

Combining the Physics of Metal/Oxide Heterostructure, Interface Dipole, Band Bending, Crystallography, and Surface State to Understand Heterogeneity Contrast in Oxidation and Corrosion

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Numerous effective medium models of metal oxidation and corrosion have been proposed over the years. These models are based on the macroscopic descriptions, and the driving forces for mass transport are conventionally expressed in terms of the electrochemical potential drops at the metal/oxide, oxide/environment interfaces, and the electric field in the oxide. Implicitly they average in some sense over microstructure, composition, and crystallography. An important issue with any effective medium approach is the degree of heterogeneity contrast, that is how much relevant properties or parameters vary spatially. Here the existing literature and, with additional density functional theory calculations, the magnitude of the heterogeneity contrast are analyzed. The physical phenomena in metal/oxide heterostructure, p/n semiconductor junction, and oxide surface such as the presence of interfacial dipole, band bending, doping effect, crystallography variation, and surface reconstruction is found, as well as surface state, lead to large heterogeneity contrasts. This implies that the simple, linear, effective, medium approaches may fail to describe the behavior properly.

KEY WORDS: corrosion, density functional theory, effective medium theory, heterogeneity contrast, interface states, interfacial dipoles, oxidation, surfaces

INTRODUCTION

The annual cost of corrosion is estimated to be more than 3% of the world's GDP. It is a topic which is both old and new: old as it mattered to the Romans with their iron weapons; new because most of the key processes occur at the nanoscale. Although many of the broad details are known, there are still many gaps particularly in the details. Much of the current knowledge is from the mesoscale down to several nanometers, but multiple processes occurring over wide spatial and temporal scales control the nucleation, stability, and morphology of protective oxide films. Understanding the early stages of oxide growth at the (sub) nanometer scale is critically important if we are to move beyond simple cost-prohibitive remedies.

There have been two generic approaches to understanding oxidation and corrosion. One is to look at the detail processes and has moved forward recently due to increased usage of sophisticated tools such as environmental microscopies¹; the other is a more global description using what should be described as transport models in an effective medium. Various forms of these transport models exist,²⁻¹⁷ where the transport equations are solved with different approximations. Effective medium approaches are common across science in areas ranging from dielectric and elastic/plastic properties in three

dimensions to two-dimensional problems such as friction and wear, the later having many similarities to oxidation and corrosion.

An important question with any effective medium theory¹⁸⁻³¹ is the magnitude of the variation in relevant properties or parameters, which is called the "heterogeneity contrast." It may also be important whether the relevant properties are linear, or have to be considered in a higher-order nonlinear approach. If the heterogeneity contrast is small, then a rule of mixture may be applicable, for instance, shared load bearing in a mechanical system. If it is large, the effective medium may be dominated by the strongest component, as in many fiber-reinforced systems, or by the weakest part as in the fracture at grain boundaries. The effective properties may also depend upon statistical properties, as in friction and wear. For instance, the classic Amontons' law of friction was shown by Bowden and Tabor³²⁻³³ to be due to multiple asperities where the two sliding bodies are in contact. As the load increases, more asperities become involved, so the effective medium response is simple, although in most cases Amontons' law is not obeyed for the single asperity contact. Similar physics, which are closer to oxidation and corrosion, occurs for Archard's law for wear which is also a statistical consequence of many nanoscale abrasive processes.

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To illustrate the relevance of heterogeneity contrast in oxidation, consider the classic Cabrera–Mott³⁻⁴ formulation for the growth rate of an oxide film with the thickness x and at a time t :

$$dx/dt \sim \exp(-\Delta E_{\text{act}}/kT) \exp(qaV_M/2kTx) \quad (1)$$

where ΔE_{act} is the activation energy barrier, T is the temperature, k is the Boltzmann constant, q is the charge of ion, a is the hopping distance, and V_M is the Mott potential. Suppose that instead of having a single potential, there is a Gaussian distribution due to the interface dipole, crystallography, and other contributors discussed later, a probability density $P(V_M)$ is

$$P(V_M) = (\sigma\sqrt{2\pi})^{-1} \exp(-(V_M - \bar{V}_M)^2/2\sigma^2) \quad (2)$$

where the local Mott potential V_M now varies spatially about the mean of the distribution $\bar{V}_M$, and σ is the standard deviation. Suppose this is reduced to an effective medium model; the average growth rate still has the functional form of Equation (1). If an effective Mott potential V_M^{eff} and an effective thickness $\bar{x}$ are used, then Equation (1) becomes

$$\begin{aligned} \exp(\Delta E_{\text{act}}/kT) d\bar{x}/dt &\sim \exp(qaV_M^{\text{eff}}/2kT\bar{x}) \\ &= \int P(V_M) \exp(qaV_M/2kT\bar{x}) dV_M \end{aligned} \quad (3)$$

with

$$V_M^{\text{eff}} = \bar{V}_M + \sigma^2 qa/4kT\bar{x} \quad (4)$$

The effective Mott potential now is not a constant, and apparently changes with oxide thickness. This perhaps unexpected result has the correct physics; effective medium approaches do not have to be parameterized by values that can be calculated from a simple model, they are reductions of a probabilistic distribution. For this specific case, the magnitude of the apparent thickness dependence is determined by the heterogeneity contrast which can be parameterized as $\sigma^2/\bar{V}_M kT$. (One could, alternatively, define an effective hopping distance similarly.)

Any real material has grains of both the substrate material and protective oxide, dislocations, grain boundaries, and different crystallographic interfaces between the substrate and oxide as well as the oxide and external medium. To better understand the connection between the nanoscale and effective medium approaches, it is important to examine the degree of heterogeneity contrast due to these different factors. The focus of this note is a closer examination of the contributions due to the crystallographic dependence of terms that influence the electrostatics across the oxide, combining approaches such as density functional theory (DFT) as well as considerations of polarization, interface state, and surface state. (There are additional sources of heterogeneity contrast due to, for instance, enhanced diffusion at grain boundaries which lie outside the scope of this paper.) To this end, both specific cases based upon our DFT calculations, as well as results from the existing literature where comparable scientific results are already available but often have not been considered into a corrosion or oxidation context, will be discussed. The overall results show the crystallographic dependence of terms such as interfacial state and dipole, and indicate that oxidation and corrosion are large heterogeneity contrast problems with significant nonlinear contributions.

The structure of this paper is as follows. In the next section, a brief overview of the existing transport models is

provided, both in terms of what hypothesis they rely on and how the electrochemical terms distribute, i.e., the potential changes at the interface, external surface and across the oxide. This is followed by a brief overview of the existing literature mainly outside of oxidation and corrosion, where the physics of the interface and surface potential changes have been discussed. After this, selected DFT results are described for a number of systems to supplement the existing literature, focusing upon the electrical dipole at the metal/oxide interface and surface state and the synergy of dipole, band bending, surface state, and chemisorption. Finally, some general features of the results are discussed.

OVERVIEW OF THE EXISTING METAL OXIDATION AND CORROSION TRANSPORT MODELS

Many models of metal oxidation and corrosion have been proposed since the pioneering work of Wagner² and Mott.³⁻⁴ Before briefly overviewing the existing models which are outlined in Table 1, several terms to help focus the description are introduced: **Drivers**, **Triggers**, **Mechanisms**, and **Dependencies**.³⁴

Drivers correspond to a reduction in the free energy of the system that controls the thermodynamics either in a closed thermodynamics sense or open thermodynamics where the total system is considered including the environment.

Triggers are the local process which subsequently leads to a change such as the breakdown of the protective oxide film.

Mechanisms are the atomistic or nanoscale process that leads to the change. They frequently are associated with specific structural Triggers and have to be in response to some Drivers.

Dependencies are how all of the above depend upon the external environment, for instance, the pH, temperature, time, and applied potentials.

The global drivers for oxidation are the free-energy change when forming the oxide from the metal and oxygen, as well as the free-energy change of dissolution at the oxide/fluid interface or (if appropriate) the free-energy of evaporation. These translate into local drivers which, in general, are a combination of an electrostatic potential gradient across the oxide and a chemical potential gradient. In response to these two gradients atoms migrate, and this is typically considered to be dominated by diffusion although at higher temperatures dislocation climb in the oxide can play a role³⁵ and dislocations can also be involved in motion of the metal/oxide interface³⁶⁻³⁸; the question of whether point defects and/or dislocations matter is the mechanism, not the driver. Frequently, the electrostatic and chemical potential gradients are combined into an electrochemical potential, although this may be a severe approximation if dislocation activity is important. In the conventional oxidation/corrosion models, the electrochemical potential for the transport of species can be expressed as³⁹

$$\bar{\mu}_i = \mu_i + z_i F \Phi \quad (5)$$

where $\bar{\mu}_i$ is the electrochemical potential of species i , μ_i is the chemical potential, z_i is the valency (charge), F is the Faraday's constant, and Φ is the local electrostatic potential.

Turning to the existing models, many if not most approximate the complicated evolution of the oxide film in three-dimensions into a simple one-dimensional approach, a variation along a single axis (e.g., x) that is normal to all of the interfaces, with the assumption that there is no variation along

Table 1. Summary of the Main Characteristics of Various Oxidation and Corrosion Models^(A)

Models	Drivers			Mechanisms	Dependencies
	$\Phi_{M/O}$	Φ_{OX}	$\Phi_{O/E}$		
Cabrera–Mott model ⁵	Independent of time or oxide thickness	Independent of time or oxide thickness	No	Migration of interstitial cations, electrons	Temperature, oxygen pressure
Point defect model ^{6-8,12}	Function of applied potential and pH of the electrolyte	Independent of time or oxide thickness	Function of applied potential and pH of the electrolyte	Migration of cation vacancies and anion vacancies, electrons	pH, temperature, applied potential
Mixed conduction model ⁹	Function of applied potential	Independent of oxide thickness	Function of applied potential	Migration of cation vacancies and interstitials, anion vacancies, electrons	Applied potential
Generalized model ¹³⁻¹⁴	Independent of time or oxide thickness	Functions of time or oxide thickness	Functions of time or oxide thickness	Migration of cation vacancies and interstitials, anion vacancies, electrons	pH, temperature, applied potential, time
Coupled current charge compensation model ¹⁵	Independent of time or oxide thickness	Functions of aliovalent ions and space charges	No	Migration of anion vacancies, electrons	Temperature, alloy composition
Diffusion Poisson coupled model ¹⁰⁻¹¹	Functions of time or oxide thickness	Functions of time or oxide thickness	Functions of time or oxide thickness	Migration of cation vacancies and interstitials, anion vacancies, electrons, holes	pH, temperature, applied potential, time
Mass charge balance model ¹⁶	Functions of time or oxide thickness	Functions of time or oxide thickness	Functions of time or oxide thickness	Migration of cation vacancies and interstitials, anion vacancies, electrons	pH, temperature, applied potential, alloy composition, time

^(A) "No" means that it is not considered in the model.

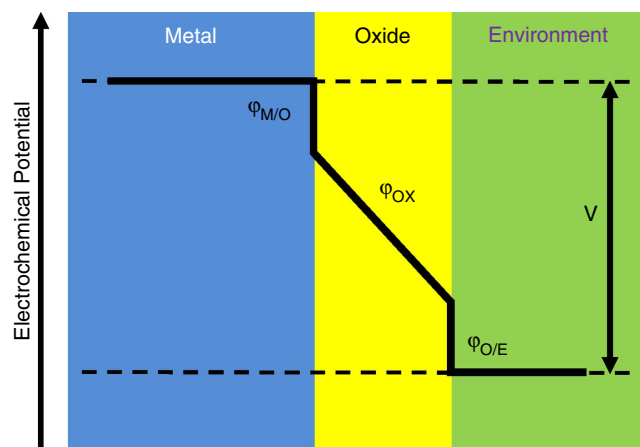


FIGURE 1. The classic description of the electrochemical potential change in the metal/oxide/environment system.

the other two directions. It is commonly accepted that the electrochemical potential drop can then be divided into three parts (Figure 1):

- (1) the potential change at the metal/oxide interface ($\Phi_{M/O}$) that controls the internal interfacial reactions;
- (2) the potential change at the oxide/environment interface ($\Phi_{O/E}$) that controls the external interfacial reactions; and
- (3) the potential change in the oxide layer (Φ_{OX}) that controls the transport mechanisms across the oxide film.

The existing models differ in their hypotheses on how the driving force is distributed, how the potential distribution changes as the oxide film grows, and in some cases whether the potential of relevance is electric, chemical, or both. For example, the potential drop across oxide is the electrostatic potential and is assumed to be independent of oxide thickness in the Cabrera–Mott model.⁵ Alternately, the potential difference at the metal/oxide and oxide/solution interface depends on applied potential and pH of the electrolyte under the stationary conditions in the Point Defect Model.^{6-8,12} The Mixed Conduction Model⁹ adapts the formalism of the Point Defect Model to the case of alloys, which emphasizes the coupling between ionic and electronic defects in quasi-steady-state passive films. The Generalized Model¹³⁻¹⁴ takes into account the interfacial potential drops and their evolutions with time during the oxide growth. The Diffusion Poisson Coupled Model is similar to the Point Defect Model except the potential profile is not assumed but calculated in solving explicitly the Poisson equation.¹⁰⁻¹¹ The Coupled Current Charge Compensation Model¹⁵ considers that the aliovalent ions compensate space charges in the oxide, which modifies the electric potential driving force as well as the oxidation kinetics in zirconium alloys. The Mass Charge Balance Model¹⁶ takes into account the distribution of the driving force using a constraint of mass and charge balance.

The various models are summarized in Table 1.

The models above use a one-dimensional, continuum description of the electrochemical potentials at the metal/oxide and oxide/environment interfaces. Beyond oxidation and corrosion, a number of similar scientific problems for metal/oxide

heterostructure, p/n semiconductor junction, and oxide surface where there can be an interfacial dipole, band bending, doping effect, crystallography, and surface reconstruction, as well as surface state, have been extensively studied. The literature, discussed below, focuses upon the electrostatic potential. In general, there are inhomogeneous electrostatic potential changes due to the local structures and compositions which need to be considered and incorporated into the classical electrochemistry framework, as discussed in the rest of this paper.

OVERVIEW OF THE ELECTRONIC STRUCTURE OF METAL/OXIDE INTERFACE, OXIDE BAND BENDING, AND OXIDE SURFACE

For a complete analysis of the electrostatic contributions, one needs to consider what is taking place in three parts of the metal-oxide-environment system separately.

1. At the metal/oxide interface. Both the atomic and electronic structure in terms of the interfacial dipole, Fermi-level pinning, and whether the interface is Schottky or metalized (i.e., Ohmic) should be considered.
2. Within the oxide. The band bending, particularly the static screening by displacements (rumpling) of the ionic atoms as well as the changes in electronic screening, need to be considered.
3. At the oxide/environment interface. Surface reconstruction, chemisorption, surface electronic state, and the rehybridization of the state need to be taken into account.

Many of these have been analyzed for specific metal/oxide combinations using DFT methods, with the focus generally upon the details for the particular case considered. Table 2 provides an overview of the existing literature including many of the key parameters that have been described; in some cases, there is incomplete information. The parameters are chosen to reflect (1) interfacial composition, i.e., whether the oxygen content at the metal/oxide interface vary; (2) lattice mismatch between the oxide and metal; (3) thickness of the oxide, i.e., the number of oxide layers used in the computational models; (4) the type of contact between the metal and oxide (Schottky or Ohmic); (5) work function change of the oxide/metal junction compared to the pristine metal surface; (6) charge transfer and dipole direction at the interface; and (7) interlayer separation which can change the ionic screening. The information summarized in the table shows large variations, which implies significant heterogeneity contrast.

A few pieces of general science that go beyond what is included in the transport models of Table 1 are well established. In semiconductor physics, band bending is associated with variations in the concentration of dopants. While there may be some point defects leading to intrinsic doping, in many cases the concentration will be small. More important will be a direct coupling of the external electric field to the internal polarization via the Born effective charges even in the absence of defects. One of the earliest analyses of this was by Stoneham and Tasker⁴⁰ who considered the image potential coupling between a dielectric oxide film and a metal, including mention that this will change the Mott–Cabrera growth kinetics. A more atomistic analysis for a number of MgO/metal interfaces has been described by Goniakowski and Noguera.⁴¹ The polarization terms can also play a significant role in later breakdown of the oxide film as first suggested for electrostrictive related stresses by Sato⁴² and has been analyzed in more detail recently by Tang

and Ballarini⁴³ and extended to qualitatively include flexoelectric contributions by Heuer, et al.⁴⁴ Similar phenomena including ferroelectric transitions in epitaxial thin oxide films have been a topic of some recent interest for other applications, see for instance the reviews.^{45–46} Many of these terms may be important, particularly the less commonly discussed flexoelectric contribution which will lead to delamination. Some general reviews on the later can be found in references.^{47–49}

As a second generalization, the electrostatic interaction is not specific to oxygen chemisorption or oxides but is quite general for any electron acceptor such as gold or donors such as transition metal atoms for a metal/insulator system.^{54,59–64} For instance, there is experimental evidence for thickness-dependent stabilization of charged species chemisorption.^{59,60,65} There is also evidence for changes in the surface diffusion rate (e.g.,⁶⁶) which one would expect—for instance, the activation energy barrier will be influenced by the image force of the perturbed electrons in the metal. There are also electrostatic interactions possible beyond individual atoms, particularly for nanoparticles.⁵⁴ This will be similar to the strong interactions of metal nanoparticles with some oxide supports, what has become known as “strong metal-support interactions” that involves these electrostatic terms as well as epitaxial considerations.^{67–93}

Continuing the survey of the existing literature, in many cases rather than focusing upon the electrostatic potential, the focus has been on the work function—which is a manifestation of the energy level at the external surface. For instance, Jaouen, et al., showed that the work function of thin MgO films could be changed by Mg atom incorporation at the MgO/Ag(001) interfaces^{94–95} while in other research DFT calculations suggested that the work function of MgO/Ag (001) could be changed by interfacial oxygen impurities.^{52,96} The effects of different metal supports on the work functions, and adsorption energies of oxide surfaces have been investigated for multiple metal/oxide systems.^{52,55–58,62,95,97–105} Not surprisingly, the work function and surface charge of oxide will change with the coverage.^{54,106}

The existing literature strongly indicates that surface states can be important.^{107–109} A few specific cases where corrosion was the focus of the research have also been considered,^{110–114} although these have often been relatively thin oxide model DFT calculations which may not be fully representative; it is well documented that one has to use relatively thick bulk models with DFT to obtain realistic surface properties.

Lastly, in the existing literature, there is data on the role of the buried metal/oxide interface although not always fully defined in terms of classic semiconductor models. As most oxides of relevance are large band-gap semiconductors, the interface can be classified as being either Ohmic or Schottky in character,^{115–124} and they may contain interfacial dipoles.^{125–126} (In the literature that are two conventions for interfacial dipoles; the one used here is the potential, not the charge transfer.) In such a formalism the nature of the band bending near the interface will depend upon whether there are available p-type or n-type states at the interface, not just the relative band offsets of the metal and oxide Fermi energies (and work functions). A respectably large number of papers have looked at specific cases such as MgO on Ag.^{96,127}

The above description is for gaseous environments, where there is no external potential. In solution, there will be an extension of the potential into the liquid particularly if it contains ions. Different approaches have been used based typically

Table 2. Summary of the Type of Oxide, Surface and Interfacial States, Contact, and Dipole Direction in Different Metal/Oxide Junctions from References^(A)

	Ni/Ni	MgO/Ag	MgO/Ag	MgO/Al	MgO/Mo	MgO/Au	MgO/Mg	MgO/Ti	MgO/Mn	MgO/Ni
Interface O	No	No	Yes	No	No	No	No	No	No	No
Lattice misfit (%)	20.27	2.16	0.96	2.52	5.46	1.67	6	4	21	21
Number of oxide layers		3	2							
Schottky contact		No	No	No	No	No	No	No	No	No
Ohmic contact		Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Work function changes(eV) $\Delta\Phi = \Phi_{OM} - \Phi_M$		-1.27	-0.91	-1.46	-1.74	-1.60				
Charge transfer at metal/ oxide interface ($e/\text{\AA}^2$)		0.0006		0.0001	0.0009	0.02	0.009	0.0003	0.0002	0.0004
Dipole direction (Toward)	Oxide	Metal	Metal	Metal	Metal	Metal	Metal	Metal	Metal	Metal
Interlayer separation d($\text{\AA}$)	1.77	2.67	2.72	2.73	2.14	2.73	2.38	2.19	2.05	2.03
References	50	51	52	51	51	51	53	53	53	53
	MgO/Pd	MgO/Pt	TiO ₂ /Mo	TiO ₂ (rutile)/Ti	TiO ₂ (anatase)/Ti	NiO/Au	NiO/Ag	CoO/Ag	CuO/Ag	ZnO/Ag
Interface O	No	No	No	No	No	No	No	No	No	No
Lattice misfit (%)	8	7.9		2.6	1.6	0.72	0.96	8.89	1.68	4.3
Number of oxide layers	2	2	3	4	4	2	1	1	1	1
Schottky contact	No	No	No	No	No	No	No	No	No	No
Ohmic contact	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Work function changes (eV) $\Delta\Phi = \Phi_{OM} - \Phi_M$	-1.5	-2.0	+1.19	+1.65	-0.58		+0.5	-0.2	+0.9	+0.4
Charge transfer at metal/ oxide interface ($e/\text{\AA}^2$)	0.0006		0.06	0.098	0.10	0.002	0.08	0.03	0.14	0.03
Dipole direction (Toward)	Metal	Metal	Oxide	Oxide	Oxide	Oxide	Oxide	Metal	Oxide	Oxide
Interlayer separation d($\text{\AA}$)	2.38	2.2	0.72			2.30				
References	53-54	54	55	56	56	57	58	58	58	58

^(A) A key point to note is the large variations, which implies significant heterogeneity contrast

upon a classic electrical double layer method.¹²⁸⁻¹³¹ To put this into a common context, one can consider that there has to be continuity of the energy levels of the states associated with the chemisorbed species at the surface. This means that just as there can be pinning of the Fermi level at the metal-insulator junction, there can be effective pinning of levels at the oxide-liquid interface. Hence, one has to consider how adsorption of water can form hydroxide at the surface, as well as the effect of competitive chemisorption of other ions such as chloride. These, as well as the electrical double-layer, will couple to the band bending within the oxide, an area which to date does not appear to have been well studied.

One important caveat needs to be mentioned—what structures have been assumed for the surfaces of the oxides in both experiment and in calculations. Frequently they have been assumed to be simple terminations of the bulk, or used simple concepts such as polarity as first discussed by Tasker¹³² and more recently by Goniakowski, et al.¹³³ In many cases an ionic model has been assumed, sometimes unintentionally. Simple bulk terminations are sometimes but rarely present—this can be a highly inappropriate approximation. While it is *necessary* to consider concepts such as polarity of oxide surfaces, these are not *sufficient* for a full explanation. The available experimental data indicates strongly that local chemical considerations have to be taken into account, essentially the local bonding.¹³⁴⁻¹³⁶ That said, the controlling factors for reduced oxide surfaces are not well known. As one example, the reduced surface of TiO_2 (100)¹³⁷ contains oxygen vacancies below the outer surface. These vacancies are not directly in equilibrium with the external medium (e.g., oxygen gas), only with the bulk oxide. This is a case where the catalytic Mars-van Krevelen mechanism¹³⁸ is active where oxide incorporation takes place at defects which can break the strong oxygen-oxygen double bond, and not homogeneously on the external surface.

It is clear that the current macroscopic mean-field models used for oxidation and corrosion oversimplify the full physics of

the electrostatic potential. What we have, in general, based upon the available literature from a number of different specializations, is a much more complex picture.

1. The metal/oxide interface may contain donor or acceptor states and dipoles, leading to either Schottky or Ohmic character to the contact.
2. The oxide/environment surface may contain surface states and reconstructions, both of which may influence chemisorption.
3. The electrostatic field across the oxide will be perturbed by the polarization of the ions in the oxide as well as image potential interactions with the metal.
4. In general, one can expect a drop in the chemisorption energy as a function of oxide film thickness, but atomic details of the system will influence exactly what takes place.

The following sections will examine some specific cases to fill gaps in the available literature that are relevant for oxidation and corrosion.

COMPUTATIONAL MODELS AND METHODS

While a large number of different cases have already been analyzed in the literature, as discussed above, there are some specific gaps. In addition, the existing literature has focused in most cases upon electronic effects associated with different atomic configurations, rather than the consequences for oxidative corrosion. A number of calculations are performed herein to fill in these gaps.

The DFT calculations involving NiO-based systems were performed using the Vienna *Ab initio* Simulation Package¹³⁹⁻¹⁴¹ with a plane wave cutoff of 550 eV. For these calculations, the projector augmented wave method¹⁴² was used and the exchange-correlation energy was evaluated using the Perdew-Burke-Ernzerhoff (PBE) functional¹⁴³ within the spin-polarized generalized gradient approximation. For relevant cases where

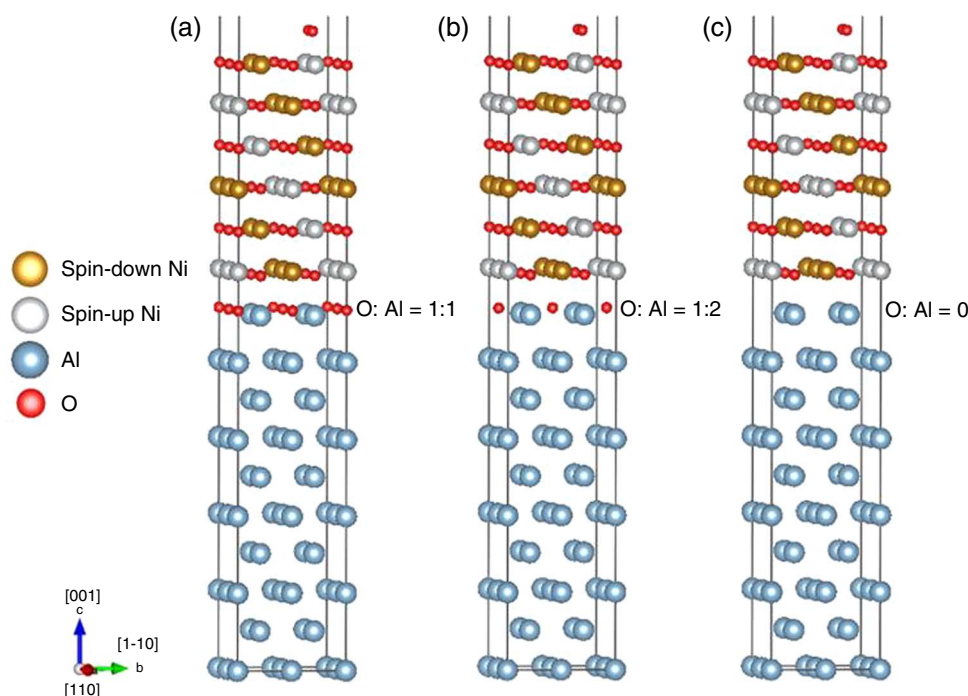


FIGURE 2. (a through c): computational models of (100) Al/(100) NiO junctions with different interfacial oxygen contents.

the d-band electrons are not well described by the PBE functional, a conventional plus Hubbard U correction was used following the approach of Dudarev, et al.¹⁴⁴ Based upon calibration calculations, for nickel in nickel oxide, a value of $U_{\text{eff}} = 5.3$ eV for the correlated Ni 3d orbitals was used in all simulations leading to reasonable values for the band gap, formation energies, magnetic moment, and bulk modulus.¹⁴⁵ A $9 \times 9 \times 1$ k-mesh was used for the k points sampling using the Monkhorst-Pack scheme¹⁴⁶ during structural relaxation until the forces on each ion were less than 0.01 eV/Å, and a $12 \times 12 \times 2$ k-mesh was used in the electronic structure calculation with a convergence of 10^{-5} eV for the total energy.

As a representative example, slab models of Al(100)/NiO(100) are shown in Figure 2. The interface between the two was

constructed from 10 Al(100) layers (lattice parameter $a_0 = 4.04$ Å) and variable NiO(100) layers (lattice parameter $a_0 = 4.10$ Å) with a 20 Å vacuum region. Three interfacial configurations were considered (a) with four interfacial O (O:Al = 1:1), (b) with two O (O:Al = 1:2), and (c) without interfacial O (O:Al = 0). No large period atomic reconstruction of the external surface was considered. The bottom two Al layers were fixed, and the rest of the atoms were relaxed. Spin-polarized calculations were performed using the antiferromagnetic ground state for nickel oxide.

When there were ambiguities for chemisorption, different adsorption sites were tested to find which was the lowest in energy. For instance, for the O_2 molecule on (100) NiO surface, three adsorption positions were considered: (a) on the top of Ni atoms, (b) in the hollow of Ni atoms, and (c) on the top of

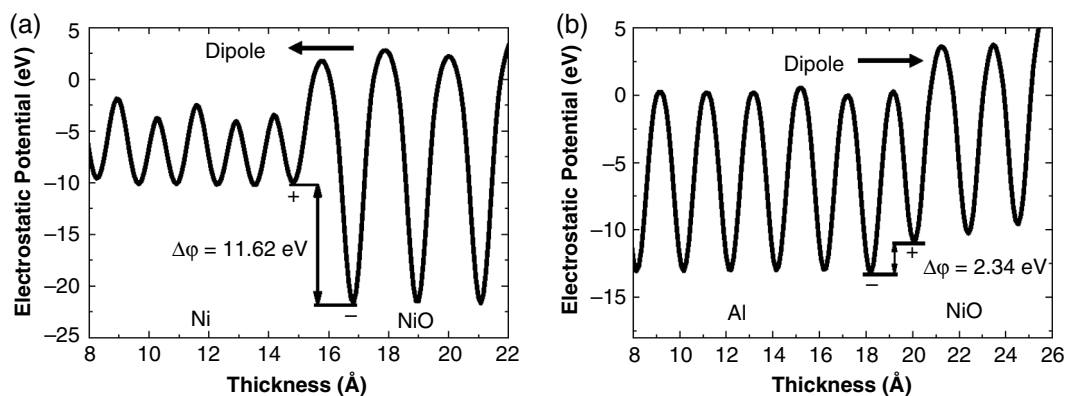


FIGURE 3. Electrostatic potentials (x - y average) along z -direction for (a) (100) Ni/(100) NiO and (b) (100) Al/(100) NiO models.

Table 3. Summary of the Type of Oxide, Surface and Interfacial States, Contact and Dipole Direction in Different Metal/Oxide Junctions^(A)

	NiO/Al	NiO/Al	NiO/Ni	MgO/Al	MgO/Li	MgO/Li	MgO/Ag	MgO/Ta	MgO/Ta
Interface O	Yes	No	No	No	Yes	No	No	Yes	No
Lattice misfit (%)	1.87	1.87	18.69	2.52	1.30	1.30	3.36	0.11	0.11
Number of oxide layers	3	3	3	3	3	3	3	3	3
Metal work function (eV)	4.20	4.20	4.90	4.20	3.07	3.07	4.38	4.73	4.73
Oxide work function (eV)	4.91	4.91	4.91	4.70	4.70	4.70	4.70	4.70	4.70
Schottky contact	Yes	No	No	No	No	No	No	No	No
Ohmic contact	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Surface States	Yes	Yes	Yes	No	No	No	No	No	No
Work function changes (eV) $\Delta\Phi = \Phi_{\text{O/M}} - \Phi_{\text{M}}$	-1.57	-0.87	-1.08	-0.9	+2.01	-1.27	-0.68	-2.74	-3.04
Charge transfer ($\text{e}/\text{\AA}^2$)	0.24	0.07	0.02	0.01	0.04	0.12	0.09	0.01	0.04
Dipole direction (Toward)	Oxide	Oxide	Metal	Metal	Metal	Metal	Metal	Metal	Metal
$\Delta\phi$ (eV)	11.11	2.34	11.62	2.83	7.87	13.8	11.45	2.74	8.85
Interlayer separation Δd (Å)	2.30	1.93	2.00	2.56	2.05	1.99	2.54	2.23	2.32
$E = \Delta\phi/\Delta d$ (V/Å)	5.76	1.28	5.81	1.11	3.83	6.93	4.51	1.23	3.81
Rumpling interface (Å)	0.35	0.05	0.08	0.05	0.09	0.01	0.03	0.04	0.03
Rumpling surface (Å)	0.03	0.02	0.02	0.01	0.06	0.05	0.04	0.05	0.04

^(A) What density functional method was used is described in section "Computational models and methods."

O atoms. Total energy calculation showed that the adsorption of O_2 molecule on the Ni hollow site has the lowest energy. Therefore, the Ni hollow with two spin-up Ni atoms below the O_2 molecule was chosen for the adsorption site for all of the calculations. (This spin configuration was slightly lower in energy, as expected considering the spin state of O_2 .)

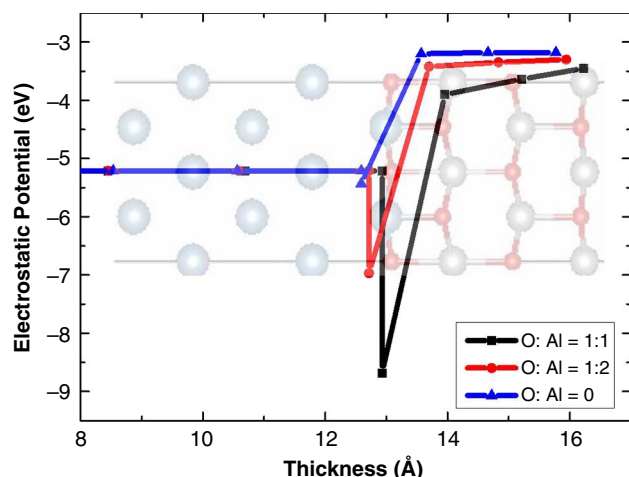


FIGURE 4. The macroscopic electrostatic potential across (100) Al/(100) NiO interfaces with different interfacial compositions.

For a number of other systems (MgO/Al, MgO/Li, MgO/Ag, MgO/Ta), calculations were performed without spin polarization with the all-electron augmented plane wave + local orbitals WIEN2K code¹⁴⁷ using the PBE¹⁴³ functional. These cases were chosen to avoid significant misfit at the interface; the effect of misfit and interfacial dislocations is a topic which bears further examination in future work. In all cases, inversion symmetry surface slabs were used with a fixed number of cells and vacuum size normal to the surface, and valence neutral structures to avoid artifacts with charged cells or highly reduced or oxidized compositions. Lattice parameters were those for the DFT relaxed bulk structures. All surface slabs had inversion symmetry, with the cell size normal to the surface approximately 4 nm, with 2/3 of the cell occupied by atoms, so the region of vacuum was approximately 1.3 nm. Atom positions except those fixed by symmetry were relaxed to an accuracy of 1 mRyd/au or better using a parallel quasi-Newton algorithm.¹⁴⁸

RESULTS

We will describe results here for a number of different cases to supplement and expand upon the available literature, paying attention to cases which are relevant to oxidative corrosion. The dependence of the electrostatic potential is not simple, and as might already be inferred from the previous sections, is highly dependent upon atomic details of the two interfaces as well as the crystallography. The result is broken into two parts which will be described separately: (1) the electrical dipole at the metal/oxide interface and the surface state of

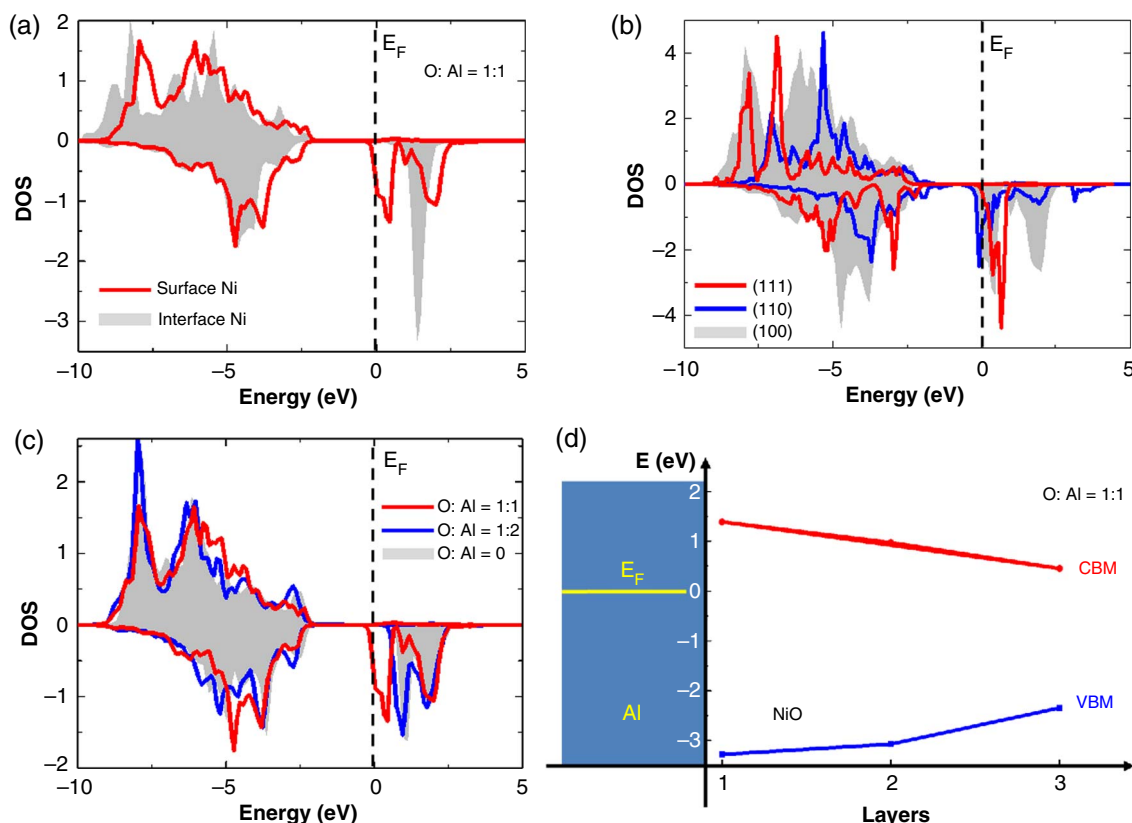


FIGURE 5. (a) The density of states (DOS) of surface and interface Ni in the (100) Al/(100) NiO (three layers) model, the interfacial O to Al ratio is 1:1. (b) The DOS of surface Ni in the (100) Al/(100) NiO, (110) Al/(110) NiO, and (111) Al/(111) NiO models. (c) The DOS of surface Ni in the (100) Al/(100) NiO models with different Al to O ratios at the interfaces. (d) The band bending in the (100) Al/(100) NiO (three layers) model, the interfacial O to Al ratio is 1:1.

oxide; (2) the synergy of dipole, band bending, surface state, and chemisorption. We will return to a global overview in the discussion.

5.1 | The Electrical Dipole at the Metal/Oxide Interface and the Surface State

The simplified picture presented in Figure 1 has a potential step at the metal/oxide interface. As already mentioned, often there is a dipole at the interface. The first result detailed is that the magnitude of this dipole varies as a function of both the chemical nature of the interface as well as the structure of the interface.

As shown in Figure 3, for different metal/oxide junctions, such as Ni/NiO, (Figure 3[a]) and Al/NiO (Figure 3[b]) the metal/oxide interfacial electrostatic potential changes $\Delta\phi$ and the electric dipole have different magnitudes and directions. Table 3 gives more examples of various metal/oxide junctions with the dipole direction and magnitude $E = \Delta\phi/\Delta d$ included, where Δd is the interlayer separation at the M/O interface.

A second not unexpected result is that the dipole is a function of the interfacial composition. To probe this, three interfacial compositions (Al:O = 0, 2:1, and 1:1) as shown in Figure 4 were calculated by adding O atoms at the Al/NiO interface. The additional interfacial O leads to a larger potential drop thus a larger electric dipole at the interface in Figure 4. The larger dipole, in turn, leads to a higher electric field in the oxide which manifests as a steeper slope of the potential.

A third result, again to be expected in general, is that the metal/oxide interface is not the only one which is not simple, the external surface is as well. Surface states that depend upon the surface crystallography, surface chemistry, and reconstruction are well established. To provide some examples of relevance here, Figure 5(a) shows how the change in local coordination of the (100) surface Ni leads to a splitting of the conduction bands into two manifolds: one shifts to higher energies as the other shifts to lower energies at and below the Fermi energy (E_F). The density of states (DOS) of Ni at metal/oxide interface has no such splitting.

Figure 5(b) shows the crystallography dependence of the surface state. The DOS of Ni on NiO/Al (001), (110), and (111) surfaces (with approximately the same thickness of oxide (~7 Å)) show that both (100) and (110) surface have filled surface states below the Fermi level, whereas they do not exist for (111) surface.

Furthermore, the dipole and surface state couple via the band bending across the oxide. Figure 5(c) plots the DOS of (100) surface Ni with different interfacial compositions. The surface states are observed in all of the three cases. However, only the surface states for Al:O = 1:1 were occupied. A clear shift of the DOS toward the deeper energy levels can be seen as the content of interfacial O increasing, which is consistent with the larger interfacial dipole and electric field in the oxide layers.

Figure 5(d) shows the band bending in the oxide for the Al:O = 1:1 model. The valence band maximum (VBM) in the NiO increases from the interface to the surface, and the conduction band minimum (CBM) decreases, which indicate a reduction of the band gap.

5.2 | The Synergy of Dipole, Band Bending, Surface State, and Chemisorption

To explore the sequences of interface dipole, band bending, and surface state on the chemisorption, the adsorption

behaviors of O₂ for different NiO thicknesses, Al/NiO interfacial structures, as well as surface crystallography are calculated.

We will first describe the general trend with thickness (Figure 6). The oxygen adsorption energy was calculated as $E_{\text{ads}} = E(\text{Slab} + \text{O}_2) - E(\text{Slab}) - E(\text{O}_2)$. With four interfacial O (Figure 6[a]), the adsorption energies as a function of the number of layers indicate that O₂ adsorption (oxidation) becomes less favorable (energy increasing) as the thickness of the NiO increases. This correlates with the elongation of the O-O distance of the adsorbed O₂ molecule shown in the same plot, indicating a weakening of the bond consistent with previous chemisorption studies.¹⁴⁹ A Bader charge analysis¹⁵⁰⁻¹⁵² shows that the charge transfer to the O₂ molecule decreases with an increasing number of layers; see Figure 6(b). The charge transfer and the O-O bond distance have a thickness dependence with three plateaus for 2-3, 4-7, and 8-9 layers. These regions correspond to charge transfer of approximately two, one, and less than one electron to the O₂ molecule. The decrease of charge transfer as the oxide film becomes thicker reduces the quenching of the magnetic moment for the triplet ($S = 1$) O₂ ground state, as shown in Figure 6(b).

For a fixed Al:O composition of the interface, the results appear to be consistent with a Cabrera-Mott model and the prior work on aluminum/alumina.¹⁴⁹ However, when the composition is changed it becomes clear that there is more taking place. Increasing the number of interfacial oxygen favors O₂

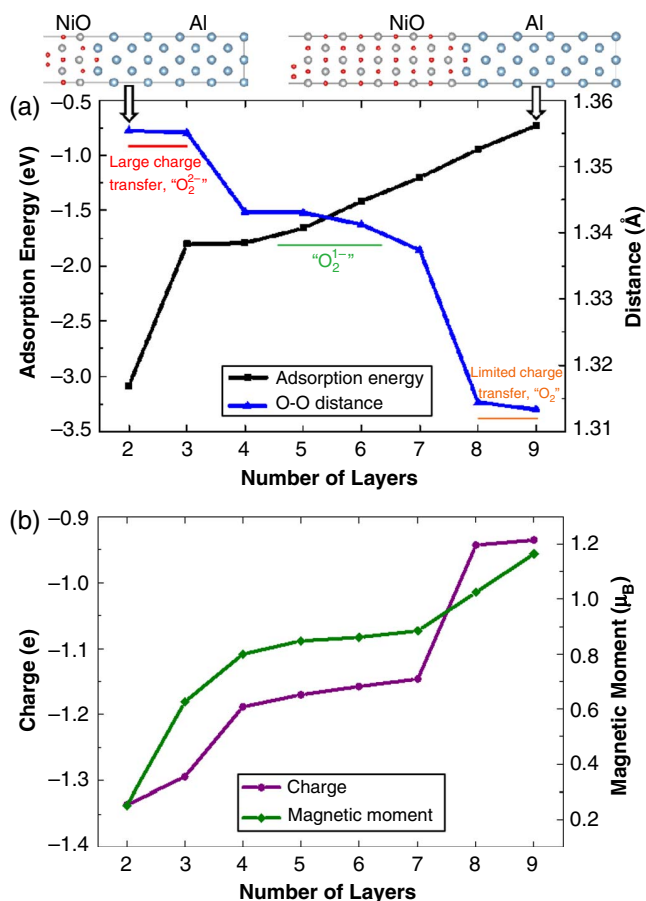


FIGURE 6. (a) Adsorption energy and O-O bond length change with the number of NiO layers in the (100) Al/(100) NiO (interfacial O to Al ratio is 1:1) slab. (b) Bader charge and magnetic moment of O₂ change with the number of NiO layers.

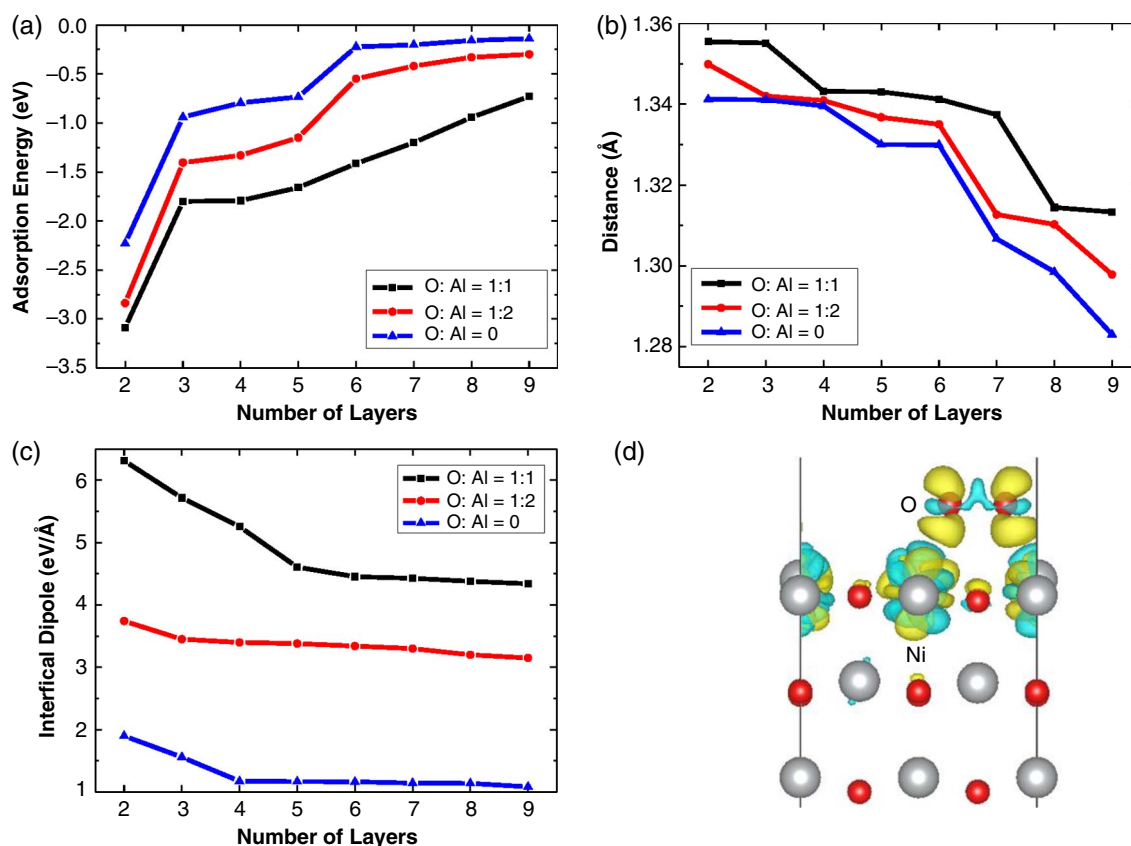


FIGURE 7. (a) Adsorption energy changes with the number of NiO layers in the (100) Al/(100) NiO models, the interfacial O to Al ratio is 1:1, 1:2, and 0, respectively. (b) O-O bond length changes the number of NiO layers. (c) The interfacial dipole magnitude changes with the number of NiO layers. (d) A representative charge density differential plot of the slab after and before O_2 adsorption, yellow is positive (obtaining electrons) and blue is negative (losing electrons) with the isosurface value of 0.006 e/Bohr^3 .

adsorption for all of the studied film thicknesses, as shown in Figures 7(a) and (b). The behavior is attributed to the presence of an interface dipole ($\Delta\phi$), which increases the high electric field in the oxide, and also the available surface states, as discussed previously. From the electrostatic potentials, as the interfacial oxygen content increases, the magnitude of $\Delta\phi$ increases and it also slightly decreases with thickness, as shown in Figure 7(c). When the O_2 molecule approaches the surface, the occupied d state of Ni will transfer electrons to the unoccupied orbitals of O_2 . This is apparent in the charge differential plot after and before the adsorption Figure 7(d), showing the formation of a Ni-O bonding at the surface. Figures 8(a) through (c) show the density states of surface Ni and adsorbed O after adsorption were aligned with the vacuum energy level of each slab model. The Ni-O hybridization states were formed near the Fermi level, as shown in the partial density of states.

To explore the role of surface crystallography, Figure 9 compares the adsorption energy of oxygen molecule, the O-O bond length and the magnetic moment after O_2 adsorption on three surfaces with approximately the same thickness of oxide ($\sim 7 \text{ Å}$). The results show that the adsorption on (100) is strongest and on (111) is weakest, while adsorption on the (110) surface is in the middle.

Figure 10(a) shows how the O_2 adsorption energy changes with thickness on the three surfaces. Although the adsorption energies become more positive for all of the three surfaces with increasing thickness, the adsorption energy on the

(100) surface is more negative than that on the (110) surface when the oxide is ultrathin, e.g., below three monolayers. When the oxide is thicker, the adsorption energies on (100) and (110) become similar and slowly decay to zero, which means no adsorption. However, adsorption on (111) is much weaker than those on the other two surfaces, and more rapidly decreases to zero.

We also calculate the Bader charge difference per atom of interfacial Al and surface Ni after and before O_2 adsorption: $n(\text{after}) - n(\text{before})$ in Figures 10(b) through (d). The negative Bader charge difference means losing electrons due to the charge transfer. For the (100) and (110) surfaces, Figure 10(b) and (c), the surface Ni contributes most of the charge transfer, which indicates that the charge transfer mostly occurs on the surface. For the (111) surface in Figure 10(d), the charge transfer from the interfacial Al dominates, while the surface Ni has almost no contribution. The collective results show that the charge transfer mechanism transitions from surface domination on the (100) surface to interfacial domination on the (111) surface.

DISCUSSION

As stated in the Introduction and background sections, there is a significant amount of existing information about electronic states in the metal/insulator and metal/semiconductor junctions, and some information for metal/oxide/vacuum systems from other fields. The question of whether the metal/

oxide interface has additional states and dipoles as well as the consequences of this for band bending is well established, similarly for the role of surface states. All of these depend upon the surface crystallography.

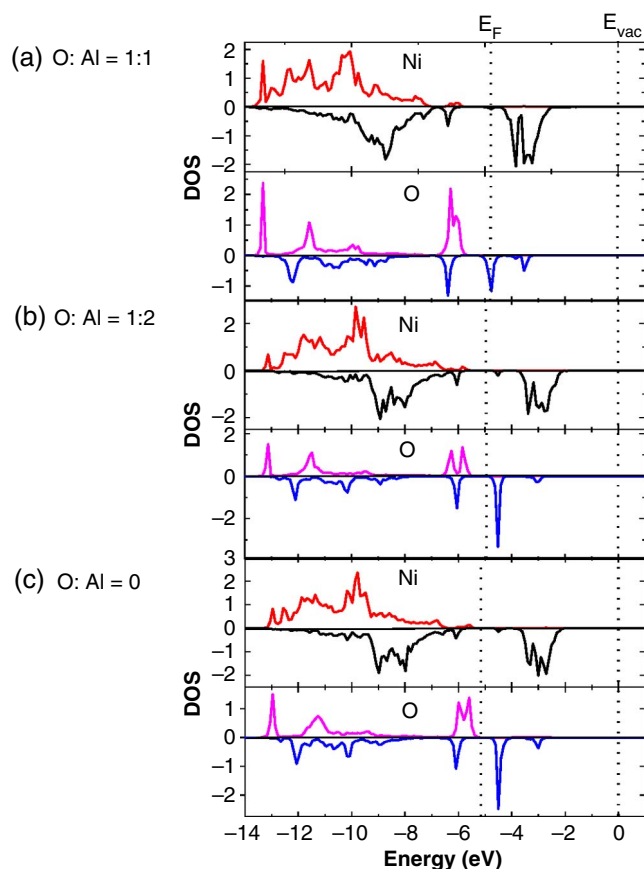


FIGURE 8. The DOS of surface Ni and adsorbed oxygen after adsorption in the (100) Al/(100) NiO models. (a) Interfacial O to Al ratio is 1:1. (b) Interfacial O to Al ratio is 1:2. (c) Without interfacial oxygen. Positive (negative) DOS indicates the majority (minority) spin states.

Where less is known, which is the primary scientific focus of this paper, is the consequences this has for oxidative corrosion and the electrostatic component of the electrochemical potential, and the consequences this has for effective medium formulations and overall behavior. Both the existing literature as well as these current specific calculations indicate that the potential jumps at the interfaces will be spatially varying in the range of 0.5 eV through 1.0 eV. Since the total potential change over the oxide film is in most cases going to be less than the band gap, this is a very large variation. While the heterogeneity contrast is not as large as it is, for instance, in a fiber composite, it will be significant. In addition to the crystallographic heterogeneity contrast, there will be heterogeneity contrast due to the grain boundaries and other defects.

To illustrate that heterogeneity contrast will matter with real oxide systems, Figure 11(a) shows the transmission electron microscopy image of a thin oxide film on the Ni-22%Cr (wt%) alloy formed by the oxidation at 600°C for 10 min in a vacuum chamber (oxygen partial pressure: 2.67×10^{-3} Pa with 2.0×10^{-5} Pa base pressure). Figure 11(b) shows a thin oxide film formed under aqueous conditions in $K_2S_2O_8$ and Na_2SO_4 solution for 3 h. (More details of these will be described elsewhere.¹⁵³⁻¹⁵⁴) The oxides in both cases are highly inhomogeneous, which will lead to large heterogeneity contrasts.

A subtle but important question is whether the significant heterogeneity contrast will lead to classic weakest-link behavior, statistical properties comparable to the Bowden-Tabor explanation of Amontons' law³²⁻³³ or more complex behavior. We suspect that there is no single answer and depending upon the dependencies (and perhaps local triggers) as discussed earlier the behavior will be different. As argued previously, there is good evidence for a weakest-link interpretation for the effect of chloride,³⁴ as will be discussed further with experimental data elsewhere.¹⁵⁴ This is consistent with a local morphological instability¹⁵⁵⁻¹⁷¹ interpretation. There is also evidence for more complex collective (statistical) behavior in pitting breakdown.¹⁷²⁻¹⁷⁶ In contrast, when oxidation and corrosion are slow, some form of straightforward, effective medium model does appear to be consistent with experimental data. There is a need for more analysis of the formulations and approximations inherent in the transition from a real nanoscale material to an effective medium

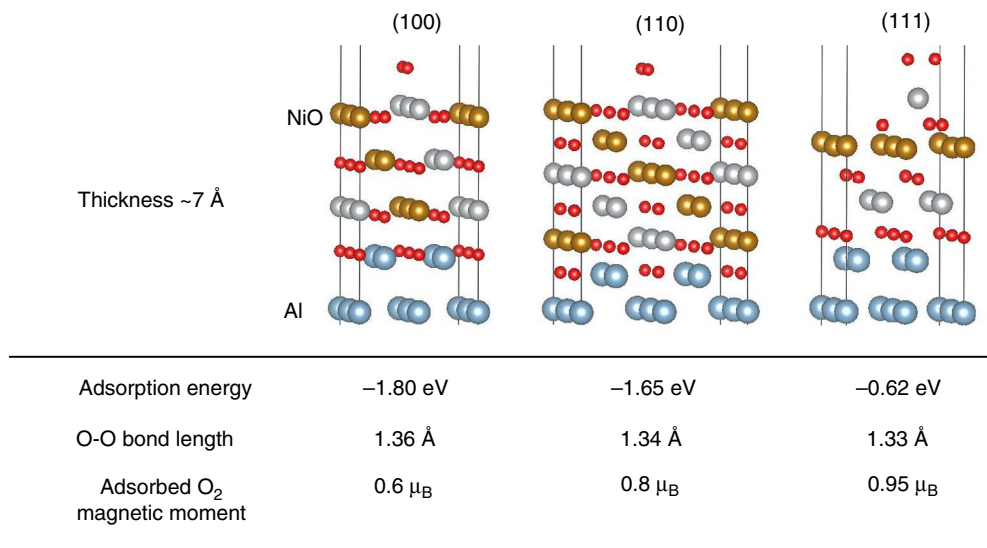


FIGURE 9. The adsorption energy, the O-O bond length, and the magnetic moment after O₂ adsorption on the surface in the (100) Al/(100) NiO, (110) Al/(110) NiO, and (111) Al/(111) NiO models, with approximately the same NiO thickness (~7 Å).

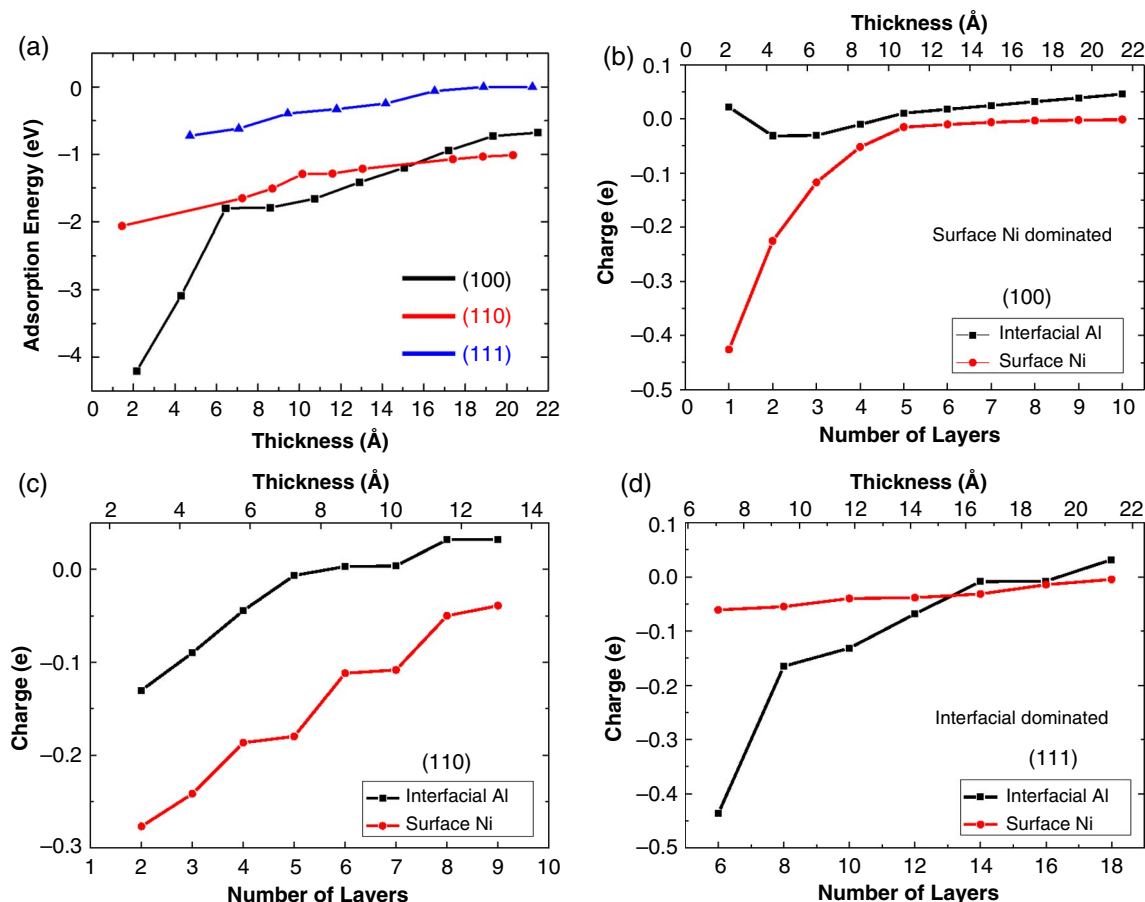


FIGURE 10. (a) Adsorption energy of oxygen changes with the thickness of NiO layers on the NiO (100), (110), and (111) surfaces. (b through d) The Bader charge difference (interfacial Al and surface Ni before and after O_2 adsorption) changes with the number of NiO layers. (b) (100) Al/(100) NiO model, (c) (110) Al/(110) NiO model, and (d) (111) Al/(111) NiO model.

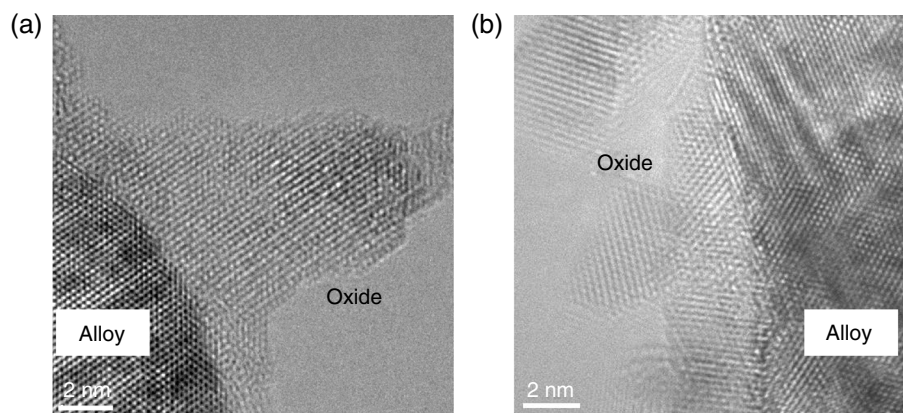


FIGURE 11. (a) TEM image of a thin oxide film formed on the Ni-22Cr (wt%) alloy by the oxidation at 600°C for 10 min. (b) TEM image of a thin oxide film formed on the Ni-22Cr (wt%) alloy during the aqueous corrosion in $K_2S_2O_8$ & Na_2SO_4 solution for 3 h (More details of these will be described elsewhere.¹⁵³⁻¹⁵⁴)

formulation, as there may be new phenomena. Based upon the example given in Equations (1) through (4), one approach would be to try and extract the effective Mott potential as a function of temperature; however, this may be too simplified an approach in general. An alternative, not trivial, would be to measure growth rates for different crystallographic

orientations and then combine this with crystallographic texture data and mean-field reductions of experimental data on polycrystalline samples.

Finally, we hypothesize that some general features extracted can be used as the basis of (perhaps weak) design rules to assist with future alloy design.

Any metal, which has occupied d-states on the cation, will have a higher probability to chemisorb oxygen. Hence, they will be less likely to resist corrosion, which is consistent with the use of cations without occupied d-states in most protective oxide films.

All systems where there is a negative dipole at the metal-oxide interface, i.e., the positive charge points into the metal will increase the electrostatic field across the oxide and therefore enhance field-assisted diffusion.

Counteracting 2, there can be a compensating/opposing effect where dipoles reduce the occupancy of surface states, therefore reduce their ability to act as electron donors that enhance chemisorption of oxygen.

Also connected with 2, any additional minor alloying elements which segregate to the interface and change the dipole can have a significant effect upon the electrostatic potential. Similarly, connecting to 3, any elements without occupied d-states that segregate to the surface may also have a significant effect.

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