Atomic Scale Simulation of Defects in Bulk Materials and Monolayer Surfaces

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by
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To three great women:
Susan ,
my love and my life.
My Grandmother, Winifred Atkinson,
who inspired me to work,
through her own hard work.
Mrs Beanland,
who first noticed my dyslexia,
thus unlocking my potential.

Abstract

When engineering alloys come into contact with an environment a corrosion reaction will occur at the interface and reaction products form. The stabilities of such products are key to the corrosion performance of the alloy. A detailed understanding of how corrosion products behave at the atomic level would be of great significance for the development and optimisation of alloy compositions.

In this thesis atomic scale simulation techniques have been used to model the incorporation of foreign elements in corrosion products and the impact on transport properties. Two systems are studied: NiF_2 which is formed on nickel alloys in fluorine environments, and M_2O_3 corundum structures that form on aluminium and steel alloys in oxidising environments.

It is recognised that further simulation advances will be required before atomic defect simulation can be used to predict large volume and long time scale processes. As such, a simulation method is reported which offers advantages over traditional techniques and can predict atomic surface structure evolution over extended timescales. Here, model systems consisting of a gas monolayer on atomically rough metal surfaces are investigated; results are presented in analytical and graphical forms.

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Finally, I would like to thank anyone who reads this thesis. You are braver than I. In the first instance it will be my examiners. I hope you find my words of some interest. I warn you in advance, section 4.4.3 is tediously boring. I strongly recommend a wee tipple to help the reading, a fine single malt would do nicely, Jura perhaps.

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Nomenclature

The notation devised by Kröger and Vink [1–3] will be used to describe various defect species in reactions. The upper case characters A, B, C and D will be used to denote 1+, 2+, 3+ and 4+ charged cations respectively. Anions will be denoted by their atomic symbol. Thus, for example, the generic representation for binary fluorides with a stoichiometry similar to CaF_2 will be BF_2. The generic representation of a 3+ cation on a 4+ host cation site will be C_D'. To indicate a defect concentration, the defect species is enclosed in square brackets, for example $[C_D']$.

Throughout this thesis reaction energies are be referred to by the symbol ΔH_{sub}, where *sub* will identify a reaction the energy is associated with. In the case of intrinsic reaction energies *sub* will indicate a reaction type (e.g. $an-fren$ for an anion Frenkel reaction) and is specific to the relevant chapter. In the case of other types of reaction *sub* will indicate an equation number which will identify the reaction it refers to. Additionally, a label denoting the reaction type may appear with the equation number. For example, $\Delta H_{sol(5.8)}$ indicates that this energy is for equation 5.8 which is a solution reaction.