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INTERACTION EFFECTS IN MAGNESIUM OXIDATION: A LATTICE-GAS SIMULATION

Elsebeth Schröder[1]

Dept. of Applied Physics, Chalmers University of Technology and Göteborg University,
SE–412 96 Gothenburg, Sweden.

Abstract

The oxidation of magnesium proceeds in several stages, beginning with the oxygen dissociation process and ending with the formation of magnesium oxides. Our focus is on the intermediate oxidation state at the magnesium (0001) surface. Our calculations show that the oxygen atoms adsorbed into on-surface or subsurface sites form dense clusters. We find that isolated oxygen atoms and small clusters prefer to adsorb into on-surface sites. However, for clusters larger than a few oxygen atoms the oxygen-oxygen interaction effects drive the oxygen atoms into the magnesium subsurface layers and bulk. We use density-functional calculations to characterize our model parameters: surface and subsurface oxygen-site adsorption energies and the corresponding oxygen-oxygen interaction energies. Monte-Carlo simulations identify the optimal distributions of oxygen as a function of concentration.

Keywords: Oxidation, Monte-Carlo simulation, density functional theory, lattice-gas model.

[1]Corresponding author: Fax: +46 31 772 8426; E-mail: schroder@fy.chalmers.se

1. Introduction

The oxidation of metallic surfaces is an important but complicated process. The oxidation proceeds in several stages, beginning with the dissociation of the oxygen molecule above or at the surface and ending with the correctly restructured oxide. In the complex intermediate stage the oxygen atoms may adsorb onto the surface or into the metal layers immediately below the surface, either in a uniform distribution or in small or large groups, all depending on, e.g., the material and the surface structure. In general we have a large number of atoms in an unknown non-uniform distribution and we must explore a huge configuration space to characterize this intermediate stage. The dissociation and the oxide phase may be accessed via first-principles calculations, albeit at a high cost even for simple materials [1]. The fractional monolayer coverages of the intermediate stages cannot be systematically analyzed by first-principles calculations and it is imperative to construct simplified models that capture the characteristics of the oxidation process. Such simple oxidation models permit us to gain insight into the underlying fundamental principles of both the initial and intermediate oxidation steps.

Here, we investigate the intermediate oxidation processes for the magnesium (0001) surface. Simple metals like magnesium and aluminum have interesting oxidation processes resulting, for example, in applications such as the very hard Al_2O_3 cutting tools material. For simple metals it is possible to accurately calculate energies of specific configurations. However, at the aluminum surfaces the interlayer spacings change enormously (60-100%) during oxidation [2, 1], which complicates any approach based on the oxygen being embedded in a passive surrounding (the metal). The emphasis on the magnesium surface provides an extra simplification in the oxidation since induced bond length changes can essentially be ignored.

We present a lattice-gas model of magnesium oxidation, including subsurface adsorption, with parameters found from Density Functional Theory (DFT) methods. We document how the oxidation process depends on the adsorbate interactions, and we find that the oxygen atoms shift from on-surface adsorption to subsurface adsorption early in the oxidation process. We further find that the oxygen atoms form islands already after the adsorption of two oxygen atoms.

The oxidation of magnesium was studied in soft X-ray photoelectron spectroscopy by Driver et al. [3] who found indirect evidence for a penetration of oxygen below the outermost magnesium surface layer even at low coverages. Also, using DFT and molecular dynamics methods for coverages up to one atomic monolayer Bungaro et al. [4] found that the oxygen atoms cluster below the magnesium surface.

Two-dimensional lattice-gas models of the on-surface oxygen adsorption were previously studied for the Ru(0001) and W(110) surfaces [5, 6], and a three-dimensional model for the oxidation of Al(111) was proposed in Ref. [7]. Models such as those and ours provide an important step from calculations on the atomic length scale (e.g. DFT calculations) to mesoscopic scales (nearly micrometer scale in Ref. [7]).

2. Single-particle adsorption

First we study the initial adsorption of a single oxygen atom at the otherwise clean Mg(0001) surface by using DFT calculations. We employ the generalized-gradient approximation (GGA) of Perdew-Wang. Initially, a clean Mg(0001) surface is constructed and permitted to relax. This constitutes the unperturbed surface. The vertical size of the system is six layers of magnesium and the equivalent of eight layers of vacuum, with 2×2 unit cells in the lateral direction. The bond lengths of the three lower-most magnesium layers are always kept at their bulk values whereas the three topmost layers are allowed to move according to the forces on the atoms derived from the electron density. We use 18 irreducible k-points to sample the Brillouin zone and a cut-off energy of 340 eV. Details of the DFT calculations will be provided elsewhere [8].

Searching for the possible oxygen adsorption sites, an oxygen atom is introduced into the clean Mg surface and the whole surface (except the three "bulk layers" at the bottom) is allowed to relax according to the calculated forces. All tetrahedrally and octahedrally coordinated sites as well as the hcp and fcc surface sites are investigated. The ten adsorption sites found per unit

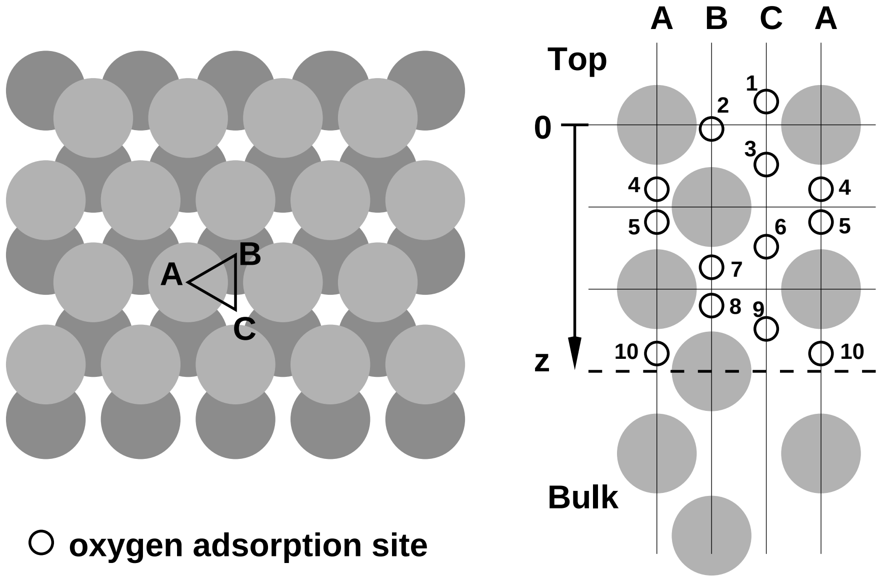

Figure 1: A sketch of the upper layers of the magnesium (0001) surface. Gray circles illustrate the positions of the magnesium atoms. *Left:* The surface seen from above, without indication of adsorption sites. The triangle illustrates the "cut" used for the illustration to the left. *Right:* A cut perpendicular to the surface. The small circles show the possible oxygen adsorption sites. For convenience the sites are numbered. Note that the positions of the topmost sites (sites "1" and "2") are not symmetric with respect to the top magnesium layer.

cell are sketched in Fig. 1. It turned out that for single oxygen adsorption two probable hcp sites above and below the mid plane of the topmost magnesium layer both relax to one single site close to the mid plane, denoted site "2" in Fig. 1. This is in contrast to the findings of the post-GGA calculations in Ref. [4].

We find that the changes in Mg-Mg bond lengths after adding an O-atom are very small: at most 0.05 Å, or less than 3% change of distance between two neighboring layers. In the following DFT calculations of lattice-gas model parameters we shall therefore use the unperturbed Mg-surface as the background for oxygen adsorption. In addition, we find that even though the O-atom was allowed to move both vertically *and* laterally, the lateral position changes very little from the symmetric position: the largest changes are less than 0.02 Å, or less than 0.6% of the lattice constant. The specification of the lateral position can thus be unambiguously given by the A, B, and C site notation as illustrated in Fig. 1.

The left panel of Fig. 2 shows the vertical position for each adsorbate site measured from the top of the unperturbed magnesium surface *and* the adsorption energy of the site relative to half the energy of an undissociated O_2 molecule. In addition to the adsorption sites found by fully relaxing the surface, we also found the corresponding adsorption sites and energies for oxygen adsorbed into a fixed background of the unperturbed magnesium surface. These are the energies that are needed in the lattice-gas model for consistency. The main effect of fixing the magnesium atoms is an almost uniform lowering of the adsorption energy by approximately 0.08 eV, the only serious exception being the 0.2 eV lowering for site 2. This is expected because the site-2 adsorption in a fully relaxed system gives rise to the largest Mg-Mg bond-length changes.

3. The lattice gas model

In general a clean metal surface relaxes or restructures when oxygen is adsorbed. The change in bond length may be as much as e.g 60% for the Al(111) surface when oxygen is adsorbed in subsurface sites [2]. However, if the surface relaxation is less significant, as for the Mg(0001) surface, we may identify the adsorption sites in the metal with fixed sites in a lattice-gas model, independently of the number of oxygen atoms adsorbed.

The simplest lattice-gas model that includes subsurface adsorption is given by the Hamiltonian

$$H = -\sum_i E_i^{\text{single}}\, n_i + \frac{1}{2}\sum_{i,j} E_{i,j}^{\text{pair}}\, n_i\, n_j \tag{1}$$

where n_i is the occupation number (0 or 1) of the ith adsorption site, E_i^{single} are the adsorption energies and $E_{i,j}^{\text{pair}}$ the pair-correlation energies. In principle the model allows for any combination of occupied adsorption sites, however, a large interaction coefficient between the sites may effectively prevent simultaneous occupation of e.g. very close sites. For simplicity we exclude triple- and higher order correlations.

The interaction coefficients of the Hamiltonian, E_{ij}^{pair}, are systematically calculated using DFT

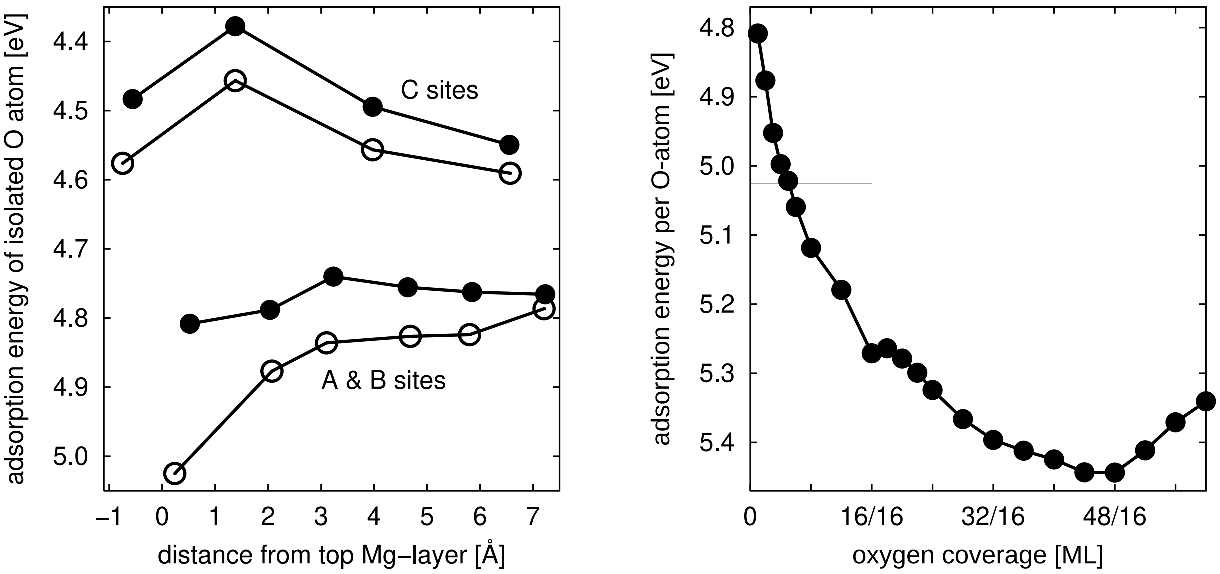

Figure 2: *Left:* The adsorption energy of a single oxygen atom relative to $\frac{1}{2}$ O_2 at sites at the magnesium (0001) surface and in subsurface layers. The sites are indicated by vertical position and correspond to the sites sketched in Fig. 1. Open circles are for fully relaxed bond lengths, dark circles are for the system used in the model (see main text). The C-sites (top two curves) are connected to guide the eye, as well as the A/B sites (bottom two curves). Note that the C-sites in both calculations are energetically unfavorable sites. *Right:* Adsorption energy per atom in clusters of the lattice-gas model. The horizontal line indicates the adsorption energy of an oxygen atom in site 2 in a fully relaxed DFT calculation.

calculations similar to the fixed-background single-adsorbate calculations. All pairs of sites within a range of one lattice spacing a (= 3.19Å in the DFT calculations) are included, amounting to 32 different types of pair interactions. Including the ten single-adsorbate coefficients E_i^{single} the model thus has 42 independent parameters, obtained from 42 different DFT calculations. In the model we impose periodic boundary conditions and the correct sixfold symmetry with respect to nearest-neighbors of identical sites.

The number of adsorption sites within one lattice spacing a from a particular unit cell is approximately the number of sites in seven unit cells, i.e. 70 sites. Distributing a certain number m of adsorbates in these seven unit cells can be done in $K(70, m)$ ways. A coverage equivalent to

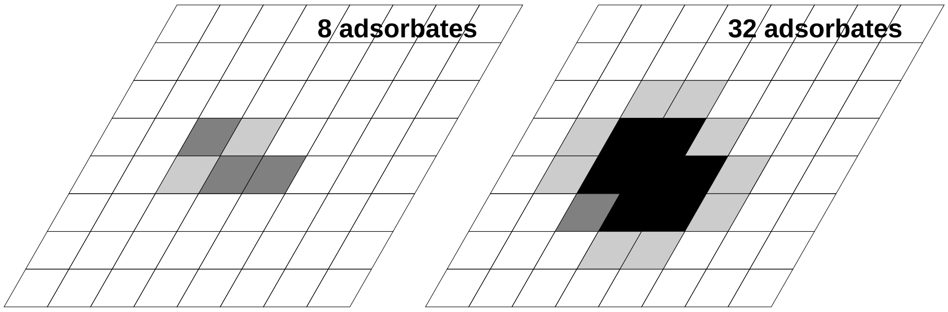

Figure 3: Cluster formation in an 8×8 system. The number of adsorbates in a unit cell is indicated by a gray scale, from zero (white) to three (black) adsorbates. In these examples all adsorbates are in subsurface sites (sites 4 and 7 for 8 adsorbates; sites 4, 7, and 10 for 32 adsorbates).

two atomic layers thus can be distributed in approximately $K(70,14) \approx 2 \cdot 10^{14}$ ways. Clearly we cannot search the vast energy space of the model systematically. Instead, we employ a Monte Carlo search method of the energy landscape in which neighboring states are obtained by moving one adsorbate to a different adsorption site not more than a distance of a away. To secure a high probability of obtaining the global energy minimum we use the method of simulated annealing with exponential cooling on an ensemble of 200 calculations ("walkers"). All walkers are initiated with adsorbates in the top sites of the model.

4. Results and discussion

The metastable states of the discrete lattice-gas Hamiltonian identify the most probable candidates for the true physical distribution of adsorbed atoms in the magnesium, at a given number of adsorbed O-atoms. Certainly, a Hamiltonian that is defined on a discrete and finite set of adsorption sites cannot accurately describe the dynamics of the oxygen atoms on their way to or between the adsorption sites. However, the model Hamiltonian tells us, as a function of the oxygen concentration, whether it is energetically favorable for the oxygen atoms to stay at the surface or enter the subsurface layers. The model Hamiltonian also provides us with probable distributions of the adsorbed oxygen atoms, again as a function of the oxygen concentration.

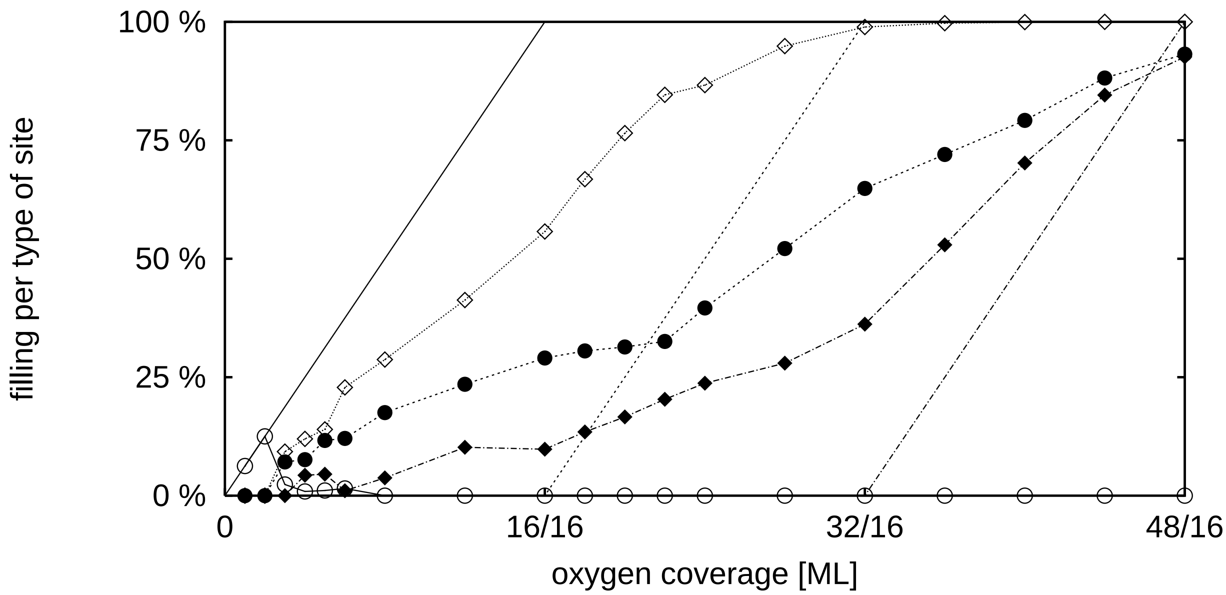

Figure 4: Degree of filling in sites 2 (open circles), 4 (black circles), 7 (open diamonds), and 10 (black diamonds). All other adsorption sites are, on average, almost vacant. The diagonal straight lines indicate the filling that would be found if all oxygen interactions were neglected, from left to right: site 2, site 4, site 10. Note that the occupation of site 2 rapidly vanishes as the coverage is increased, in contrast to the no-interactions result, thus documenting the many-body effect.

Whether the physical system in fact reaches the lowest-energy distribution of our model or instead reaches a distribution with a slightly higher energy depends on the energy barriers that the adsorbates need to cross in order to reach the sites. We are therefore interested in and have investigated not only the distribution corresponding to the global energy minimum of our model, but also in the metastable distributions that have energies close to the global minimum.

Independently of the number of adsorbates in the system our calculations show that the adsorbates collect to form dense clusters. Two examples of clustering are shown in Figure 3 for an 8×8 system with 8 or 32 adsorbates. In the clusters the system locally obtains the MgO stoichiometric 1:1 ratio of oxygen to magnesium atoms, best seen in the 32-adsorbates example where the kernel of the cluster has 3 oxygen atoms per unit cell. For coverages 1 or higher the clusters tend to form bands that span the system across the periodic boundaries.

For most of our calculations we imposed a dilution of adsorbates, in the absence of site-to-site barriers in the model, by restricting the system size to 4×4. For oxygen-atom coverages from 1/16 to 60/16 we searched for the global energy minimum among the adsorbate distributions. The adsorption energy per atom for these distributions is shown in the right panel of Figure 2. We notice a lowering of the adsorption energy as the clusters grow in size, up to the 48/16 coverage. The corresponding filling of the sites is shown in Fig. 4, averaged over distributions with adsorption energies in the range 99%-100% of the optimal energy. We find that the only sites occupied in the calculations up to coverage 48/16 are the sites numbered "2", "4", "7", and "10". These are all hcp or tetragonally coordinated sites. Octahedral sites ("C sites") are not occupied. At low coverages (small clusters) the on-surface site 2 dominates. However, for clusters of four or more atoms clustering in the subsurface sites 4 and 7, and eventually 10, is preferred. Thus as the coverage is increased not just the added adsorbates but all adsorbates are driven from the surface and into the subsurface layers by the adsorbate-adsorbate interactions. If pair interactions were absent, the site 2 would instead be filled for any coverage, as illustrated by the straight lines in Fig. 4.

The exact cluster size at which the surface-to-subsurface transition happens depends on the details of the model. For consistency reasons we use the fixed-background DFT calculations for the single-particle adsorption energies. However, in the fully relaxed DFT calculations the site 2 is the only site with any significant change in Mg-Mg bond length and adsorption energy. We therefore expect the on-surface site 2 to dominate for cluster sizes a few units larger than those found in our model.

At coverages larger than 48/16 the site 1 starts to fill (not shown) at a significant cost in adsorption energy (Fig. 2 right panel). We interpret this as an overfilling of the system with adsorbates that in a real physical system would move further into the bulk. This is supported by the fact that the lowest-lying site, site 10, is filled to a lesser degree than the two intermediate subsurface sites, sites 4 and 7, until a coverage of three full layers is reached.

On-surface lattice-gas models, with DFT-determined pair- and higher order coefficients, modeling the behavior of oxygen atoms not entering subsurface sites have been proposed, e.g., by Stampfl et al. [5]. It is important to distinguish the two-dimensional character of an on-surface model from the three-dimensionality of the model proposed here. In the two-dimensional model the adsorbates stay on the surface, not leaving the system. In contrast, our model of surface and subsurface-layer adsorption allows for a net flow of adsorbates into the subsurface layers, treated explicitly in the model, and a further flow into the bulk, inferred indirectly from the sharp rise in adsorption energy at coverage larger than three atomic layers.

In conclusion, we have proposed a lattice-gas model with parameters based on density functional theory calculations to describe the intermediate stages of oxidation of the Mg(0001) surface. Using Monte Carlo methods we searched for the energetically favored distribution of oxygen atoms on the surface and in the subsurface layers. We found that the adsorbate interactions cause the adsorbed oxygen atoms to form clusters, with a transition from on-surface occupation to subsurface occupation when going from small clusters (a few oxygen atoms) to large coverages (up to 1:1 ratio of oxygen to magnesium atoms).

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