Part I

Introduction

“A beginning is the time for taking the most delicate care

that the balances are correct.”

–the words of Princess Irulan

Chapter 1

Motivation, Scope and Basic Principles

1.1 Motivation

It is ironic that much of our civilisation's wealth and effort has been expended in extracting metals from their ores, yet once separated these metals immediately begin to revert back to ores by combining with elements in the environment. Consequently, a constant technological battle is waged to form kinetic barriers against this inevitable thermodynamic fate for metal structures. The work presented in this thesis is concerned with certain of the important processes involved in the formation of corrosion products. In thinking about these processes one is unavoidably brought face to face with the atomic scale. Fortunately, our civilisation has developed many theories that explain atomic behaviour in materials. In particular, theories that replace an idealistic view of the perfect arrangement of atoms in materials by one where atomic imperfections play a leading role. The fascinating world of atomic imperfections, or defects, is unfortunately so far removed in scale from our own that it becomes egregiously difficult to probe with instrumentation. However, the recent advent of cheap, high speed computing provides a valuable tool which can help to examine this atomic frontier of science.

Simulation will, of course, never replace experimentation, indeed it would not have advanced so far without it, and experimentation will always benefit from ideas suggested by simulation. Both avenues naturally complement each other; simulation can quickly compare and contrast the many variables in a given system to provide an optimum data set suitable for more refined experimental investigation. In turn, experimentation provides vital validation (or not!) of the theory behind the simulation. It is this cooperation between the two approaches that ushers in new advances. So, to summarise, the great value of simulation is that it can probe where experimental data is limited, difficult or hazardous to obtain. Some of these areas are explored in the following chapters.

1.2 Scope of Work

The simulations presented in this work have their foundation in the fundamental principles of atomic behaviour and the forces that hold materials together. The first part of this thesis therefore includes this section (chapter 1) which details some basic principles that underpin discussion in later parts. The principle models used to represent atomic interactions are common throughout the thesis and are discussed in chapter 2. From this two distinct methodologies emerge. The first is applicable to the study of defects in crystal lattices (results of which are presented in part II) and the second probes the fundamental aspects of gas monolayer growth on surfaces (see part III). In part II an approach, based on energy minimisation, is used to simulate defects in crystal latices. The methodology is detailed in chapter 3. This is followed by two separate studies of the behaviour of crystal lattice defects in important corrosion products. The behaviour of a passive film on a nickel alloy is investigated in chapter 4; the focus of which is the importance of defect concentrations to transport in this passivation layer. The nickel system is found to work well with the underlying theory used. Some important conclusions are made about how the underlying nickel alloy might be changed to provide an enhanced performance. In chapter 5 a similar approach is used for a wider range of possible corrosion products, formed as oxides on aluminium and steel. The complexity of these systems is overwhelming and represents the limit to which current energy minimisation methods can be applied. This highlights a problem with theoretical simulation: as the target system becomes more complex then the computational effort becomes greater. In order to fully investigate the system (particularly where dynamic mechanisms are of interest) larger simulations and longer simulation times are required. Ultimately, this brings the simulation technique to a crossroads where a choice must be made between simulating for longer time periods or simulating a larger system. The only alternative is to employ further approximations. Consequently, in an attempt to explore the boundaries of what is possible, an alternative simulation methodology is presented in chapter 6 (part III). This method is based on statistical rules which define the behaviour of discrete regions of the system under study. Since the technique and simulation code are in its infancy, only idealised systems are currently accessible. The simple case of argon gas evolution onto an imperfect calcium surface is simulated and the results are presented in chapter 7.

One appendix is included, in part IV, which presents a detailed study of the atomic arrangement in a group of materials with a common rutile structure. This serves as an example to explain several simulation issues as well as providing some interesting observations about this structure.

1.3 Basic Principles

1.3.1 Defects in Materials

The simulations in this work are largely concerned with defects in crystal lattices. There are many classes of defects but they can generally be thought of as either a missing atom in a regular structure (a vacancy defect) or an extra atom where one is not usually found in the regular structure (an interstitial defect). Such defects are native to the material under investigation and are termed intrinsic defects. It is also possible for a foreign element to occupy a site normally occupied by a native atom (a substitutional defect). Such defects are not native to the lattice and so are termed extrinsic defects. Extrinsic defects can be of the same charge as the ion they replace (isovalent) or they can have a different charge state (aliovalent). The specific mechanisms by which defects form will be discussed in the relevant chapters as they arise. It is important to note that defects occur in materials due to the thermodynamic laws that govern their behaviour.

1.3.2 Passive Surfaces and Transport

All the work presented is in some way concerned with surface layers, whether they be a protective layer on a nickel alloy or a monolayer of argon on a calcium metal. Some thermodynamic driver causes the environment to react with the substrate and form an interface. An interfacial product can then act as a barrier to further reaction between the substrate and the environment.

Chapters 4 and 5 will be concerned with systems in which the surface layer is termed passive. The term passive can be confusing as it implies that there is no further interface growth beyond the initial formation. However, the reality is that the thermodynamics still favour further formation of interface product but the kinetics are severely hindered. Often the hindrance is due to the rate of transport across the passivation product. In this situation the transport flux, J, is described by Fick's first law and associated relationships as described in several general texts [4–6]. Fick's first law states that the flux of material that moves across an interface is a function of the concentration gradient:

$$J = \mathbf{D}\frac{d\mathbf{C}}{dx} \tag{1.1}$$

where $\mathbf{D}$ is the diffusion coefficient and $\frac{d\mathbf{C}}{dx}$ is the concentration gradient. The diffusion coefficient has several parts [4]: a configurational term, γ, the jump distance, λ, and the jump frequency, Γ, such that,

$$\mathbf{D} = \gamma\lambda^2\Gamma \tag{1.2}$$

It is found experimentally that $log\mathbf{D}$ plotted against the inverse temperature, $\frac{1}{T}$, results in a linear relationship that can be expressed as,

$$\mathbf{D} = \mathbf{D}_0 exp\left[\frac{-(Q_f + Q_a)}{kT}\right] \tag{1.3}$$

where $\mathbf{D}_0$ is a constant; Q_f and Q_a are respectively the formation energy of the migrating species and the activation energy for the migration mechanism and k is Boltzmann's constant. If there is no formation energy then Q_f is removed resulting in a simpler form of the equation. This analysis describes the situation in which atomic diffusion is thermally activated and thus the jump frequency, in equation 1.2, can be related to the activation energy of the migration.

$$\Gamma = \nu\, exp\frac{-\Delta G}{kT} \tag{1.4}$$

where ΔG is the activation energy and ν is the vibrational attempt frequency. Substituting equation 1.4 into 1.2 results in,

$$\mathbf{D} = \gamma\lambda^2\nu exp\left[\frac{-\Delta G}{kT}\right] \tag{1.5}$$

Now, by comparing 1.3 and 1.5 a detailed definition of $\mathbf{D}$ is arrived at,

$$\mathbf{D} = \gamma\lambda^2 \nu exp\left[\frac{-(Q_f + Q_a)}{kT}\right] \tag{1.6}$$

the energy terms in this relationship are considered to be dominant and it is the values of these that are of interest when transport through the lattice of a passivation product is discussed.

In chapter 3 a method for establishing the saddle point energy (which is closely related to Q_a) is described. This is then used in chapter 4 to make predictions about the migration in the passivation layer that forms on nickel alloys.

1.3.3 Thermodynamic Approximations

When reaction energies are discussed in the following chapters they will generally be internal energies. This is because the techniques used do not account for entropy and PV (pressure × volume) terms in the Gibbs energy are ignored. While this can represent a significant error it is not thought to be significant given the following thermodynamic approximation and the fact that predicted data is used to discuss relative energies, never absolute values.

The thermodynamics below follows that laid out by Kröger [2]. Consider an equilibrium reaction between two reactants A and B forming products C and D,

$$A + B \rightleftharpoons C + D \tag{1.7}$$

where the free energy of the reaction is ΔG. The equilibrium constant $\mathbf{K}$ for this reaction is defined as,

$$\mathbf{K} = \frac{[C][D]}{[A][B]} \tag{1.8}$$

where,

$$\mathbf{K} = exp\left(\frac{-\Delta G}{kT}\right) \tag{1.9}$$

Expanding this equation using $\Delta G = \Delta H - T\Delta S$ suggests that,

$$\mathbf{K} = exp\left(\frac{-\Delta H}{kT}\right) \cdot exp\left(\frac{\Delta S}{k}\right) \tag{1.10}$$

However, since ΔS is small $exp(\frac{\Delta S}{k}) \approx 1$. Therefore, the following approximation is possible,

$$\frac{[C][D]}{[A][B]} \approx exp\left(\frac{-\Delta H}{kT}\right) \tag{1.11}$$

The above suggests that it is a reasonable approximation to assume that $\Delta G \approx \Delta H$ for this type of equilibrium reaction. Certainly this approach has been successful in the past [7]. Of course, as computational facilities continue to expand it will eventually be possible to carry out extensive calculations in which vibrational entropy terms are included.