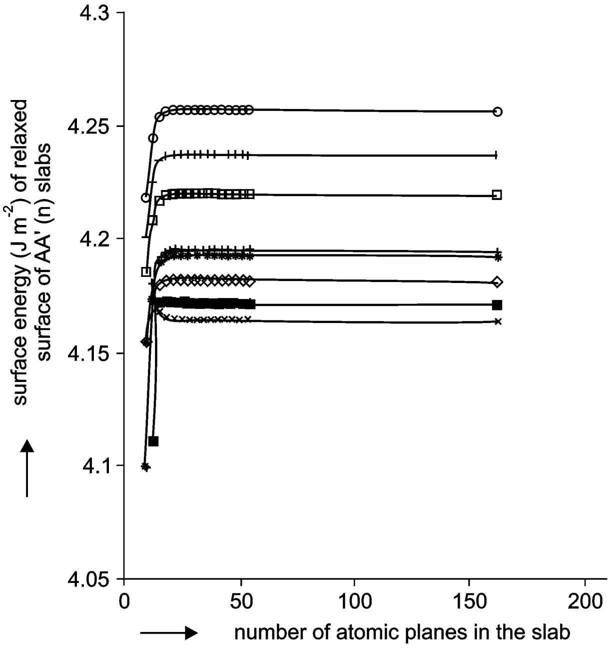

Figure 5. Dependence of the surface energy (J m^{-2}) of the relaxed surface of AA'(*n*) slabs on the number of atomic planes in the slab. *Npl* is the number of relaxed top planes.
○ - *Npl* = 1, + - *Npl* = 2, □ - *Npl* = 3, × - *Npl* = 4, △ - *Npl* = 5, ∗ - *Npl* = 6, + - *Npl* = 7, ◇ - *Npl* = 8, ■ - *Npl* = 9, × - *Npl* = 10

Table 1. Surface energy of unrelaxed and relaxed (001) surfaces of α–alumina (J m^{-2}).

cut	unrelaxed surface	relaxed surface	difference*
AA'	4.27	4.16	-0.11
BB'	8.02	7.95	-0.07
CA'	4.49	4.42	-0.07

*The difference of surface energy of relaxed and unrelaxed surface.

Table 2. Relaxations of top ten atomic planes of considered cuts of the (001) surface (%).

plane	cuts		
	AA'	BB'	AC'
1	5.8	-3.4	-7.3
2	-0.5	17.8	8.6
3	17.6	-6.4	-0.8
4	-6.1	1.3	3.3
5	2.3	-5.0	3.6
6	-6.2	3.9	3.5
7	4.2	3.6	-5.8
8	2.9	-5.4	3.3
9	-3.4	3.1	2.2
10	3.2	2.6	1.1

reliable results. Similar results were obtained for BB' and CA' slabs (for CA' slab, 27 atomic planes is needed to obtain satisfactory stable surface energy).

The resulting surface energies of relaxed slabs and unrelaxed slabs (of sufficient thickness and sufficient thickness of vacuum gap) are shown in table 1, whereas table 2 contains the relaxations of individual atomic planes. The relaxed AA' cut represents the most stable (001) surface in accordance with findings of other simulation computations ([6] and citations therein). The cut BB' with top plane containing oxygen atoms is the less stable one. The surface stabilisation *via* statical relaxation is maximal for the AA' cut. Comparing the surface energies with those of Mackrodt [13] (5.95 J m^{-2} for unrelaxed and 2.03 J m^{-2} for relaxed surface, respectively) one sees quit large relative differences. This can be partially ascribed to difference in computational method (this demonstrates the surface energy of non-relaxed surface) and possibly in the slab thickness, what could indicate the energy difference between surface energy of relaxed and unrelaxed surface. Unfortunatelly, the paper cited does not contain the information concerning the slab thickness used in that paper; looking at dependences of this quantity on the slab thickness obtained in the present work we see the higher relaxation and higher stabilisation *via* relaxation in the range of too thin slabs. This could lead to assumption that the slab thickness used in the paper [13] could be also in this region. Anyway, one has not to forget that the surface energies are obtained as differences of two big numbers what has such consequence that very small differences in total energies will lead to very high relative differences of the surface energies.

The surface energy of the same surface obtained using quantum-chemical calculation [5] was 3.77 J m^{-2} for unrelaxed and 1.76 J m^{-2} for relaxed surface, respectively. The used number of atomic planes was 9 what is deep under the limit obtained in the present work. The discussion of the differences between surface energies obtained in the last cited paper and in the present paper is in principle the same as above.

The relaxations of individual atomic planes are for all studied cuts relatively small in comparison with the values referred in the literature [3, 5, 6, 13, 14]. Maximum relaxations according to present work do not exceed 20 % in absolute value whereas the literature cited refers maximum absolute values over 50 % (in some cases are referred even much higher relaxations, e.g. the quantum-chemical DFT study [14] refers 86%, *ab initio* crystal orbital HF STO-3G study [3] refers 80 % relaxation of the top plane of AA'(6) slab). The 6-12 potential used in the present work was used also in our previous paper [3] where for the AA'(6) slab provided relaxation of the top atomic plane 65 % what was in qualitatively good accordance with results obtained using other type potentials and quantum chemical calculation and also with the results of other authors. Thus, the difference of relaxation can be ascribed to the use of more realistic model of the semi-infinite crystal; the high relaxations cited were obtained for too thin slabs.

CONCLUSIONS

The 2 nm thick vacuum space between layers is sufficient for correct description of the surface relaxation in case of use of the 6-12 potential parametrised according to [3].

Slabs consisting of 27 atomic planes (approx. 2 nm) are sufficiently thick for the modeling of statical relaxation of the top (001) α–Al_2O_3 surface when the bottom planes are left unrelaxed. At this slab thickness the value of the surface energy is stabilised and the use of more thick layers leads only to addition of the energy corresponding to the energy of the bulk material to the total energy of the slab.

The relaxation of 10 - 12 top planes is sufficient for obtaining the surface energies of the (001) α–alumina surface. Relaxation of next atomic planes causes only unsignificant changes of the surface energy which are comparable with the round-off errors of the computational algorithm used.

The most stable surface of the (001) direction corresponds to the AA' cut.

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TEORETICKÉ MODELOVANIE (001) POVRCHU α–Al_2O_3

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Modelovala sa štruktúra (001) povrchu α-Al_2O_3 za použitia empirického párového potenciálu typu 6-12. Určili sa povrchová energia, statická relaxácia desiatich povrchových rovín ako aj podmienky výpočtu, potrebné na správne modelovanie povrchov tohto typu.