Toward multiscale modelling of localised corrosion

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Abstract

Localised corrosion is a cause of unanticipated and sometimes catastrophic failures of equipment, transport vessels and infrastructures. Therefore, the development of modern corrosion-resistant materials and inhibitors by design is both technically and economically attractive. In the coming decades, industrial components will be engineered from molecular structures. This prospect provides the designer with a truly enormous range of choices in design, which is a situation that demands predictive tools that can link molecular structures with the final component performance. In particular, the development of alloys and inhibitors can replace the use of toxic compounds in protecting metal surfaces. To execute a tailored design programme, it is necessary to understand how corrosion and the associated processes occur from the molecular level to the component level and how the overall system behaviour emerges because of the inherent links among different scales. Therefore, in the present work, the literature on theoretical modelling of localised corrosion and related experimentation are reviewed from a multiscale viewpoint. The review addresses (a) the challenges in the theoretical formulation of the important phenomena that influence localised corrosion and (b) the hurdles facing computational methods. It is shown that (i) the existing models lack the resolution to design effective corrosion-resistant systems, (ii) the numerical strategies for linking the scales are in a state of evolution and (iii) there are gaps in the experimental characterisation of the corrosion system, particularly at the lower end of the scales. Suggestions are provided towards the construction of a multiscale model for localised corrosion.

Keywords: localised corrosion, pitting corrosion, crevice corrosion, multiscale model, materials by design, density functional theory, inhibitors

List of abbreviations

ANN	Artificial Neural Networks
BEM	Boundary Element Method
BV	Balance Volume
CA	Cellular Automaton
GGA	Generalised Gradient Approximation
CCST	Critical Crevice Solution Theory
CSCT	Critical Solution Chemistry Theory
CVFEM	Control-Volume Finite Element Method
DFT	Density Functional Theory
DPD	Dissipative Particle Dynamics
DPDE	Dissipative Particle Dynamics with Energy Conservation
FDM	Finite Difference Method
FEM	Finite Element Method
FVM	Finite Volume Method
HFM	High Field Model
IRDT	IR Drop Theory
kMC	kinetic Monte Carlo
LCAO	Localised Combination of Atomic Orbitals
LDA	Local Density Approximation
LMPM	Lattice Material Point Method
MC	Monte Carlo
MD	Molecular Dynamics
MSM	Multiscale Model
OCP	Open Circuit Potential
PDF	Probability Density Function
QM	Quantum Mechanics
QSAR	Quantitative Structure-Activity Relationship
SIESTA	Spanish Initiative for Electronic Simulations with Thousands of Atoms
SPH	Smoothed Particle Hydrodynamics
VASP	Vienna Ab-initio Simulation Package
XPS	Photoelectron spectroscopy

1.0 Introduction

Localised corrosion is the accelerated attack of a passivated metal at discrete sites in a corrosive environment. In a metal, it may initiate because of (i) a breakdown of the otherwise protective passive film and/or (ii) the presence of metal surface heterogeneities, such as grain boundaries or inclusions. Localised corrosion poses challenges for detection, and once initiated, the damage propagates rapidly, which results in unanticipated and sometimes catastrophic failures of the materials [1]. Localised corrosion may induce significant repair, maintenance and replacement costs of equipment, transport vessels or buildings [2]. Therefore, a successful development of purpose-designed corrosion-resistant alloys and inhibitors may have significant commercial benefits.

It is conceivable that future materials will be engineered from individual atoms or molecules, and researchers will be able to design molecular configurations and processing routes to obtain the required performance [3]. Key elements of a material are being designed on the molecular level (e.g., inhibitors and their interactions with metal surfaces), and the complexity and dimensions of these deliberately designed molecular elements will presumably increase in the near future. However, molecular design will permit myriad combinations (and permutations) that require validation to determine the most effective combinations. Combinatorial and high-throughput methods [4] are accelerating the pace of material discovery and optimisation. However, although they are faster than the traditional methods, these techniques are not sufficiently rapid and typically generate data only in the laboratory with no clear method of linking to the in-service performance. Combining computational modelling with high-throughput methods can not only significantly increase the speed of material discovery but also provide a link to the in-service performance. Using computational design, designers will be able to access realistic predictions of the properties and the performance based on the actual microstructure and the operating environment. In this regard, computational modelling may be considered a vertex of a triangle, where the other two vertices are represented by experimentation and the formulation of theories [5]. This comprehensive approach is especially beneficial in studying localised corrosion, where the inherently low rates of material removal make experimentation a relatively lengthy process, even under accelerated conditions.

Localised corrosion is inherently multiscale (see Fig. 1) because the nucleation and the propagation of pits are affected by phenomena on vastly different length and time scales (e.g., the surface interactions at the atomic scale vs. the environmental conditions that are described in the continuum scale). Thus, the corresponding computational design must be based on a multiscale approach. Fig. 1 illustrates the length scales of local corrosion from environmental conditions in the continuum, i.e., the macroscopic length scale, (e.g., [6]) to the mesoscopic scale that defines the material microstructure and ultimately to the atomic scale in charge transport phenomena (e.g., [7]). Despite this complexity, as a design tool, an effective multiscale model (MSM) [5, 8-11] must seamlessly combine the continuum and the atomistic descriptions of matter [12]. Future design [13, 14] at the molecular level will require this type of MSM. From this perspective, in the current work, the literature on such topics as the theoretical modelling of localised corrosion, the numerical techniques, the experimental knowledge required for model inputs and validation, and the limitations in software are critically reviewed. Several thoughts that are relevant to the development of a suitable framework for an MSM are also provided, and the challenges in the development task are highlighted. To the best of the present authors' knowledge, there is currently no comprehensive MSM in the public domain that simulates localised corrosion in metals from the atomic scale to the continuum scale, although an example of a prospective type has recently been stated [13]. However, there are MSMs for glass [11] and carbon [8] corrosion.

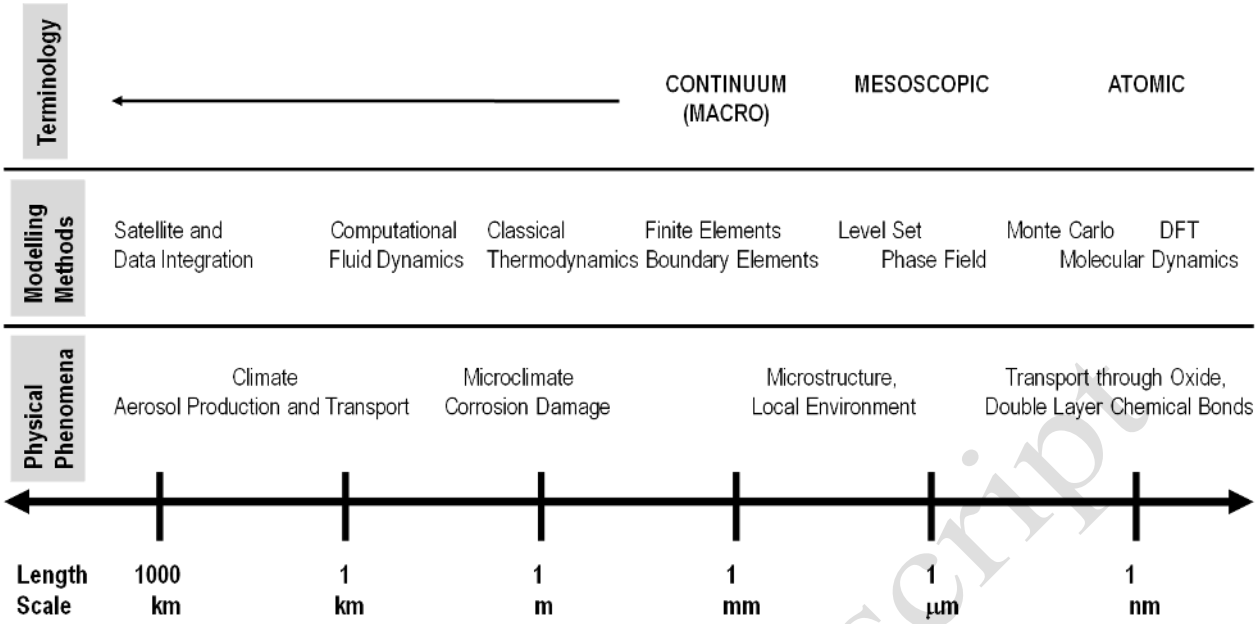

Figure 1: The spectrum of models to describe the electrochemical phenomena at various length scales (approximated)..

2.0 New paradigms for predictions

A prospective MSM on localised corrosion should provide more accurate and service-relevant predictions than the traditional approaches such as (i) the E-pH or Pourbaix diagrams (thermodynamics), (ii) the polarisation or Evans diagrams (kinetics) and (iii) the Nernst-Planck equation and the transport models that are based on the concentration solution theory. For example, the E-pH diagrams do not account for: (a) the transient behaviour (because they describe only the equilibrium states for given concentrations), (b) the localised variations in conditions such as concentration gradients, and (c) the highly influential features such as the alloy microstructure. Essentially, this thermodynamics-based empirical tool cannot be relied upon to predict the corrosion rates or the degree of passivity or for use in a non-equilibrium situation, although some useful extensions have been made [15] since its introduction. In addition, most Pourbaix diagrams only address pure metals and not alloys (an exception is Fe-Cr-Ni [16]). The polarisation diagrams do not consider mass transport limitations, which are important when there are concentration gradients in the electrolyte. In addition, different half-reactions (i.e., oxidation/ reduction) are activated at different potentials, and they depend on the microstructural features of the electrode and the microenvironment in the electrolyte; thus, several permutations and combinations of these polarisation curves are required to adequately describe an engineering system. Furthermore, the transport models heavily depend on the approximation of macro-homogeneity and local electroneutrality. Thus, the transport models neglect the atomistic details of the reactions and the inhibition mechanisms that occur on the metal or oxide surfaces. In addition, a common drawback of the above schemes is that they provide information at only one level. An ideal MSM should include strategies to overcome such limitations and the lack of resolution that accompanies the traditional techniques. For example, the alloy microstructure should be sufficiently described in terms of the metallurgical phases, their relative amounts, and their spatial distribution. However, to develop an MSM that provides a major advancement over traditional methods in the medium term, presently unavailable experimental data at the lower scales must be generated to describe the localised corrosion at an atomic level. Traditional electrochemical, surface analytical and spectroscopic studies only provide integral information on the electrochemical processes that occur at the solid/liquid interfaces, but they do not provide information on local atomistic events and the influence of surface imperfections on the interfacial processes [12]. In addition to such considerations, the MSM should seamlessly link the scales and be as computationally efficient as possible. In a recent review of MSMs in materials science, Elliot [5] noted that there are some promising strategies that are making progress at reducing the computational burden of models, in particular, at the lower scales. Thus, it is likely that a full-scale MSM can be solved within reasonable time frames in the not-so-distant future.

Types of existing models

3.1 Single scale models

Based on the assumptions about the behaviour of events (i.e., deterministic vs. stochastic) and the scales involved (atomic vs. continuum), currently, the available single-scale models may be divided into various categories (Table 1).

Table 1: Types of single-scale models that relate to localised corrosion.

	Main category	Sub category	Description	Example references
Categorised based on the assumptions relating to behaviour of events modelled	Determi-nistic	Atomic scale	Quantum Mechanics (QM) calculations are performed at the atomic level.	[17-21]
			Molecular Dynamics (MD) calculations are performed at the atomic scale	
		Continuum scale	Partial differential equations are solved using one of the following methods: analytical, Finite Element Method (FEM), Finite Difference Method (FDM), Boundary Element Method (BEM) or Finite Volume Method (FVM).	[22-30]
		Cellular Automaton (CA) models	In the CA models, the new state of a cell is a function of all states in the cell's neighbourhood at the previous moment in time. Most CA models follow deterministic rules to update the cell states (although the choice of the deterministic rule itself can be randomised)..	[31]
	Stochastic	Atomic scale	A Monte Carlo (MC) model that incorporates stochastic variability for the pit initiation and the pit widths.	[32]
		Continuum-Using Probability Density Functions (PDFs)	PDFs describe the likelihood that a pit would initiate at a given location at a given time under given conditions. PDFs are also applied in some cases for the pitting frequency, the pit incubation time and the pit generation rate.	[33-37] and review [38]
		Continuum - Using Artificial Neural Networks (ANNs)	The relationships between the causal parameters and the observed effects are developed without a deep knowledge of the physics. ANNs are criticised [39] for their "black box" nature, greater computational burden, etc.	[40-44] and review [45]
	Hybrid	Continuum scale	Combine elements of the deterministic models with those of the statistical models.	[46-48]

Currently, the deterministic models generally focus on the growth of a single, previously established pit (or crevice) or a collection of pits with predetermined anodic and cathodic sites. However, these models do not incorporate pit initiation events because the currently available experimental knowledge is insufficient to deterministically model the pit initiation, which is an atomic scale event

that is difficult to observe physically. Reigada et al. [32] note that this incomplete knowledge has led modellers to consider pit initiation as a sporadic and stochastic event, whose random nature manifests itself in both the distribution of induction time and the amount of current at a constant applied potential. Furthermore, the computationally intensive molecular dynamics (MD) methods such as the kinetic Monte Carlo (kMC) method are required to simulate atomistic events over distances that are relevant to pitting. Therefore, the extents of the systems that may be covered in those simulations are greatly limited, which reduces the practical value of such efforts, unless a multiscale approach was employed. Regardless, given the expanding body of evidence that pertains to the preferential initiation of pits at the microstructural features such as inclusions (e.g., [49]) and second-phase particles (e.g., [50]), it is increasingly likely that atomic scale deterministic models will be developed in the coming years.

Although the stochastic models are elegant tools to model the mechanisms that are not fully understood, ipso facto, they cannot be interrogated to gain a deeper understanding of the influences that are exerted by causal factors. Thus, these models lack the resolution to define a process at the level of detail that is necessary to design corrosion-resistant systems. In addition, the stochastic models that the present authors found were developed in the macroscopic scale, except for the MC model by Reigada et al. [32], which solved both the electrochemical responses and the morphological features by assuming that the pit propagation is a tunnelling process.

The unified models (e.g., [46-48]) have sought to combine the elements of the deterministic models and those of the statistical models to redress the limitations of the two approaches. For example, Laycock et al. [47] developed an experimentally validated hybrid model, where a purely stochastic model for pit initiation was combined with a deterministic model to propagate single pits in stainless steel (SS). Such an approach is perhaps most suitable for the early versions of the proposed MSM.

3.2 Linking of the scales

MSM may speed up computations by replacing the atomistic models with a less computationally demanding continuum assumption at locations that are removed from the region of interest. In addition, it extends material behaviour to the larger scales that represent the continuum realm. Thus, an MSM makes predictions relevant to the engineers.

Ingram [9] has discussed different frameworks that may be adopted to link the scales (Fig. 2). This figure shows how the two-scale domains may be linked in terms of the balance volumes (BVs) using six different frameworks. The broken lines show the regions where such balance volumes overlap. The BVs of the mesoscopic- and macroscopic- (continuum-) scale submodels are represented by $\sum_{\mu}$ and $\sum_{M}$, respectively. In a multidomain model (Fig. 2(a)), the BVs occupy the adjacent, non-overlapping parts of a system domain. In some cases, there is a small interface region between the domains where both models apply (Fig. 2(b)). In an embedded framework (Fig. 2(c)), $\sum_{M}$ spans the system domain, whereas $\sum_{\mu}$ describes only a portion of that domain. In the parallel framework, both models, which are labelled 1 and 2 in Fig. 2(d), span the system domain. In the serial framework (Fig. 2(e)), $\sum_{\mu}$ does not exist because the associated conservation equations are transformed into constitutive relationships. Finally, in the simultaneous framework, the whole system domain is described by $\sum_{\mu}$. No balance volume is associated with $\sum_{M}$ equations, since no conservation relations are used at this scale. More details on these frameworks, including how information is transferred between BVs, are provided by Ingram [9].

To circumvent the large computational load at the lower scales, the multiscale approach adopts coarse graining towards the higher scales. For example, in an embedded MSM [9, 51], an atomistic model may be embedded within a mesoscopic model, which can be embedded within a continuum scale model. Then, the lower-scale model can update the higher-scale model at regular time intervals with the corrosion damage information (e.g., [52] the simulating fracture). Moreover, one should also

consider the potential application of meshless methods [53-56] to pit propagation because these state-of-the-art techniques are being used increasingly successfully to simulate crack propagation (e.g., [53, 54]) in the field of computational material science. These methods are better suited to tackle the moving discontinuities such as crack propagation along arbitrary and complex paths, whereas the traditional FEM methods would involve considerable meshing and re-meshing. There are significant inherent challenges in attempting to link the scales, and these challenges are well understood [5, 12]. Elliot [5] and Tan [12] discussed several numerical methods that have been used for such linking at the boundaries of the two domains.. In Section 5.0, the present authors discuss the numerical difficulties that must be surmounted before a comprehensive MSM for localised corrosion may be successfully built.

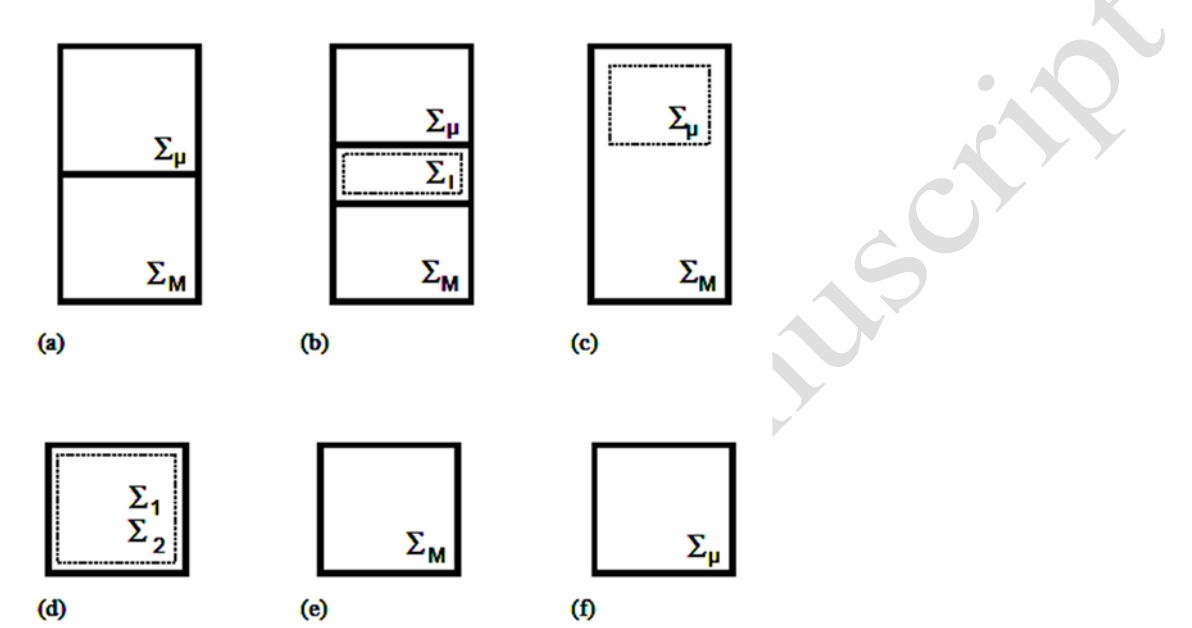

Figure 2: Framework class definitions [9] for the two-scale models: (a) multidomain, (b) multidomain (with interface zone), (c) embedded, (d) parallel, (e) serial, and (f) simultaneous.

4.0 Formulation of crucial phenomena

This section discusses the barriers and the data requirements for MSM, namely, the crucial parameters and events [57, 58] that influence the localised corrosion. This discussion on formulation ends with a pictorial summary (see Fig. 5 later) of the types of models that are currently used.

4.1 Microstructure of the metal substrate – its formation and influence

The microstructure of a metal or an alloy and its processing route control the sites of inclusions, the second-phase particles, the solute segregated grain boundaries, the flaws, the dislocations and the degree of surface roughness, all of which overwhelmingly influence the preferred locations for pit initiation. These quantities are discussed in detail elsewhere [15, 50, 59-61].

The present review suggests that the existing continuum models are too limiting in their treatment of the microstructure. However, there are early MSMs that may be used as starting points to build future MSMs which comprise microstructure evolution during solidification and link a microstructure to in-service performance.

4.1.1 Continuum models – rudimentary description of microstructures

Several early single-scale (continuum) corrosion models (Sharland [62]) and many recent works (e.g., [29, 63, 64]) did not consider the microstructure. However, the modellers who did, assumed the microstructure as a given. The modellers who followed the deterministic path (e.g., [65-67]) have defined the microstructure either in their computational grids [65, 66] or treated them as a regular array and used analytical solution methods [67]. The modellers who work in the stochastic realm have used PDFs (e.g., [68]) to account for the probabilistic nature of the features. Brown and Barnard [65, 66] incorporated the microstructure that defines a certain electrochemical property (e.g., different Tafel dissolution kinetics for individual phases) for each Finite Difference Method (FDM) computational cell. Their latter model [65] could predict the distribution of cathodic regions. Jakab et al. [67] also developed a simplified deterministic model by treating a heterogeneous AA2024-T3 electrode as a regular array of Cu-rich favoured cathodic sites (partially covered with an inactive aluminium oxide layer) in a benign Al matrix.. Furthermore, Zhang et al. [68] developed a stochastic model for the same ally AA2024-T3, which, according to the authors, provided a new approach to the prediction and the quantification of localised corrosion kinetics based on the alloy microstructure. Their PDFs for grain dimensions had parameters that were fitted based on the observed three-dimensional grain sizes, and a 'brick wall model' was used to model the grains (and the inter-granular regions) in 3D. There are also empirical models that correlate the corrosion consequences with the microstructural aspects. For example, Cavanaugh et al. [69] developed an empirical relationship between the accumulated corrosion damage in AA7075-T651 and the physical and electrochemical characteristics of the intermetallic particles, and this model predicted the pit radii (assuming hemispherical pitting) as a function of the immersion time in the 0.1 M NaCl. However, such models have limited applicability and cannot be relied upon for any experimental conditions other than those for which they were developed. In summary, the traditional continuum models that incorporate the microstructure have assumed it as a given quantity and have described it in relatively simplistic terms. No work appears to have considered details such as the recently observed [70] non-random clustering of buried intermetallic particles in AA2024.

4.1.2 MSMs for solidification and prediction of service life – early versions are promising

4.1.2.1 Microstructure evolution during solidification

The formation of microstructure originates at the atomic scale, where the initial nucleation and the growth of critical nuclei occur [10]. This formation is followed by the growth of microstructure at the intermediate mesoscopic scale. Rafii-Tabar and Chirazi [10] have reviewed several deterministic, stochastic, hybrid models and some early multiscale models that predict the microstructure evolution; they have also developed a well-documented, validated, generic MSM that spanned the nano-meso-continuum scales for microstructure formation (Fig. 3).

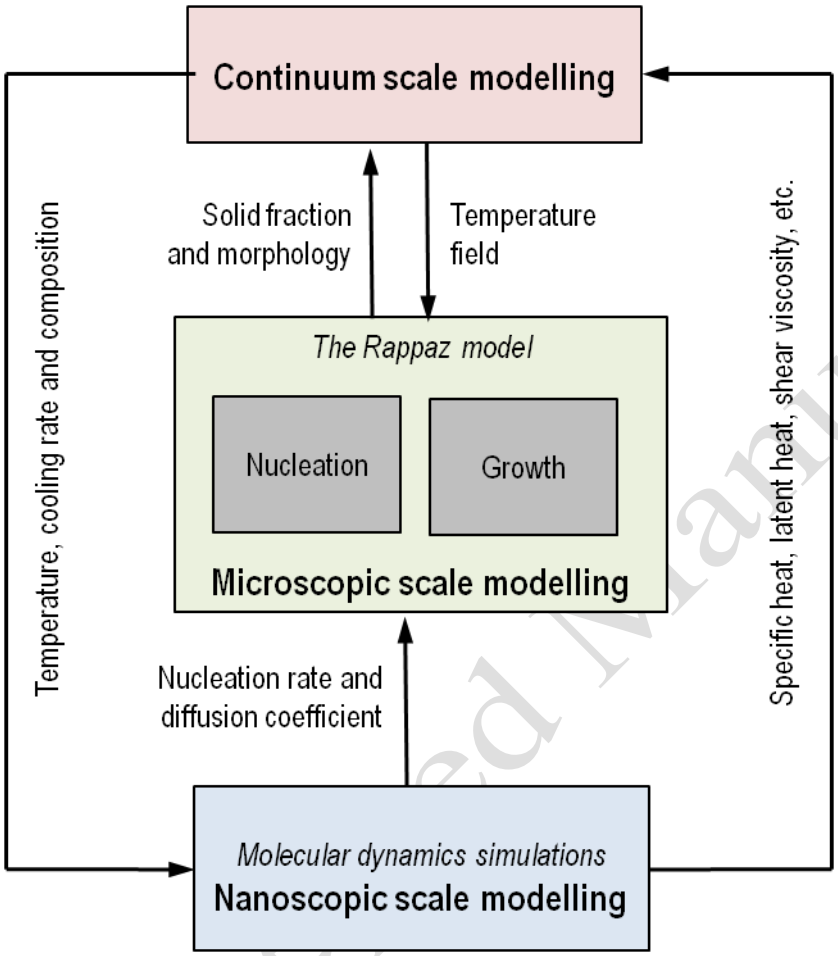

Figure 3: A multiscale model for solidification by Rafii-Tabar and Cherazi [10].

Their MSM is representative of the limited number of available MSMs for microstructure prediction that can be linked to an MSM for localised corrosion. In the Rafii-Tabar and Chirazi model (Fig. 3), MD simulation techniques were used at the atomic scale and linked to a cellular-automaton (CA) - based mesoscopic model for microstructures. The Rappaz model [71] that was used for the microstructure combined a stochastic approach to the nucleation of grains (which was implemented using CA) with a deterministic, diffusion-controlled approach to their growth. The parameters that were used in the Rappaz model were calculated using MD simulations. Finally, the continuum scale simulations were performed based on finite-element (FE) and finite-volume (FV) techniques. The models at different scales were executed independently and coupled through databases using a serial framework (Fig. 2(e)). The procedure was to associate an MD simulation box with a CA volume to couple the nano-meso models, followed by associating a CA volume with a finite volume to couple the meso-macro models. Because only one-way coupling is possible in a serial framework, and because the three scale models were run separately using different codes, it was necessary to run the meso and macro models more than once to achieve the two-way coupling between the scales through

iteration. For example, in its first run, the meso model generated the inputs for the macro model, and in the second run, which was performed after the macro model had predicted the temperature evolutions, it predicted the microstructure based on the temperature histories and the cooling rates.

4.1.2.2 Influence of microstructure on the in-service performance

The MSMs to link microstructure with the in-service performance at continuum scales for steel were published by research teams that were led by Olson [72, 73]. From these MSMs, some concepts and strategies could be borrowed to incorporate the influence of microstructure on the corrosion performance at higher scales. The Olson models link the microstructure of steels with failure scenarios such as ductile fracture by predicting the relevant properties. The microstructure was decomposed into multiple scales using a nested domain framework (i.e., an extension of the embedded framework, Fig. 2(c)). The continuum scale was linked to an embedded microscopic scale (primary inclusion particles) and again to another embedded sub-microscopic scale (secondary inclusion particles). Thus, their finite elements solutions could account for the influence of inclusions during fracture in terms of the particle size and the carbide/ matrix debonding stress.

4.1.3 Recent advances

Amongst MSMs for solidification that span all scales, because the Rafii-Tabar and Chiraz model [10] applies in its current form only to binary alloys, the important effect of the alloying elements on the corrosion morphology [50] cannot yet be modelled. Therefore, the more recently developed and validated MSM models [74-76] are more attractive for the corrosion modellers who work with engineering alloys, although these models span only the meso to continuum length scales and the associated temporal scales. These latter models are useful because they are capable of handling both ternary [74, 76] and quaternary [75] alloys that are industrially more relevant. These 3D models can also account for the influence and the interaction of multiple phases (solid/liquid/gas) during the microstructure development. In addition, some of the latter models (e.g., Wang et al. [75]) have further enhanced their realistic nature by accounting for the effects of the cooling rates and the alloy content in their prediction of the microstructural features that included the shape, the size and the distribution of the intermetallics and the defects such as porosity. The main output of these models is typically a suggested deterministic microstructure. The information flow between the two levels in the Wang et al. [75] model was facilitated through the coupling of temperature and pressure variables (see Reference [76]). In addition, the lower-scale model was implemented as a subroutine of the macro model, which was solved using FEM in an embedded multiscale framework (Fig. 2). The meso-scale sub-region formed a total volume fraction of approximately 0.001% of the domain volume that was covered by the continuum scale model, which allowed for the mesh sizes in the meso model to be on the order of μm. In summary, the microstructure-evolution-related MSMs treated the nucleation events stochastically (e.g., with a pre-set nuclei density and a nucleation potential with a Gaussian distribution PDF [75]) and modelled the growth events deterministically using a hybrid strategy. Thus, there is no purely deterministic microstructural model. Regarding MSMs for linking the microstructure to the prediction of service life, validated works [72, 73] by Olson's teams appear to be the most preeminent, and their strategies may be used as a basis to link the microstructure to the in-service corrosion performance in MSMs.

4.1.4 Proposed improvements

Because the existing models on corrosion treat microstructure as a given quantity or have a simplistic description of microstructure, the ability of an MSM (that incorporate such models) to tailor materials is limited. An MSM on microstructure prediction should ideally be linked to an MSM on localised corrosion, so that through a feedback loop, the alloy system may be optimised for corrosion performance. Furthermore, none of the existing models account for the formation of the oxide layer (Section 4.2 below), and they do not provide other corrosion-related information such as the interfacial energies at the grain boundaries and the grain mismatch, which are indicators [77] of the propensity of various sites to corrode in some cases. Therefore, in the long term, it is desirable to have

the microstructure model also predict the composition and the morphology of the oxide film. Recently, promising efforts at atomistically simulating the precipitation kinetics in the solidification of multicomponent interstitial/ substitutional alloys [78] have been published. It is also desirable to predict the surface roughness characteristics. However, in the short term, the prescription of the entire final microstructure as a given quantity remains a convenient starting point.

4.2 Passivating oxide film, its thickness and its porous nature

The phases that make up an oxide film that forms on the surface of a substrate are often traditionally identified using Pourbaix diagrams [59], although these diagrams only describe the equilibrium phase distributions. The passivating nature of the film is attributable to its limiting influence on charge transport between the electrolyte and the substrate. The oxide film thickness varies between nanometres (e.g.,[79, 80]) and single-digit micrometres (e.g., [81]). Different oxides have different degrees of stability depending on the environmental parameters [82] such as [81] the pH, the corrosion product concentration and the ionic species. Almost all passive films have multilayer structures, usually with the inner oxide and the outer hydroxide parts, the former is the barrier layer against cation transfer, and the latter is an exchange layer with the electrolyte [83]. A review [7] on passive films at the nanoscale has provided rare insights into the structure and the growth of oxide films based on recently observed atomistic level details. In addition, the passivating films of Zn and Fe are crystalline oxide grains with grain boundaries, whereas those of Al alloys and SSs are amorphous in structure [84].The electrochemical behaviour of the oxide film, its thickness and its chemical composition depend on numerous parameters [79, 85-88]. Because this oxide film is somewhat analogous to the artificial coatings [86, 89, 90] that are designed to decelerate corrosion, some comments in this section are equally applicable to those coatings. The Pourbaix diagrams cannot be accurately applied to passive films that are non-equilibrium structures, the existence of which depends upon an appropriate relationship between the rate of formation and the rate of destruction [91]. The recently introduced Kinetic Stability Diagrams (KSDs) [91, 92] may provide a means to calculate the corrosion rates for alloys if they are further developed; however, their construction is tedious because there are numerous possible combinations of electrode potentials, ionic concentrations and pH.

The present review notes that the continuum models do not have sufficient resolution to describe the atomistic mechanisms, and a lack of experimental data at lower scales makes it more difficult for atomistic models to be developed in the short term to describe the behaviour of oxide films.

4.2.1 Continuum models – lack resolution

4.2.1.1 Transport through the oxide film

Crystalline oxides: Several continuum phenomenological growth kinetic models have been proposed to model the growth of oxides and the rate-limiting cation-transport mechanism through the oxide thickness. Many of these models have been reviewed by Hendy et al. [21]. All of these models assume the homogeneity of the crystalline oxide to which they are applicable and have several free parameters that must be fitted empirically. Hendy et al. [21] showed that by comparing their own ab initio simulations with those of the phenomenological models, that the latter models were consistent with the calculated barrier energies only if it was assumed that the grain boundary diffusion of cations dominated. These results are consistent with the sentiments of Marcus et al. [28], who proposed that the cations would preferentially migrate through the more electrically conducting inter-granular regions. These findings highlight the importance of considering the grain boundary structure and their inter-connectivity in the modelling efforts.

Amorphous oxides: For these oxides, models that relate to ionic conduction have been relatively scarce. In a model that was proposed by Wang and Hebert [93], the current was carried by defect

clusters, which were created by the inward displacement of O^{2-} ions around an O vacancy in response to the vacancy's electric field. The model hypothesised that the displacement created a gap between the first layer and the second layer of O^{2-} ions that surrounded the vacancy, within which the metal ions could easily migrate with little required activation energy. The analytically solved steady state equations were satisfactorily validated using experimental results.

4.2.1.2 Interactions between the oxide film and the electrolyte

The interactions between the oxide and the electrolyte determine the rate of electron transfer presumably by altering the electronic work function at the interface (e.g., Vago et. al [94]). However, although phenomena such as O_2 reduction, oxide transformations and electron transfers to redox species in a solution occur at an atomic scale, it would seem that atomic scale models are not yet available in the public domain. Only continuum scale analytical models by Jakab et al. [67] and Chen et al. [95] appear to address this phenomenon. In some cases such as the ZnO system, the ability of oxides to act as reducing sites can significantly change the nature of the cathode and reduce the diffusion limits [96]. For example, when pH<5, the cathodic reactions in the Zn system are rate-determining [61]. In such cases, the model must account for the scenario where the porous layer on the metal surface either competes with or complements the oxygen reduction reaction (ORR) that occurs on the metal surface. This scenario can be affected by many factors, and a recent continuum scale porous-electrode model [97] has incorporated some of those influences. Nevertheless, an atomistic-level deterministic treatment of the interactions is preferred because the mechanisms at play operate at that level.

Although the metal surface can ideally be represented using a crystalline lattice, the oxide layer may or may not be crystalline depending on the metal and the conditions under which the oxide is formed. Most amorphous solids are initially hard, deform notably little, reach their plastic limit early and break because they have a high strength and a low ductility ([98]). Multiscale modelling of amorphous solids is far less advanced than in crystals because of the limited understanding of the behaviour of plasticity in amorphous materials. The integrity of the oxide layer on an active metal is highly influenced by the stresses that the metal beneath experiences. These stresses can locally rupture the oxide layer, which leads to cracks (also known as holidays), through which the corrosive solution can percolate and reach the surface of the metal. In addition, when the oxide layers host a cathodic oxygen reduction, the net corrosion rate becomes vastly different from a situation where the oxide layers do not host such an electrochemical reaction. FEM could ideally handle this situation in the continuum description. Note that unless the oxide layer is electrochemically active, we may not be required to model the entire oxide layer in a multiscale manner even if the oxide breaks down locally.

4.2.2 Atomistic models and paucity of data at the atomic scale

The continuum assumption of a uniform passivating layer for the complex heterogeneous structure of the oxide film is quite inadequate. In addition, as noted by Williams et al. [99], although the continuum models for migration and accumulation of point defects in the film are appropriate to describe the behaviour of high-purity single-phase metals, they are inefficient for the engineering alloys. Thus, atomic scale models are required. Maurice and Marcus [7] reviewed some of the atomistic models and highlighted their usefulness in helping one understand the mechanisms that occur at the lower scales. The ab initio model of Bouzoubaa et al. [18] predicted that the surface undulations on the oxide film played a major role in its chloride thinning mechanism. Kim et al. [100] used DFT to understand the origins of the natively n-type characteristics of ZnO by modelling the interaction of a Zn interstitial with an oxygen vacancy. The 3D atomistic model of Diawara et al. [101] successfully modelled the selective dissolution and the passivation of Fe-Cr alloys by simulating the formation of oxide nuclei from chromium-rich clusters on the surface. This model confirmed the experimental observation that Cr preferentially diffused towards the Cr clusters on the surface, whereas iron atoms showed no such preferential diffusion. Their kinetic Monte Carlo (kMC) model also showed that passivation occurred within a matter of seconds. The ab initio modelling work by Costa et al. [20] on SSs studied the effect of water coverages in the Cr_2O_3 film on the surface, and

the energies of adsorption that it predicted were successfully validated with experimental data. Similarly, Hendy et al. [21] calculated the energy barriers that were associated with the transport of cations through the oxide film by combining ab initio simulations with experimental observations at the atomic scale. These investigations reinforce the value in modelling the film at the atomic scale. However, in this connection, Maurice and Marcus [7] noted that the development of such models will be limited by the complexity involved in considering the three phases (alloy substrate/ oxide/ electrolyte), their interfaces, the electric field, the temperature, the orientation of the oxide film, its nanostructural defects and the surface defects. The issue of heterogeneous passive films on engineering alloys makes it critically important to select *what* is modelled. The examples above are limited in terms of computational load when attempting to model engineering alloys even with a reasonably low concentration (in relation to the number of atoms that can be considered in the ab initio methods) of second-phase particles. This problem is even more challenging when pit initiation is considered. Current ab initio models are rather weak at modelling the defects that exist at second-phase particles in a matrix because the required number of atoms is too high.

The relative scarcity of models at the atomic scale is unsurprising given the computational burden that we discussed above and because the experimentalists could not observe the oxide film in detail at an atomistic level [28, 79] until recently. Nevertheless, there is an increasing amount of literature (e.g., [79, 99, 102, 103]) that addresses such measurements, slowly filling the present gap in knowledge at such length scales.

4.2.3 Proposed improvements

The oxide film is a classic example of the need for a multiscale approach to corrosion modelling because its atomic scale thickness is coupled with its mesoscopic-scale microstructure, which is punctuated with continuum scale defects. Thus, either a 3-scale approach or a less comprehensive 2-scale platform (meso/ continuum scales) may be chosen to model the film. However, in the latter approach, a generic phenomenological model that adequately describes in the meso or continuum scales those mechanisms ([104, 105]) which actually occur in the nanoscale - through derived transport and kinetic parameters - will be considered mandatory. The advanced version of a prospective MSM should have the capacity to predict the oxide composition and structure (both geometric and electronic), including its thickness and its porosity distribution, based on a given microstructure of the substrate and the electrochemical environment. Of course, this hypothesis assumes that sufficient experimental data become available for validation in the short to medium term. For a deterministic model to have a strong predictive capability in relation to the electrochemical behaviour of the oxide film, the following must be undertaken [106]: (a) the kinetic and the transport parameters that are pertinent to different metallic constituents of the film must be determined either based on the available values or using advanced experimental techniques, and (b) the energy heterogeneity of the transport medium must be considered using the distribution functions for the diffusion coefficients of individual species in the compact film and by quantifying the role of the grain boundaries in the transfer of matter and charge through such a film. The model should also account for the interaction between the film and the environment using kinetic data (and thermodynamic data if the temperature influence is considered) on the adsorption, the surface complex formation and the re-precipitation reactions of various cations at different pH levels and locations of the oxide. It is also desirable that the atomistic modelling of nano-scale events such as the oxide penetration/ thinning mechanism (e.g., [18, 28]), which leads to the prediction of nucleation sites. In addition, some of the free parameters required for the phenomenological models may be determined from first principles through such simulations where theories are available, rather than being fitted empirically. However, given the enormous effort and time required to achieve all of the above, the early versions of an MSM are likely to incorporate approximations for many of the aforementioned aspects.

4.3 The influence of aggressive ions (pH and Cl^-) and the role of inhibitors

The acidity or the alkalinity of the environment significantly affects the corrosion behaviour of metals, and there are several rules and exceptions that govern such behaviour [50, 57, 59, 61, 107]. Traditionally, the influence of pH on the corrosion tendency of metals in aqueous solutions of a given concentration has been described using the Pourbaix diagrams, the limitations of which have been mentioned in Section 2.0 (see also [92]). The inhibitor molecules in the electrolyte also significantly influent the corrosion rates, but unlike Cl- ions, they slow down corrosion. Inhibitors are an attractive option when thick coatings are either unacceptable for isolating the metal from the electrolyte or when coatings may become damaged. In addition, inhibitors work by adsorbing onto the metal surface at its interface with the electrolyte [108] and creating nanometre-thick films instead of the usually millimetre-thick coating layers.

The current review found that the continuum scale models could not be used in a generic MSM because of their lack of generality, and the rapidly improving suites of atomistic modelling software packages are increasingly facilitating the modelling in this area at lower scales.

4.3.1 Continuum models – lack of universal applicability

Traditional models [25, 47, 62, 109-114] have either neglected the influence of pH or Cl- or incorporated their influence in a rudimentary manner. Sharland [62] has reviewed some of these models. More recently, as noted by Frankel and Sridhar [115], a Point Defect Model (PDM) [116] incorporating empirically determined parameters correctly predicted the logarithmic dependency of pit initiation on Cl^- concentration, although it could not calculate the often observed bi-logarithmic dependence. The Cl^- influence was integrated in the PDM by hypothesising that its concentration altered the generation and the transport of cation vacancies. A simplified PDM for iron [117], which was based on the High Field Model (HFM) formulation, also predicted the correct qualitative trend for the dependence of the film thickness on the pH of the electrolyte. Nevertheless, neither PDM nor HFM can be universally applied (they are only valid for crystalline materials) and are limited by the assumptions (e.g., homogeneous oxide) and the need to fit the parameters empirically for each scenario. Lastly, the effect of the inhibitors has not been tackled by continuum models as much as the present authors are aware, which is understandable given the patent lack of resolution of such models in accounting for the surface/liquid interactions at the molecular level. In summary, traditional approaches such as the Pourbaix diagrams are inadequate, and the continuum models lack universal applicability and resolution in describing non-homogeneous microstructure. Thus, although some traditional models may have to be used in early versions of an MSM, a truly generic advanced MSM will require more detailed modelling at the lower scales.

4.3.2 Atomistic models – promising, but currently at early stages

The atomistic models of more recent origin have shown promise in this area by incorporating the influence of ions in the aqueous solution from a more fundamental point of view. Molecular or atomistic modelling brings to multiscale modelling a unique tool that can discriminate behaviour on the molecular scale [118, 119] and allow a molecular design. Consider the development of organic corrosion inhibitors. Their performance is strongly controlled by bonding (electron sharing) and the type of pendant functional groups that are attached to aromatic rings. However, the exact molecular structure has a critical impact on the inhibition performance; because conventionally, inhibition is measured by exposure of metal plates in inhibited solution or by electrochemical tests, a direct correlation to the inhibitor's efficiency does not exist because of the multiple scales that are involved. Hence, incorporating molecular modelling into a multiscale modelling framework offers the possibility of forming a continuous link from the molecular structure to the inhibition of anode and cathodic activity on the surface, which inhibits corrosion.

4.3.2.1 Density functional theory methods

A detailed account of the evolution of how the Schrodinger's equation is solved in DFT can be found in texts, e.g., [120]. In the modelling of surface/molecular interactions (such as inhibitors), the most commonly used basis sets are plane waves (see Table 2). The localised basis sets first approach (e.g., in SIESTA) the edge plane waves (e.g., in Quantum Espresso) because of the lower computational requirements that are associated with modelling the vacuum space.

Table 2: DFT software packages.

Package/Code	**Available levels of exchange correlation approximation**	**Basis set formulation**
VASP or Vienna Ab-initio Simulation Package	LSDA, GGA, Meta GGA, Hybrid	Plane wave
SIESTA or Spanish Initiative for Electronic Simulations with Thousands of Atoms	LSDA, GGA, Hybrid*	Linear Combination of Atomic Orbitals (LCAO)
Gaussian	LSDA, GGA, Hybrid	Gaussian Type Orbitals (GTO)
Quantum Espresso	LSDA, GGA, Hybrid	Plane wave

LDA - Local Density Approximation
GGA – Generalised Gradient Approximation
LCAO – Localised Combination of Atomic Orbitals

Taylor [121] has reviewed some works in this space. Bouzoubaa et al. [18] modelled the aggressive role of Cl^- in breaking down the passivity of the crystalline NiO using a periodic DFT. They intended to investigate the interaction of these ions with a stepped surface on the hydroxylated NiO film, which is characteristic of the barrier oxide layer on passivated nickel. The results suggested that adsorption of Cl by exchange with surface hydroxyls is energetically favourable but may not promote dissolution. Sub-surface insertion into the lattice was found to promote dissolution only if the Cl surface coverage was > 70%, which is unlikely because of the Cl-Cl repulsions. Thus, this work, which was performed on a defect-free surface, did not confirm the existing hypotheses of adsorption-induced surface thinning or Cl subsurface penetration. Bouzoubaa et al. later extended their work to include various halides [17]. Although a final word on the hypotheses cannot be provided until a more realistic surface with defects is simulated, the above works display the power of atomistic simulations besides putting conventional wisdom to the test.

4.3.2.2 Inhibitor/surface modelling

Inhibitors also have been modelled at the atomic scale by several workers (e.g., [122-129]), and the literature contains a wide range of approaches to model their interactions and electrochemical effects, some of which were reviewed by Gece [122]. In addition, although several software codes such as VASP, Gaussian and Quantum Espresso have been used, a relatively recent entrant known as SIESTA [128] appears promising in the area of inhibitors because its underlying method can describe well the interaction event. Much of the current work models the structures of inhibitors in vacuum [130, 131] and obtains the correlations [132, 133] with percent inhibition for a metal in an inhibited saline

solution. However, more recent studies [134] include solvation effects, examine an inhibitor's binding to the surface, consider the charge double layer [135] and model the actual kinetics of the cathodic reaction [124, 136]. The effect of solvation is considered by placing water molecules in vacuum. However, two issues must be overcome [134]: a) the probable water structure must be estimated prior to its placement (otherwise, the DFT code will spend all of its time to optimise the water structure), and b) the long-range interactions such as hydrogen bonding and dispersion/Van der Waals forces must be included. To include the dispersion forces, it is necessary to add an auxiliary force field to the DFT calculation with a number of approaches that are developed to do so including: a) the non-local functional (vdW-DF functional) of Langreth and Lundqvist [137], b) the modified pseudopotentials (von Lilienfeld et al.[138], c) the highly empirical (hybrid) metaGGA functionals [139], and d) the interatomic (pairwise or beyond) dispersion corrections such as that of Grimme [140]. The approaches vary widely; for example, Langreth and Lundqvist explicitly incorporated the pairwise point-point interaction while ignoring the non-additive many-body interactions, whereas Grimme's approach is a highly empirical approach based on the parameterisation of the interaction energies.

4.3.2.3 Modelling the electric double layer

Generally, the double layer effect on metal surfaces is modelled by adding or removing a charge from the unit cell of the metal and balancing with a homogeneously applied counter [140]. This approach can be problematic in plane-wave methods such as those used in VASP because the charge may not be well localised. Spohr [141] has reported an increase in the use of ab initio models to simulate the interfacial interactions between the electrolyte and the solid substrate by modelling the electric double layer. One such work is by Taylor et al. [142], who examined the double layer regions for water over a range of metals and compared the equilibrium potentials for the initial steps of water reduction and oxidation at the surface with known experimental quantities. Spohr [141] and Yeh [143] found that the inclusion of an explicit solvation provides more realistic reaction energetics in comparison to the solutions in vacuum. Similarly, in a related work, Janik et al. [124] simulated the electronic double layer by adding various numbers of electrons in a Pt unit cell and adding a compensating background charge. However, Taylor et al. [144] noted that the effect of charge addition highly depends on the orientation of water dipoles of the chosen solvation structure, and the fluctuations of the water molecule orientation can induce instabilities in the charge localisation. This phenomenon allowed the potential at the surface to be controlled by adding fractions of charge. They concluded that: (i) the increasing use of molecular simulations allows the combination of statistical mechanical description of the double layer with a description of elementary chemical processes on the electronic structure level; (ii) the free-energy methods are applied to describe the chemical reactivity within and beyond the framework of the continuum Marcus theory of electron transfer [145], and (iii) at sufficiently high concentrations, direct simulations of the two-phase systems with an aqueous solution and a charged or uncharged solid phase or surface can model the entire double layer region. Taylor [121] also discussed the specific types of information that may be garnered from DFT simulations of various metal-environment interactions and the associated challenges. To summarise, the atomistic models that address different mechanisms at the electrolyte/electrode interface, including the influence of ions, have begun to appear in the open domain and have provided useful insights into the interfacial dynamics. In the large domain of inhibitors, although significant progress is being made, major challenges must be resolved, including how to effectively model the solvation, the potential and the chemical reactions at the double layer of the metal/solution interface.

4.3.2.4 Bridging the nano-gap

The design of inhibitors must span the scales from 10^{-10} m to 10^{-1} m (the scale of a test plate) and cover a wide range of phenomena (see Fig. 4). The properties derived from DFT in vacuum studies may not be relevant to the inhibitor surface binding and the link between the molecular properties and the mesoscale phenomena such as anode/ cathode development, pit initiation, and pit growth is not evident. Thus, a large gap currently exists between the DFT models and the measured inhibitor efficiency in terms of both scale and phenomena. This gap is often [133] covered using a pattern recognition or a neural network approach such as the Quantitative Structure Activity Relationships

(QSAR). In the near future, the DFT models will likely accurately include the solvation effects and model the competitive reactions (i.e., oxygen reduction vs. inhibitor absorption), and the local electrochemical techniques such as local EIS can be used to develop refined local parameters and their spatial variation (e.g., coating resistance or diffusional properties), whereas the post-test analytical procedures can examine the structure of the protective layers on the metal surface (i.e., using photoelectron spectroscopy (XPS), etc.) down to the sub-micron scale. Two additional developments can further close this gap. The DFT studies can be linked to MD studies, which will allow an order-of-magnitude expansion on the molecular scale [125]. Lastly, most electrochemical formulations are based on the Butler-Volmer equation, which provides an average free energy formulation of charge transfer but does not examine the individual processes that are involved in such transfer. Recent phenomenological models [146] break down the charge transfer in the solution into a number of components and allow each component to be addressed, which effectively refines the electrochemical scale.

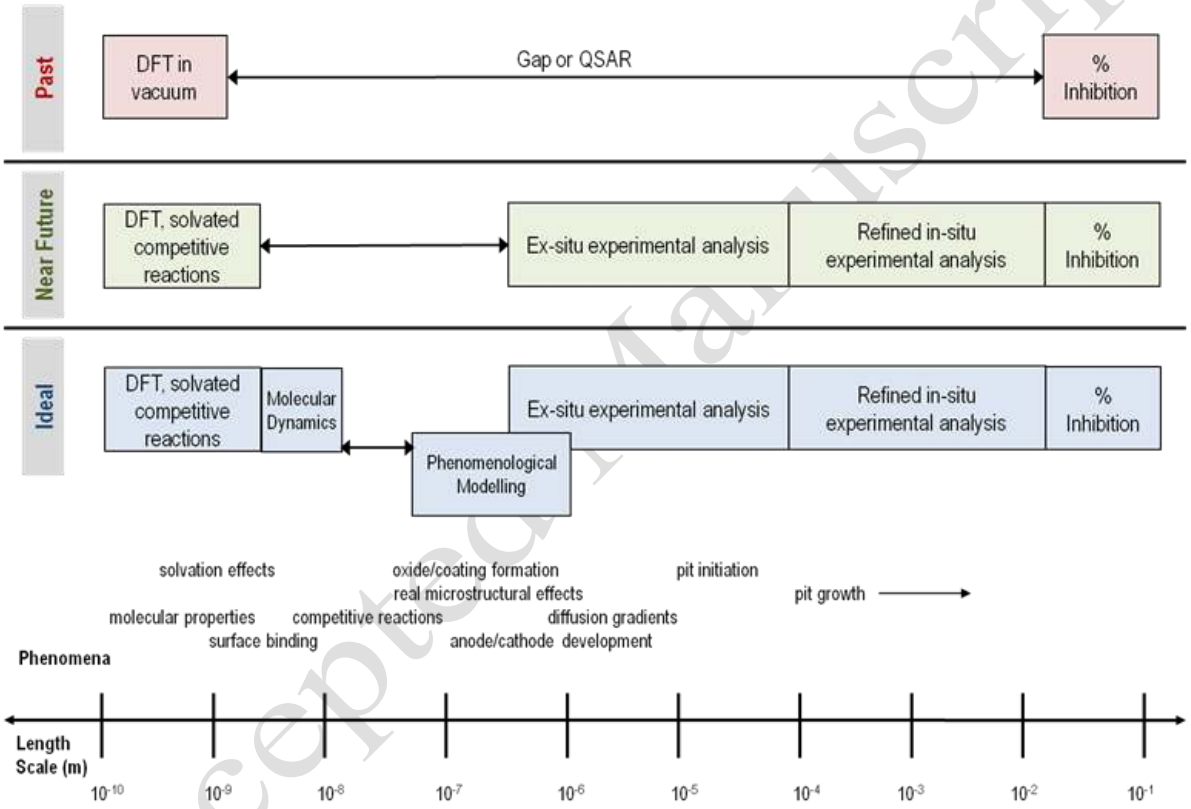

Figure 4: The "nano-gap" between the DFT models and the measured inhibitor efficiency.

At this point, a brief note about the use of ex-situ techniques such as XPS is appropriate. In such techniques, the specimens are removed from the experimental solution and placed in vacuum for examination. Such inspection under vacuum may significantly alter some aspect of the surface; for example, dehydration can occur, and the physio-sorption between the inhibitor and the surface will not be maintained, although chemical bonding and chemo sorption in particular will be. Thus, such techniques must be used with care, but they can provide valuable information.

4.3.3 Proposed improvements

Based on atomic modelling, a more fundamental approach can be used for both crystalline oxides [21] and the amorphous variety [147] and is well-suited to describe the solid/oxide bonding [148] and oxide/electrolyte interactions [17, 18, 141]. This approach is likely the preferred option for a design-optimisation MSM because of the fine resolution that it provides. There is currently no such exhaustive and generic model, and until one becomes available, empirical correlations that are based on mesoscopic and continuum scale models must be used to build an MSM. In the intervening period, however, it may be possible to explore the use of KSDs to model the influence of pH and aggressive ions at the higher mesoscopic and continuum scales. The current DFT work addresses the accuracy of surface-binding studies and can also examine the competition between inhibitor binding and the cathodic reactions. Hence, the objective of correlating DFT or MD [149] studies with a coarse parameter such as the experimental inhibition efficiency may have to be modified in the light of data from electrochemical and analytical techniques such as XPS, which probes the surface. Lastly, most electrochemical kinetic models are based on the Butler–Volmer equation, which provides an average free energy formulation of charge transfer but does not examine the individual processes that are involved in such transfer. The proposed MSM should also address the commonly used but inaccurate assumption that uniform conditions exist in the bulk solution; for example, this assumption often neglects the concentration gradients that extend into the bulk solution from a pit or a crevice.

4.4 Establishment of anodic and cathodic sites

Anodic and cathodic sites are characterised by different potentials because of the variations in chemical composition encountered in the alloy and/or the electrolyte. These two quantities (i.e., potential and composition) are coupled in the electrolyte through the Nernst equation under equilibrium conditions. For a large cathode area with a small anode area [150], the distance between these sites [151] and the protective films that formed on their surfaces affect the corrosion rate. A small anode area results in the rapid penetration of the pit or the crevice because the current density at the small anode is notably high, and the anodic polarisation in chloride solutions is extremely limited. When the cathode size is limited [22], the limiting corrosion current is determined by the size of the cathode (e.g.,[152]). The establishment of the anodic and cathodic sites is dictated by several factors, which are mentioned elsewhere [59, 61, 69, 150, 153-158].

The present review suggested that the continuum scale models lack the necessary resolution to describe anodic and cathodic sites and that the development of more suitable atomistic models will need to be supported by the generation of experimental data at the lower scales.

4.4.1 Continuum models - contain limiting assumptions

The continuum philosophy considers that whilst the potential difference on the corroding surface is zero, there are anodic partial currents across the metal-electrolyte interface at microscopic surface sites, the total of which is balanced by an equal value of the total cathodic current that is similarly distributed under free corrosion conditions. This balance is achieved at the open circuit potential (OCP) of the “homogeneous” metal substrate, and is determined by the rates of the partial electrochemical reactions [159] (which are described by either the Tafel or the Butler-Volmer equations). This information is sufficient for modelling the O_2 reduction-driven cathodic tendency only when the influence of the microscopic inclusions and the alloying elements are ignored. There is a limited number of continuum works (e.g., [160]) that address the anode-cathode separation, and they are rudimentary. A model that automatically predicts the anode-cathode separation by solving the mixed potential problem was developed by Venkatraman et al. [64] for corrosion under a differentially aerated NaCl droplet, which was deposited on a Zn substrate. The surface was assumed to be homogeneous; thus, no microstructural details were considered. The previously visited model of Brown and Barnard [65] could predict the cathodic regions. More recently, researchers have started to address the microstructural inhomogeneity-driven phenomena that are relevant to the anode-cathode

separation in alloys, e.g., the previously discussed model of Jakab et al. [67] (Section 4.1). In addition, Alodan [161] simulated O_2 reduction using an approximated alloy-like microstructure and employed circular discs for the cathodes (inclusions), which were surrounded by an annulus-like region for the anode (aluminium). Although these latter models represent a step forward in the simulation of engineering alloys, they still suffer from the over-simplification of the microstructure. Valutrin-Ul et al. [31, 162] developed a cellular automata (CA) -based mesoscopic model with a random walk of H^+ and OH^- ions, where the spatial separation between the anodic and the cathodic sites could be made smaller than that in the continuum scale; thus, the model could more realistically locate discrete cathodic and anodic sites as interwoven within a propagating pit (i.e., not only on the side walls) based on the solution pH at the mesoscopic vicinity. This model was unlike most continuum models, where the cathodic sites are usually located outside the anodic pit or crevice or simply assumed to be along the side walls of a pit. Although it constituted a step up from the continuum scale models in terms of details, the model still lacked the resolution to handle the microstructural details of engineering alloys and was limited by the approximations that described atomistic phenomena at the mesoscopic scale. Therefore, lower-scale models must be developed for the anode-cathode separation; any continuum treatment that assumes homogeneity in the microstructure is inadequate for design purposes.

4.4.2 Paucity in atomistic models and experimental data

Atomistic models were difficult to find for this topic. However, because characterisation studies (e.g., [50]) have started to generate relevant kinetic data in the form of polarisation diagrams for different alloy phases at the mesoscopic level, such models may soon be developed. An alternative that does not depend on experimental data is an atomistic model that is constructed bottom-up from first principles. No such model appears to exist in the current open domain for metallic corrosion, except a model that is a part of a recent MSM by Yu [11] for glass corrosion. This situation is likely to change with the generation of physico-chemical data at the atomistic level (e.g., energies for surface formation, chemisorption, and adsorption) and the increasing application of high-resolution characterisation techniques for corrosion-related studies (e.g., [79, 102]). Advancing observation techniques such as the in-situ atomic scale studies that were reported by Magnussen et al. [163], where the local removal/addition of atoms at atomic kinks at the steps of Cu crystal surfaces during dissolution in 0.01 M HCl were observed and quantified, also serve to help accumulatee knowledge at lower length scales. However, until a sufficient amount of such data exists, the microstructure-based empirical rules (e.g., for dissolution rates, such as the combination of a chemical rate law (first-order law based on $[H^+]$) and an electrochemical law (Butler-Volmer equation) as used by Suter et al[49] for MnS dissolution in NaCl) may be necessary. These rules should also quantify the effects such as the probable catalysis by $[Cl^-]$ of the MnS dissolution, which was proposed by Williams et al. [164], and any possible influences of the oxide films.

4.4.3 Proposed improvements

One of the reasons for the lack of atomistic models might be the difficulty inherent in coupling the electron transfer (current flow) between atomistic models of anode and cathode. The problem arises because, at the atomistic level, calculations are typically performed for equilibrium configurations whereas the formation of anode and cathodes are highly dynamic events. It is suggested therefore that the potential use of fluctuation theorems [165] be considered for simulating the non-equilibrium mechanisms. The central premise of these theorems revolves around comparing the probability of phase-space trajectories of the system with that of the anti-trajectories (one that the system would traverse if it were moving in the negative time direction), thus introducing the concept of time-irreversibility into the continuum processes. Thus a non-reversible, non-equilibrium process such as corrosion may potentially be modelled using fluctuation theorems at the mesoscopic level, facilitating the prediction of the evolution of favourable phase-space trajectories. Fluctuation theorems are discussed in more detail later, in section 5.3. Early versions of an MSM are likely to have varying degrees of approximations to simulate the anode-cathode separation. One of the available avenues for the development of such models is perhaps the extension of models like that of Diawara et al. [101],

discussed earlier in Section 4.3, and that of Legrand et al. [166]. These models simulate the selective dissolution of Fe and the passivation of a cluster of Cr atoms (which simulates the Cr_2O_3 layer) in Fe-Cr alloys. Another pathway is available from the previously noted work of Yu [11], who simulated the corrosion of glass. This MSM had an atomistic model that was coupled to an MC simulation of surface phenomena such as hydroxylation with cations, chemisorptions, adsorption and dissolution. Then, the continuum scale phase field simulations were performed using material properties that were fed from separate MD simulations. Although the MSM contained approximations and educated guesses and at times relied upon empirically obtained parameters, its framework provides a potential platform for the development of an MSM for localised corrosion.

4.5 Metastable pitting

Metastable pitting is generally accepted as the necessary precursor to a stable pit initiation in metallic systems that include SS [167], aluminium [88] and cast iron [168]. This stage is characterised by the consecutive formation and repassivation of sub micrometre-size pits below the OCP of an alloy, which leads to oscillations in the potential transients in the active direction in an open circuit during the incubation period for stable pitting [57, 88]. Some of the metastable pits survive beyond their usual lifetime of the order of seconds [57] and grow to transition into stable pits under favourable circumstances, which are mentioned elsewhere [25, 50, 88, 167]. Recently, additional causes such as clustering have been suggested to encourage the transition [169-171]. The phenomenon has attracted several theories, including those reviewed by Frankel [172]. In short, from the works of Burstein et al. [173] and those of others (e.g., see Frankel's comments on Sand's equation), it would appear that the metastable pits thrive as long as a critical solution chemistry is maintained using various means([173], [174]). However, they would die through repassivation following a change to this chemistry, which is precipitated by a catastrophic event such as the loss of the cover at the pit mouth or a violent rupture of the passive film covers, leading to a mixing with the bulk solution. Experimental scientists who work with alloys have reported other conditions that can lead to metastable pits (see [50], [175-179]).

The present review did not find any atomistic models, although pit nucleation is essentially a nanoscopic event. It was observed that because of an inability to adequately account for the microstructure at the required scale, the continuum models largely depended on a stochastic treatment of the subject.

4.5.1 Continuum models - mainly stochastic

Because the triggers for the initiation of metastable pits and their repassivation or transition to the stable pits were poorly understood deterministically, a stochastic model that was proposed by Williams et al. [36] based on a treatment by Shibata [180] has been frequently used. Experimental data analysis is required to fit this model to a particular system [36]. However, this model simplistically assumed that each micro pit had an equal chance of propagating into a macro pit, which disregarded the role played by the microstructure, the local microenvironment and any aspect of the pit itself, e.g., the narrowness of the mouth or the existence of a pit cover. Nevertheless, it is interesting that the likelihood of interactions between the metastable pits, which were recently observed using *in situ* techniques at the micrometre scale [170, 181], were actually predicted by a stochastic model by Wu et al. [37], which pre-dated the observations. By assuming through a "memory effect function" that each pitting event will influence subsequent events and the influence would exponentially decay with time, that model could successfully reproduce the current transients that were recorded during the metastable pitting of an SS alloy and an aluminium alloy. (However, it must be noted that the current transients may also be caused by events such as trenching or de-alloying). This temporal model was subsequently extended to a spatiotemporal version by Organ et al. [182]. However, the model remained limited by the assumption that the surface was homogeneous without any preferred sites for nucleation because the microstructural effects were not modelled. A

model developed by Walton et al. [183] (which is discussed later in Section 4.6) appears to be one of the first model that accounted for the active/passive transition based on the potentials. The Cellular Automaton (CA) models [184, 185] that addressed metastable pits concluded that their growth is controlled by the anodic dissolution probability. Other models of note are by Malki and Baroux [186, 187] and Hoerle [188]. In summary, the continuum models that accounted for metastable pitting were stochastic in nature and did not consider the influences of microstructure or other factors such as ions (the Cl^- ions were neglected). They also did not account for the non-random nature of some features such as the intermetallic particles in some aluminium alloys, which were found in clusters instead of being arbitrarily distributed [70].

4.5.2 Proposed improvements

The present authors did not find any atomistic model that addressed metastable pitting. The common drawback among the existing continuum models is that none of these consider the microstructural effects despite their significant influence [189]. Therefore, an MSM should comprise a meso-scale model that adequately describes the microstructural features, which affect the metastable pitting, including the mechanism of active/ passive transition if possible. An MSM should also be able to handle the differences in the behaviour of the current transients between systems, such as SS and aluminium (see [190]), and such events as co-operative spreading [169, 170]. In addition, because the pit nucleation events occur at the nanoscopic scale [10], an MSM that incorporates metastable pitting should preferably include a model at this length scale, but a stochastic approach may be used for the initiation phenomena until such model is available.

4.6 Stable pit initiation

Pitting is caused by the localised failure of a passive oxide film [191] or the selective dissolution of a grain boundary or an inclusion [50] on a metal surface exposed to an electrolyte, and it is characterised by accelerated corrosion in the local region. For instance, it is generally agreed that anodic dissolution of MnS inclusions results in a change of the local solution composition near the inclusions, resulting in a condition where the passive film on the SS surface can no longer be sustained [192]. In general, most pits nucleate if the potential of the alloy surface is above the nucleation potential (or film breakdown potential or pitting potential) for the local electrochemical environment. After an incubation period, a pit propagates if the surface potential remains above the pitting potential. Especially in alloy systems involving SSs [99, 167] and aluminium [88], some metastable pits nucleate at potentials that are hundreds of mV below the OCP and eventually transition into stable pits (Section 4.5). Therefore, the proposed MSM should allow either path for pit initiation. However, there are unanswered questions about the exact nature of the events that trigger pit initiation [79, 99] and the mechanisms associated with film breakdown [172]. According to Kempf et al. [79], highly sophisticated techniques are required to study pit initiation events on sub-micrometre scales. High-resolution observations are, however, increasingly becoming commonplace, allowing informed theories to be developed. For instance, Marcus et al. [28] observed experimental data on the nanometre scale and proposed mechanisms for pit initiation at inter-granular regions. Other similar observations were reported recently by Magnussen et.al. [163] and Williams et al. [99]. Reviews of the critical factors affecting the pitting corrosion of pure metals and alloys are readily available, e.g., [115, 172, 193].

The current review determined that in the absence of a consensus on how pits nucleate, various continuum models have taken different approaches. While the results of atomistic models are encouraging, additional experimentation on smaller scales is required to facilitate a convergence of views on this controversial topic.

4.6.1 Conventional theories – insufficient mechanistic detail

Two conventional theories encapsulate the traditional deterministic criteria: (a) critical solution chemistry theory (CSCT) or critical crevice solution theory (CCST) [194-196] and (b) ohmic resistance-based IR drop theory (IRDT) [63, 197]. According to CSCT/CCST, passive film breakdown occurs when the pH and the Cl^- concentration reach a critical state. However, according to IRDT, localised corrosion starts abruptly when the electric potential drop (IR) between the mouth and the interior of a pit or crevice is large enough to activate anodic potentials. Shortcomings of IRDT have been discussed by Frankel and Sridhar [115] and others (e.g.,[198, 199]). Although CSCT/CCST has been supported overwhelmingly in the past, a recent attempt [63] has been made to develop and validate a model that unifies CSCT/CCST and IRDT. However, all of these theories are for pure metals and ignore the seminal role played by microstructural inhomogeneities (including surface roughness) on pitting initiation on engineering alloys. For example, neither of these theories includes the preferential dissolution of select alloy phases as a cause of pit initiation.

4.6.2 Continuum models – multiple approaches

As mechanisms relevant to pit initiation take place on the atomic scale, the continuum treatment involves significant approximations and assumptions. In addition, the absence of a consensus view on pit initiation is reflected in the variety of approaches that have been used to model pit nucleation. Many of these studies have been reviewed by Sharland [62], Frankel [115, 172], Kennell et al. [63], Papavinasam [200] and Anderko [15], but a small sample of this research is discussed here. Anderko [15] reviewed several theories for passivity breakdown and concluded that all of them share a common theoretical result: the passivity breakdown potential varies with the logarithm of the concentration of aggressive ions, which is confirmed by experimental data. He also notes that, while this observation is accepted widely, its generalisation to systems with multiple types of aggressive and inhibitive ions is not obvious. Given the poorly understood nature of pit initiation mechanisms, it was convenient to use a stochastic approach to model pit nucleation (e.g., references in [38], [34-37]). Hybrid models (discussed in Section 3.1) typically take a stochastic approach to model pit initiation (e.g., [46-48]). These formulations calculate quantities such as pit birth rates based on probabilities or assumed statistical distributions rather than physically viable mechanisms. A common feature of stochastic models is that physical mechanisms (e.g., for passive film breakdown and pit initiation and growth) and microstructure are not included explicitly. These considerations limit the applicability of stochastic pit initiation models for alloy design. The pre-eminent deterministic models are the 1D steady-state models by Galvele [194-196] – the proponent of CSCT/CCST - that influenced deterministic thinking for decades by providing a step change in the ability to rationalise experimental results in various systems. However, as Newman [201] notes, the Galvele approach needs minor revisions to include highly concentrated metal salt solutions in pit nuclei. Other significant deterministic models are those of Alkire and Siitari [202], Sharland [203], Laycock and Newman [204], Cong et al. [205] and Walton et al. [183]. The transient 1D model by Walton et al. was one of the first that considered the electrode kinetics of both cathodic and anodic reactions with active/passive transitions. An electrode kinetic model developed and validated by Mccafferty [113] took into account the adsorption of chloride ions on aluminium oxide surfaces, the penetration of chloride ions through oxide films, and the localised dissolution of aluminium at the metal/oxide interface in consecutive one-electron transfer reactions. The 1D pseudo-steady state model of Webb et al. [192] modelled the influence of MnS inclusions on SS surfaces. However, all these continuum models suffer from the shortcomings discussed in Section 4.6.1.

4.6.3 Atomistic models – showing promise

Decades ago, Williams et al [206] attempted to develop an atomistic model of pit initiation on random binary Fe-Cr alloys. They added a scheme for passivity breakdown based on CCST to existing atomistic models [207, 208] by postulating that passivity breakdown corresponds to the critical chemistry necessary for the activation of the alloy. Their model identified the most important factors for pit initiation on SS: (a) the dissolution probability of Cr atoms; (b) the alloy composition, which

determines the cluster size distribution; and (c) diffusion and migration within the cluster volume. A more recent atomistic work by Bouzoubaa et al. [18] has proposed tenable mechanisms of passivity breakdown. Currently, experimental observations are being made on the atomistic scale – e.g., the recent observations of aluminium oxide by Zavadil et al. [105]. Rashkeev et al. [209] have performed first-principles quantum-mechanical calculations to provide an atomistic understanding of corrosion initiation on Al under atmospheric conditions. Their results suggest that atomic hydrogen penetrates oxide films and causes structural damage in oxides and at Al/Al_2O_3 interfaces. To summarise, atomistic modelling increases the understanding of pit nucleation by modelling mechanisms on their characteristic scales. Therefore, atomistic models are most suitable for modelling pit initiation.

4.6.4 Proposed improvements

Nucleation events are best modelled on atomic scales, and appropriate models have started to become available. These models, however, are still in their infancy and only explore probable mechanisms for pit nucleation, which remains a controversial topic. More investigations, like the X-ray photoelectron spectroscopy studies and MD simulations of amorphous Al_2O_3 by Chang et al.[210], may illuminate the relationship between oxide structures and passivity breakdown. First principle quantum mechanical calculations such as those carried out by Rashkeev et al. [209] and Scully et al. [171] may provide an alternative to experimentation until better techniques become available for observing pit initiation events. However, until a deterministic model is developed for pit initiation, MSMs on localised corrosion may use stochastic models. It is necessary to prescribe the microstructure to apply the early deterministic models to the selective dissolution of inclusions/second phase particles at rates based either on empirical polarisation curves (e.g., [50]) or dissolution models (e.g.,[25, 49, 211]). The effect of microstructural roughness can be incorporated by drawing from, for instance, the empirical relationship between surface roughness and pitting potential (e.g., [212]). If continuum deterministic approaches are adopted until models on mesoscopic scales are available, other approximations may be required, for example, Olson et al. [213]. They considered that surface energy must affect pit formation and treat pitting corrosion as a nucleation and growth process where surface energy promotes an activation barrier.

4.7 Pit or crevice propagation and rate

Pit growth is autocatalytic in nature in that alterations in local conditions [57] promote the further growth of a pit in its propagation stage. (These environmental changes are considered in Section 4.8.) The spatial separation between the anodic and the cathodic reactions results in a negative pH gradient between the pit and the film that sustains the electrochemical reactions. Factors that control pit growth rate are discussed by Frankel [172]. Whilst the initiation and early metastable growth of a pit are activation controlled (Butler-Volmer or Tafel kinetics equations), pit or crevice propagation above the pitting potential is mass transfer controlled [199] (Nernst-Planck equation). For an activation-controlled reaction, the current density is plotted on a polarisation plot (potential E vs. log (current I)) or Evans diagram. Current density in a pit is a measure of the corrosion rate in the pit and, thus, a measure of the pit penetration rate [57]. Pioneering modelling work based on CSCT/CCST by Galvele [194, 195] showed that a critical value for the product of the current density i_{corr} with the pit depth x, the pit stability product = $x.\ i_{corr}$, may be found in terms of the concentration of the ionic species at the bottom of a one dimensional pit. This critical $x.\ i_{corr}$ value corresponds to a critical pit acidification condition for sustained pit growth, and it can be used to determine the i_{corr} value necessary to initiate or sustain pitting at a defect of a given size [57]. However, because Galvele's treatment explicitly ignores the effects of cathodic reactions inside the pit, it is only relevant at potentials well above the OCP of the metal in its critical localised solution. A topic that remains controversial is the degree of influence exerted on pit propagation by salt films that form on electrodes when the dissolving cations and, say, Cl^- ions combine at saturation concentrations of the salt in solution [204]. Another unresolved subject is the formation of lacy covers on pits on SS that limit diffusion at pit mouths and

thus help to maintain the critical chemistry in the pits. Some authors have proposed that this phenomenon is caused by the strong dependence of dissolution kinetics on local dissolved metal ion concentration (e.g., [198]).

The present review found that only continuum models were available for propagation events. Although these models are able to model pit propagation reasonably well (as it is a relatively higher scale event), they can be applied only indirectly using empirical parameters that account for associated mechanisms rather than explaining the direct influence of causal factors such as microstructure. Thus, continuum models are not sufficiently general to be incorporated into a truly generic MSM. Additionally, a deep understanding of electrode kinetics that would facilitate the development of reliable atomistic models was lacking.

4.7.1 Continuum models – the only option available

Because the propagation mechanism is better understood than the nucleation mechanism, more continuum models are available for pit or crevice propagation. Most models, including hybrid versions, follow the deterministic path for propagation. However, a number of stochastic models also exist. Sharland [62], Turnbull [214], Frankel [172], Scheiner and Hellmich [199], Kennell et al. [63], Papavinasam [200] and Macdonald and Engelhardt [215] have reviewed traditional models and formulations for propagation–related mechanisms, and only a selection of these models are reviewed here from a multiscale modelling perspective. Stochastic models typically calculate expected values of quantities such as the induction time or the number of stable pits as functions of defined parameters such as the nucleation frequency, the survival probability and the critical age. Then, through the interpretation of measured current transients, values for the parameters are retrieved. Stochastic models of Williams et al. [36], Valor et al. [35], Alamilla and Sosa [33] are noteworthy examples. While none of these models explicitly consider the microstructure, the previously mentioned stochastic model for inter granular corrosion developed by Zhang et al. [68] (Section 4.1.1) utilised a brick wall model with a rectangular 2D geometry for aluminium grains. This rather simplistic description appears to be the closest stochastic approach published for modelling alloy microstructure. To summarise, stochastic models have not explicitly accounted for critical factors. Rather, stochastic models have relied on empirical parameters that were used subsequently to estimate various quantities associated with propagation. Deterministic models invariably followed either the CSCT/CCST or the RDT approaches. Often, early models (e.g., [160, 194-196, 202, 216, 217]) were developed for idealised 1D geometries, supported only the steady state, and contained several simplifying assumptions. Sharland and co-workers [30, 203, 218] and Engelhardt et al. [219] developed some noteworthy models, but Walton et. al. [183] appear to be the first to develop and validate a transient model applicable to a wide variety of metals and electrolytes and supported by different kinetic rate equations. Laycock and White [198] developed a 2D FEM model that successfully recreated the lacy covers observed on pits on SSs. The deterministic model of Turnbull et al. [48] contained statistically distributed parameters for the pit growth equation. When Laycock et al. applied the previously developed propagation models [198] in their hybrid version [47], they accounted for different SS alloy compositions by changing the OCP for each alloy and for surface roughness by altering the distance of the initial spherical pit beneath the metal surface in the Tafel equation for anodic dissolution. Additionally, the deterministic propagation equation in the hybrid model of Engelhardt and Macdonald [46] for manganese steel in CO_2-acidified seawater and Al in tap water contains empirically fitted parameters rather than values obtained from physical mechanisms. Such empirical modelling has been carried out for Al alloy AA7075-T651 using neural networks by Cavanaugh et al. [41]. Investigating two orientations of metal exposed to varying temperature, pH and [Cl^-], those workers concluded that pit growth generally followed $t^{1/3}$ kinetics. To summarise, most models used the 1D approach to predict pit size and transfer processes [215], and existing continuum models of pit propagation have not explicitly considered the effects of causal parameters such as alloy microstructure, oxide films or surface roughness on propagation rates. Rather, these parameters have been incorporated using quantities such as the OCP or the exchange current density (in the Butler-Volmer equation, for instance) that were obtained empirically. The lack of generality makes it difficult to use such models in an MSM for designing alloys or corrosion resistant systems.

4.7.2 Proposed improvements

There are very few atomistic models of pit propagation in the literature. The probable reasons for this situation are (a) the continuum models have tackled this phenomenon reasonably well on the continuum scale and/or (b) the computational cost does not justify applying atomistic simulations to phenomena on mesoscopic scales or continuum expanses. However, it is likely that atomistic methods will be used increasingly to simulate propagation and extend the boundaries of knowledge. There is a need for advancement in the fundamental theoretical understanding of electrode kinetics before reliable atomistic models can be developed. For instance, Macdonald and Engelhardt [215] recently noted that while Tafel constants may be calculated ab initio, the exchange current density is almost always measured experimentally because theory is not sufficiently developed to calculate this quantity from first principles. This is because Tafel constants contain relatively little kinetic information and the transfer coefficient is usually assumed to be 0.5 corresponding to a presumed symmetric barrier, whereas the exchange current density is derived from a highly kinetic and inherently complex set of mechanisms involving solvent reorganisation which are still poorly understood [220-222]. Once an understanding of the charge transfer reactions at the electrode/ electrolyte interface and related mechanisms is established on the atomic scale, however, rate equations such as Butler-Volmer or Tafel with empirically determined parameters to describe boundary conditions at the continuum scale will unnecessary. Recent phenomenological models [146] analyse charge transfer in solution in terms of a number of components and effectively refine the electrochemical scale. Lower scale models will manage the difficulties with mesh refinement on finer scales to better describe, for instance, small-scale material removal or large concentration gradients near the electrode/ electrolyte interface under diffusion control. In a nutshell, pit propagation can be modelled reasonably well on mesoscopic scales in the absence of a lower scale model. In this case, the incorporation of microstructural details at the electrode/electrolyte interface should be considered in the medium term. However, because the atomistic description gives the best resolution, efforts should be made to incorporate atomistic-scale models in advanced versions of the MSM. Development of such models may remain a challenge until issues with computational loads are resolved through hardware and/or software improvements. Finally, the potential use of mesh-free methods for pit propagation should also be explored because these methods are well suited for modelling moving discontinuities.

4.8 Changes in electrolyte chemistry in pits

The concentrations of species in a pit are affected by electrochemical reactions such as anodic dissolution and cathodic reduction at the electrode/ electrolyte boundary, chemical reactions such as precipitation (see Section 4.9) and dissolution of O_2 and CO_2 at the electrolyte/air boundary as well as dissociation and hydrolysis in the aqueous environment. As a pit grows and the pit depth exceeds the width of the pit mouth, diffusion is restricted between the confined localised pit volume and the bulk solution. This results in the depletion of consumed species (e.g., dissolved oxygen) in the pit but the enrichment of dissolved metal ions. Such enrichment results in the migration of anionic species such as Cl^- from the bulk to preserve electro-neutrality and the hydrolysis of the dissolved metal ions that releases H^+ ions in the pit and lowers the pH. This acidic chloride environment is aggressive to most metals and tends to prevent repassivation and promote pit propagation. Further information about this subject may be found elsewhere [57, 61, 223-226].

The current review established that the only models on the continuum scale were available, and the lack of resolution as well as simplifying assumptions limited the application of these models.

4.8.1 Continuum models – purely deterministic

Stochastic modelling of pitting is not commonplace. Sharland [62] reviewed some of the early studies and concluded that no single model predicted (qualitatively or quantitatively) all the available experimental observations. The Walton model [183] predicted concentration profiles more accurately than previous versions. Evitts [227] carried out an extensive review of both steady state and transient models that dealt with changes in chemistry, including the studies by Sharland [30, 203, 218] and Walton [183], and concluded that most models assumed isothermal conditions and constant bulk solution chemistry. Macdonald and Engelhardt [215] noted that most models are 1D and erroneously neglect the potential drop outside the corrosion cavity, leading to significant errors in the prediction of damage. The White et al. [228] model relied on the Nernst-Planck equation rather than the electro-neutrality condition for the calculation of potential differences and predicted concentration profiles for an SS system. Laycock and White [198] calculated the local chemistry in an SS pit and accounted for several relevant criteria including a moving boundary due to propagation. More recently, Kennell et al. [63] developed a combined CCST/CSCT-IRDT model that provided the best agreement yet with the experiments of Alavi and Cottis [229], surpassing the models of Sharland [218], Walton [183], White [228] and Evitts [227], and introduced the possibility that such a combined approach may be superior to the CCST/CSCT-only path. Taxen and Persson [230] considered concentration changes due to the evaporation of aqueous electrolyte and used a moving mesh, but the application of the dilute solution theory was discontinued beyond a certain loss of volume. Finally, Heppner et al. [231], noting that most models assumed a dilute solution, carried out theoretical calculations for non-ideal solutions where ionic interactions could no longer be neglected. Their work, which used the Pitzer model [232], simulated crevice corrosion evolution including species concentration changes and delivered better predictions than those models that did not account for ionic interactions. Thus, the use of the Pitzer model in the MSM should be explored, especially for non-ideal solutions. Moreover, in actual solutions, the activities of species can change not only with temperature but also with pH values [15]. Even for dilute solutions, traditional models relied on estimating activity coefficients from theoretical models (see [15],[183],[233]), and advanced modelling on this front should be considered. Another common feature in traditional modelling was the lack of data on chemical reaction kinetics. Therefore, several assumptions were made. For instance, Sharland and Tasker [218] assumed that the chemical reactions occurred at very high rates compared with other phenomena such as diffusion. While many such assumptions may be justified for continuum models, they are invalid for atomic scale models. To conclude, the existing models that describe chemical changes in a pit all belong to the continuum scale and thus lack detail on the mesoscopic scale for some relevant events discussed below.

4.8.2 Atomistic models – may be required for non-dilute solutions

Lower scale atomistic models that describe changes in solution chemistry are rare in the corrosion domain. This may be because the chemical changes are largely a response to other events rather than being causal events themselves. This means that, if events at electrolyte-electrode and electrolyte-air boundaries were modelled with sufficient accuracy and the important chemical reactions were properly accounted for, the chemical changes in the pit would be adequately modelled at the continuum scale without the need for a computationally intensive atomistic treatment. Nevertheless, as the theoretical work of Heppner et al. [231] showed, ionic interactions may become significant in non-dilute solutions where dilute solution theory would break down. Such cases might benefit from atomistic-level computations which can provide the necessary resolution to model the interactions in more detail. For instance, in the multiscale framework, an atomistic-scale model can be used to calculate the empirical parameters (e.g., the activity coefficients and the osmotic coefficient) for the Pitzer model [232] for deployment at a higher scale, although these parameters have been experimentally derived for some systems [234]. Furthermore, the following events may be better modelled at a scale lower than continuum: (a) the influences of alloy microstructure on local chemistry (e.g., through space-dependent dissolution) or vice versa (e.g., the local chemistry can preferentially attack metallurgical defects; (b) the passive film or its influence on the chemistry; (c) the microenvironment defined by the microscopic surface roughness; or (d) interactions between pit

sites. Such detail is desirable in an MSM that will be used in a predictive role in alloy design. MD simulations of non-ideal solutions have been performed [235, 236], and perhaps similar studies could be used to explore the concentrated solutions that develop in pits.

4.8.3 Proposed improvements

In non-dilute solutions, phenomena such as ionic interactions within the electrolyte may not be neglected and ideally are modelled on the atomic scale to arrive at an optimum generic approach that could be used widely. Another area that needs to be strengthened is the quantification of reaction rate constants for some reactions. Although these constants could be obtained experimentally for some reactions, other extremely rapid reactions present difficulties in the determination of rates because reliable experimental measurements cannot be made easily using traditional methods [237]. In the absence of dependable measurements, the application of theories such as [238] collision theory or transition state theory may be attempted for estimating reaction rates, and subsequently rate constants (see [239]). Alternatively, these may be obtained from the application of first principles (e.g.,[19]). Similarly, it appears that no current document has a comprehensive listing of all relevant parameters such as those above and others such as dissociation constants and solubility products that a modeller could conveniently access, although some handbooks contain samples of these. Therefore, there are opportunities for developing atomistic models capable of estimating these quantities.

4.9 Precipitation of corrosion products

During localised corrosion, some salts precipitate on the corroding substrate as a result of reactions between dissolved anions and species in the electrolyte in the pit or crevice (see, e.g., [85]). Precipitation occurs when the product of the ionic reactants exceeds the solubility product. The corrosive microenvironment under surface deposits is very different from the bulk solution. In particular, the pH of these microenvironments tends to be very acidic. The formation of acidified microenvironments is related to the hydrolysis of corrosion products and the formation of differential aeration cells between the bulk environment and the region under the deposits [59]. Precipitation of salts on electrode surfaces can affect the anodic and the cathodic reaction rates by modifying the extent of the areas that are in contact with the electrolyte and/or increasing the resistance of the passive film to charge transfer. For example, the dependence of the Zn corrosion rate on pH is determined by the corrosion products [61]. Conditions controlling the thickness of products in zinc [61] and SS [240] systems are discussed elsewhere. Given the rate-controlling nature of the precipitates and the alterations to solution chemistry, an MSM should have the facility to adequately account for corrosion products.

The present review found that only continuum scale models were available to address precipitation, and these models contained sweeping assumptions such as homogeneous electrodes to describe what are, in essence, atomistic phenomena that are influenced by the heterogeneous electrochemical behaviour of electrode surfaces.

4.9.1 Continuum models – severely lacking in detail, but the only type available

As with the changes in pit chemistry (Section 4.8), only deterministic models are relevant for describing precipitation. Models that account for precipitation include those of Gravano and Galvele [196], Sharland and Tasker [218], Sharland [203], Walton et al. [183], Laycock et al. [25] and Laycock and White [198]. These models provide different mathematical treatments of precipitation. For instance, Gravano and Galvele [196] treated precipitating solids as colloidal diffusing species in their work that focused on solution chemistry immediately after film breakdown. The 1D transient model constructed by Sharland [203] was one of the first models to predict the evolution of solid phases (corrosion products) as a function of time and space in addition to solution chemistry and

electric potential. All the above models assumed that the precipitation of the metal hydroxide occurred when its concentration reached the saturation level in the solution; Laycock and White [198], however, allowed up to 10% super-saturation to occur owing to their additional assumption that a hydroxide salt film could precipitate only on an existing salt film or on the corroding metal. A slightly different approach was followed by Taxen and Persson [230], who assumed that precipitation occurred when the activity coefficient for any solid species in solution exceeded unity. Another aspect of traditional modelling has been the limited use of data for rates of precipitation by many models (e.g., [218]) based on the assumption that rates of precipitation are much higher than other events such as diffusion. It was necessary to make these assumptions in the traditional models due to the general lack of data on chemical kinetics and rates of precipitation [218], which has remained the case to this day [215]. Some workers such as Farrow et al. [110] worked around this issue by using theory [241] to estimate the rates. Some works such as Nesic and Lee [242], Sun and Nesic [243], Anderko [15] and Taxen and Persson [230] dealt with the subject in the sphere of general, rather than localised, corrosion. Also worthy of mention is the work of Tidbald et al. [244] who used the well-known GILDES model [241] for atmospheric corrosion to predict the formation of corrosion products on copper substrates exposed to aqueous species. The GILDES model solves the mathematically formulated transformations and transitions that occur in the six relevant 'regimes': the gas phase, the interface between a gas and a liquid, the liquid phase, the deposition layer, the electrode region near the surface and the solid phase. With the exception of studies such as that of Farrow et al. [110] and the GILDES model [241], none of these models have accounted for the well-known influence of surface pH on precipitation by simulating the dissolution of precipitate layers in certain pH ranges – so these models were limited to pH ranges where the products were stable. None of these models also took into account the effect of microstructure and were unable to provide the details required to model mixed corrosion products, such as different oxides of alloy components or their spatial distribution that depends on microstructural features besides alloy composition. Additionally, none of these models explicitly accounted for the passive films. Because the electrode was assumed to be homogeneous on the macroscopic scale, the available models do not contain the details that a prospective microscopic or lower-scale model would be capable of furnishing. Thus, the available models need fine-tuning from the perspective of incorporating precipitation algorithms into an MSM.

4.9.2 Proposed improvements

The present authors did not find any atomistic scale models that dealt with corrosion products, although, like oxides films (Section 4.2), the usually ultrathin and porous nature of precipitate layers make them classic examples of why a multiscale-approach should be taken for modelling localised corrosion. The atomistic scale provides the ideal framework for modelling transport at not only the interfaces between the products and other components such as the passive film or the metal itself but also through the products themselves. This is also the most suitable method for modelling interactions between the electrolyte and the products including adsorption. In addition, bonding at interfaces may be modelled elegantly using an atomistic approach. Thus, there is scope for building models of corrosion products at the lowest scales in the medium to long term. These models should take into account the microstructural inhomogeneity of the metal substrate and the oxide when predicting the space-dependent structure and thickness of the precipitate layers. It may be possible to develop atomistic precipitation models for corrosion based on precipitation kinetics-related models that are becoming available in other fields, e.g., solidification - atomistic [78] and hybrid atomistic-kMC [245]. Additionally, the inverse of precipitation (dissolution) of salt films has been studied recently using MD [246], and this approach may be examined for developing a basis for precipitation models of corrosion.

4.10 Repassivation

Under certain circumstances, the increasing corrosion partial current that follows a nucleation event may cease. This is attributable to repassivation and is due to the loss of the active surface on the electrode. Despite the autocatalytic nature of pitting, even large pits can stop growing or die [57]. Whilst the repassivation of the corroding surface stifles the growth of pits, the increasing ohmic potential drop along the depth of the pit also results in the pit being stable at a low anodic current density at the bottom. That is because, as the pit deepens, the diffusion of the cations out of the pit reduces - thus decreasing the rate at which these ions dissolve from the substrate. At some point, the pit stops growing and is considered 'dead'. The repassivation mechanism/s for metastable pits are not known for certain [247]. Relatively recent high-resolution experimental works, however, are beginning to illuminate some of the mechanisms involved in repassivation. For instance, Chidambaram et al. [248] have observed, through synchrotron infrared microspectroscopy and secondary ion mass spectroscopy, that the slow migration of ions from the surface of AA2024-T3 alloy protected by chromate conversion coatings to the scratch-exposed metal surfaces leads to the repassivation of the metal. A similar mechanism might be operating in metals protected by oxide films. Furthermore, the quantitative effects of the alloying elements on kinetics have been studied by some workers. For example, Cho et al. [249] have quantified the influence of alloying elements on repassivation kinetics. Data on repassivation kinetics remains scarce. However, repassivation kinetics are considered to be a critical factor in determining the resistance of metals and alloys to localised corrosion [250] and, consequently, in influencing the accumulated damage [104]. Thus, there is little doubt that any MSM built for use in the design of corrosion resistant alloys should be able to simulate phenomena relating to repassivation.

This review found mostly continuum scale models that relied on Pourbaix diagrams for equilibrium conditions and mostly empirical data for non-equilibrium situations – and thus had little general applicability. This review also highlighted the lack of atomistic models and experimental data on the smaller scales.

4.10.1 Continuum models – inadequate

Traditionally, conditions under which repassivation occurs have been determined by the use of Pourbaix diagrams [247]. However, this phenomenon has been addressed by a handful of empirical and continuum mathematical models as engineering situations deviate significantly from the equilibrium-based scenarios. Examples of empirical models include that of Song et al. [251] . However, as the empirical models do not explicitly incorporate the influence of, for instance, the environment or material properties, they cannot be utilised as generic tools. Stochastic modelling works have attempted to incorporate the repassivation phenomenon using probabilities. For example, in the model by Williams [36] an assumption regarding the probability that a metastable pit will repassivate was made. However, these stochastic models – like their empirical counterparts – do not explicitly account for mechanisms leading to repassivation. Among deterministic models, the Walton et al. model [183] appears to be the first that is capable of simulating repassivation, as it supported the active/passive transition. Laycock et al. [25] assumed that repassivation would occur if the diffusion of metal ions away from the electrode exceeds their production through dissolution, in which case the ion concentration tends to zero. Anderko et al. [252, 253] developed mechanistic models based on statistical thermodynamics. Their models calculated the repassivation potential for selected SS and Ni-base alloys whilst accounting for the influence of solution chemistry (aggressive species, oxyanions and inhibitors), temperature, competitive dissolution, adsorption and oxide formation. In particular, the models predicted the transition from the concentration range where localised corrosion was favoured to the region where inhibition was expected. Some of the parameters in the Anderko models [252, 253] were experimentally obtained. A PDM [26, 104, 215] was capable of explaining the experimental observations of Ahn et al. [254] for the repassivation kinetics of Ti. However, as

noted by Wu and Celis [255], HFM is the most widely used explanation of repassivation kinetics, although its validity has been questioned by some. Whilst some experimental works (e.g., [255-257]) have supported the application of HFM, Wu and Celis [255] caution that HFM may not be physically realistic at very short times following depassivation. To summarise, while continuum scale models exist, they are inadequate for modelling repassivation because it is known that lower scale factors influence this phenomenon. For instance, second phase particles or inclusions in an engineering alloy would exhibit electrochemical potentials different from that of the matrix – and can preferentially passivate (or dissolve). Such resolution at the microscopic level is mandatory for an MSM aimed at alloy design.

4.10.2 Atomistic models and experimental data at this scale are scarce

Using Monte Carlo simulations, Malki and Baroux [185] determined that varying the repassivation probability on the atomic scale on the pit walls can control pit growth kinetics (t^n law), but the authors admitted that there was no experimental evidence to suggest that this unexpected prediction was tenable. This model appeared to be the only one in the open literature that dealt with repassivation, and the lack of models at this scale is probably explained by the scarcity of experimental data on this scale. However, atomistic simulations have been performed for the oxidation of metal surfaces, which is a critical step in repassivation – e.g., MD simulations by Sankaranarayanan [258] and DFT work by Schröder [258]. Perhaps strategies found in these works can be applied to develop a model for repassivation.

4.10.3 Proposed improvements

More experimental observations on the atomic scale are required to understand the mechanisms that lead to repassivation in situations that do not involve the preferential dissolution of phases or inclusions. It therefore stands to reason that atomistic scale models will be the most appropriate means to describe such phenomena. However, the existing models that account for repassivation have all been developed on the macroscopic scale. Additionally, no existing model has taken into account the role of the microstructure, for instance in the apparent repassivation of pits formed by selective dissolution. It is also necessary to determine through experimentation whether the presence of different phases or other microstructural features in the local neighbourhood would have any influence on whether a pit repassivates. Such influences may be modelled at the microscopic level and will enrich an MSM designed for alloy design.

4.11 Interactions with the immediate neighbourhood

A passive surface exposed to an aggressive corrosive environment is usually riddled with numerous pits. Due to a competitive interaction process between these pits, only the strongest survive to grow [104, 259]. A stronger pit, which generates a higher current, competes for a larger share of the charged species by attempting to expand its "living space" - the volume of electrolyte immediately adjacent to the pit. The stronger pit thus suppresses its weaker neighbours. In some cases, possibly when the competing pits are similar in strength, they coalesce. Recent high-resolution experimental observations [169, 170] have suggested that an autocatalytic explosion of metastable pits may be possible, at least in SSs. Therefore, it is useful to reproduce these interactions in detail in an MSM so that corrosion sites are predicted realistically.

Despite the dominant influence of the electrochemical properties of the *microenvironment* surrounding a pit on determining the favoured interactions (which calls for lower-scale modelling), only continuum models were found during the present review. With greater understanding of pitting at the lower scales, it should be possible to model these interactions at the atomic level.

4.11.1 Continuum models – hybrid treatment

Only a handful of existing models address this topic, and this is probably due to (a) the lack of experimental data and associated understanding, which is only just beginning to filter into the open literature, and/or (b) the probable perception that such interactions may only be of secondary importance. Available models generally take a hybrid approach treating nucleation and interaction events stochastically but employing deterministic equations for the influence of the environment. One of the first models that accounted for interactions was the previously mentioned stochastic model of Wu et al. [37], in which a memory parameter, M, was incorporated to retain the influence of a given event over time. Lunt et al. [260] extended this model and their simulation results, which agreed with experimental data obtained by the same workers on an array of SS electrodes, showed that surface damage gave the highest M value. Organ et al. [182] extended the Lunt et al. model to 2D, and this model suggested that interactions among metastable pitting events can lead to the formation of clusters of pits. White et al. [261] developed an FEM model incorporating interactions as an extension of a previously discussed model by Laycock et al. [47]. Their model confirmed that an existing pit would increase the probability of pits nucleating at nearby sites. Harlow and Wei [262] developed a stochastic model incorporating interactions for pit growth in Al alloys. Although not validated with experiments, the authors mentioned that its predictions were in qualitative agreement with observations. Significantly, the authors advocated a deterministic approach for a more realistic analysis of interactions. A mechanism of competitive interaction between pits at the early stage of their development was considered by Popov [259], who assumed that the interaction occurred due to the hydration of metal ions by the solvent. Popov derived analytical equations and proposed a 1D model of interaction between two linearly connected pits. However, this model was not validated with experimental data.

4.11.2 Proposed improvements

Only a limited number of models have addressed the phenomenon of interactions between pits. All of these models were on the continuum scale, and the electrode surface was modelled as homogeneous, without preferred nucleation sites. Therefore, a stochastic approach was followed for nucleation events, and interactions were modelled by deterministic equations that incorporated the influence of the environment on interactions. Clearly, the assumption of homogeneity reduces the detail required in a model for alloy design. Therefore, a model at the mesoscopic scale should be developed for describing the interactions on their characteristic scales. It would be an advantage to have an atomic scale model to describe nucleation events. However, limitations of atomistic models addressed earlier in section 4.4.3 with respect to non-equilibrium events must be adequately dealt with before dynamic processes such as interactions can be realistically modelled at that scale. In addition, although recent in situ experiments and modelling indicate that an existing pit would increase the likelihood of pits nucleating at adjacent sites – at least on SS, it would be desirable to have additional observations of different corrosion systems. Lastly, when more experimental data becomes available, replacement of the stochastic treatment by deterministic mechanisms would help interrogate the models and thereby increase our understanding of the controlling factors.

4.12 Summary

Fig. 5 provides a summary of approaches discussed in some detail in the preceding sections. Continuum approaches are shaded in red and atomistic in green.

Figure 5: A summary of approaches found in the literature for the various events relevant to localised corrosion. Continuum approaches are shaded in red and atomistic in green.

5.0 Numerical strategies

In this Section, issues unique to the solution of equations on multiple length and time scales are addressed.

5.1 Field variables at different scales

The primary challenges for modelling corrosion where different scales of time and length are linked can be classified broadly as *formulational* and *computational*. Formulational challenges arise when two or more apparently dissimilar modelling philosophies operating at different scales are combined to explain a phenomenon such as corrosion. It is a formidable task to combine the mathematical structure of one modelling approach with another while ensuring a seamless information exchange between the different models. Computational challenges, on the other hand, include appropriate hardware, efficient multithreaded parallel programming, approximation and fault tolerance, data visualisation and data transfer between various computing units. In this section, we concern ourselves primarily with formulational challenges of multiscale modelling and some computational challenges inherent in the development of an MSM for corrosion.

The central difficulty in coupling two methods on different scales is reconciling the definitions of computational variables. Two quantities are of primary interest: the total energy of the system and the temperature. The standard approach is to construct a potential energy functional and use its derivatives to obtain the forces necessary to evolve the system. However, Curtin et al. [263] note that the fundamental problem in bridging the continuum and atomistic methods stems from the fact that the expressions for the total energy of the system are fundamentally different in the two methods. They observe that apart from the semi-empirical nature of the interatomic potentials employed in MD, which introduce uncertainty and approximations, the quantum energy, unlike its classical counterpart, cannot be partitioned into energies on a per-atom basis. This was reiterated by Makov et al. [264] who observed that, in the case of an MSM, two potential Hamiltonian formulations could be used for the atomistic and the continuum models. When more than one model Hamiltonian is used, it is normally assumed that the energies in the system are additive. However, the additivity of the energy is scale-dependent, being valid at large scales (continuum) and invalid at short scales (atomistic) due to the existence of long-range interactions and quantum non-locality. Thus, the width of the boundary zone where the models "shake hands" must be chosen such that no forces are introduced artificially. Makov et al. [264] have described a “Learn on the Fly” (LOTF) multiscale approach in which the entire system is represented in the high level, and the region of the low level simulation is determined dynamically (i.e., continuously updated) by flagging the ‘quantum’ atoms according to a mixture of topological (bonding lengths and angles) and geometric (e.g., distance from the crack tip) conditions. The potential used to derive the forces in the boundary zone is fitted to the results of the low-level atomistic simulation, and this unique potential describes and conserves momentum.

On the other hand, Ganzenmuller et al. [265] observe that both the heat flux and the temperature are interpreted differently in continuum and atomistic domains. The continuum approach is based on discretising a continuous field of state variables at discrete spatial locations. The momentum, mass (and species), charge and heat fluxes are then evaluated between these nodal points. Many techniques including Finite Difference [266], FE [267], Control Volume [268] and their hybrid variants [269] employ this scheme. Techniques such as Smoothed Particle Hydrodynamics (SPH) [56] based on Lagrangian methods, where the evolution equations are not constrained by the need to track the movement of the fluid particles, also evaluate the fluxes using averaging techniques similar to the earlier methods. Molecular properties such as viscosity (internal friction) are usually provided as transport parameters to the simulations. The conservation equations usually are developed for mass (species), energy, momentum and charge separately and solved by effectively capturing the non-linear coupling between the variables. However, in MD, the kinetic energy of the interacting atoms depends on the

momentum exchange because no other degrees of freedom except those associated with the particle kinetic energy are present and, thus, the temperature depends solely on the momentum. Ganznemuller et al. [265] christen the average temperature in MD simulations as the *kinetic temperature* because it stems purely from the kinetic consideration of a large number of interacting atoms. They distinguish this from the *continuum temperature,* which in continuum models is defined using the concept of internal energy and heat capacity. They further assert that the kinetic temperature in an atomistic simulation relates to the average particle momentum, whereas the continuum temperature (even if coupled to the momentum conservation equation) serves only as a *state variable* without any relation to the momentum of the corresponding continuum integration node. Ganzenmuller et al. [265] further observe that a correct continuum-MD coupling algorithm must describe the heat flux between the two domains such that the continuum variable internal energy is linked locally to the MD particle velocity. They also advocate Dissipative Particle Dynamics at constant Energy (DPDE) as an ideal choice for the mesoscale coupling. DPDE, albeit an isothermal method, has provisions for assigning an "internal temperature" to each particle that can be related directly to the internal energy and the heat capacity, and the local DPDE thermostat is used in the MD domain to achieve dynamic equilibrium between both temperature definitions.

5.2 Modelling electric potential

Another closely related issue is the "conjugate problem" [269] in which two or more regions (or phases) are involved and there is a "jump discontinuity" in the material properties and state variables. In corrosion, we encounter two or more phases where some quantities must be defined unambiguously to ensure continuity. Electric potential is the only macroscopic variable that is present in both the solid and the solution domains, although a discontinuity is prescribed (i.e., the potential of the metal and the potential of electrolyte have different values) at the solid-solution boundary to quantify the electrochemical surface reaction using Butler-Volmer kinetics. The reason for these discontinuities is simply the incapability of the continuum models to describe atomistic details. In the continuum methods such as the Control-Volume Finite Element method (CVFEM), the mesh is constructed such that any given integration element falls in one and only one region, which ensures there is no ambiguity in calculating the face diffusivities in a given element. While the conjugate problem is based on a genuine phase-differentiation, the atomistic-continuum boundary zone is only a *numerical artefact*. Thus, while it is important to ensure that modelling the conjugate problem considers accommodating the atomistic details of the interface, it is equally important to ensure that the spurious forces at the "numerically created boundary zone" do not contribute to the atomistic-continuum handshaking as well.

5.3 Candidates for future MSM and mathematical coupling of scales

Tan [12], Elliott [5] and Curtin et al. [263] have reviewed a number of multiscale methods with particular emphasis on fracture. Tan discussed stress-corrosion cracking and pitting corrosion and observed that stress corrosion cracking is the result of sufficiently strong mechanical forces that separate chemically bonded atoms and also presented a case where hydrogen interacted with dislocations. However, the combined interaction of mechanical stress (developed due to deformation or loss of atoms) and electrochemical reactions underlying corrosion was not discussed in detail. Similarly, Tan discussed pitting corrosion in the context of Monte-Carlo simulations performed by Reigada et al. [32], who assumed that the probability of "tunnelling" (metal oxidation) depended linearly on the local halide concentration and exponentially on the applied potential. Bartosik et al. [270] considered that pit nucleation is a rare event at the atomic scale and that a Monte-Carlo simulation is still far too large for currently available computational resources. They also noted that the complicated spatial and temporal oscillatory behaviour exhibited by metals undergoing passivation in solutions poses a strong challenge to the development of a unified approach for covering various aspects of corrosion. Thus, at the mesoscopic scale, they have proposed a CA model that is characterised by seven species: metal M, reactive site R, passive site P, electrolyte E, anodic dissolution site A, and cathodic site B. They

enforced local rules and noted the interdependence of the A and the B sites and the underlying connectivity in the metal matrix that ensures that the electrons lost at an A site are compensated exactly and simultaneously at a B site. CA methods on mesoscales typically require huge grids, and establishing a connected path in the metal matrix for three-dimensional simulations is very time-consuming. This method, although in an early stage of development, shows promise for future MSM applications because it is one of the very few methods that accounts for global charge conservation, which is a stringent requirement for corrosion. This approach however has not yet accounted for the following phenomena: a) the diffusion and migration of species such as dissolved oxygen in the electrolyte, which determines local corrosion rates; b) the effect of metallic microstructure including local phase compositions on multi-phase/ polycrystalline metals and/or alloys; c) distributions of defects in the microstructure; and d) effects of porous semi-conducting oxides (precipitated from the solution or natively formed) that affect the permeability/ percolation of the electrolyte and host oxygen reduction reaction on their surfaces [271, 272], thus enhancing corrosion rates to more than expected levels for metals such as iron and zinc. The CA models can be refined to an atomistic level and the atomistic-mesoscopic scale coupling can be achieved by refining the cells to match the atomistic surface morphology. This refinement could place a high computational load on the current CA models especially for corrosion on a contiguous metal surface. The CA models could be combined with control-volume from CVFEM techniques, which will account for reactions and ionic movement in the solution phase. Additionally, SPH is another method that can include localised precipitation [273]

Elliot [5] observed that the atomistic-mesoscale coupling can be performed by 'coarse-graining' at the boundary-zones and integrating out redundant degrees of freedom. This is achieved either by forcing atoms onto a lattice or by grouping them into larger particles. The Lattice Material Point Method (LMPM) [12] or SPH [56] could be used for this purpose. In both LMPM and SPH, the continuum material point is modelled as an aggregate of atoms ("particles" or "atomic aggregates"), and the entire continuum is modelled as a collection of material points (or particles) although, unlike SPH in LMPM, a background mesh is always used. In both methods, a Lagrangian description is used to discretise the material into a collection of atoms whose motions characterise the deformation of the material. In LMPM, once the atoms are combined into larger particles, a quadtree or octtree method could be systematically employed to aggregate the atoms in the transition zone for 2-D and 3-D models, respectively. The stresses are calculated from velocities that are computed using Verlet algorithms [274]. However, Hoover [275] warned that the analogy linking the SPH to atomistic MD also suggests that the SPH representation of a continuum might exhibit the same chaotic instabilities that are present in atomistic systems. Ganznemuller et al. [265] proposed a coupling strategy wherein they employed SPH for the partial differential equations in the continuum to which a region with atomistic length-scales and corresponding particle dynamics was coupled and this region was described by classical MD employing a DPDE thermostat. Interpolations could help damp some of the oscillations encountered at the boundary points, but LMPM, although computationally expensive, seamlessly integrates with the framework of MD.

There is another interesting issue, mentioned briefly in sections 4.4.3 and 4.11.2, which requires discussion. It concerns with the difficulty of linking electron transfers during non-equilibrium situations such as the formation of anode and cathode at the atomistic scale, where calculations are typically carried out for equilibrium configurations. As previously indicated (section 4.4.3), fluctuation theorems [165] may provide a pathway for dealing with such events because they enable quantitative predictions on fluctuations in small systems that are monitored over short periods to be made; therefore the fluctuation theorems allow thermodynamic concepts to be extended to apply to finite systems. They describe the statistical fluctuations in time-averaged properties of many-particle systems such as fluids driven to non-equilibrium states and provide some of the few analytical expressions that describe non-equilibrium states. Incorporating the fluctuation theorems in the MD simulations (which are formulated using a Newtonian approach and not using DFT) could provide a method to predict the evolution of time-irreversible electrochemical systems of molecular dimensions. Once these modifications have been incorporated, one could expect an electronic/ charge distribution (thus non-equilibrium) to result from the calculations and subsequently the atomistic-mesoscale

coupling could be done by 'coarse-graining' at the boundary-zone by integrating out redundant degrees of freedom using LMPM.

Another problem that requires consideration is solving equations on different scales. Consider that anodic half-cell reactions constituting localised corrosion start at microscopic anodic sites and eventually spread on macroscopic scales. Often, the microscopic anodic sites couple to much larger cathodic areas on the continuum scale. Similarly, there is a vast difference in characteristic time scales between (a) the almost instantaneous phenomena such as electromigration, chemical reactions and electrochemical reactions; and (b) the decidedly slow processes such as diffusion. The partial differential equations in an MSM that describe such incongruent phenomena occurring over different length and time scales that are several orders of magnitude apart present numerical solution issues that are known as stiff problems. A stiff equation is a differential equation for which certain numerical methods for solving the equation are numerically unstable unless the step size is extremely small. The main reason for this issue is that the equation includes some terms that can lead to rapid variation in the solution. While generic solution strategies have been contrived to solve such problems, a complex set of equations, as in the case of corrosion modelling, requires a customised approach to obtain a stable numerical solution in a reasonable time frame. Developing such a successful solution strategy is part of developing an MSM. Incidentally, Macdonald and Engelhardt [215] have discussed alternative approaches to solving the system of equations containing chemical reaction and transport terms with vastly different characteristic time scales and thereby rates also. The numerical method employed by White et al. [228] separated concentration changes due to chemical reactions, which can have infinitely large rates of change, from concentration changes caused by transport so that the partial differential equations (PDEs) may be solved more easily. Walton et al. [183] and Sharland [203] decoupled equations for precipitation reactions from mass transport and corrosion equations on the basis of vastly different characteristic time scales. They used the same procedure when modelling changes in chemistry inside the pit. Thus, in addition to overcoming the formulational challenges associated with the linking of spatial scales, an MSM developer will need to resolve issues related to the different temporal scales. In the latter, the coupled equations will need to be solved using techniques that account for: (a) properly reconciled definitions of the computing variables (e.g., kinetic and continuum temperature), (b) stiffness and (c) instabilities that may propagate from the lower scales to the higher.

6.0 Some suggestions on the features of a future MSM

Initial versions of MSMs on localised corrosion will have incremental improvements over current techniques rather than satisfying all of the lofty goals outlined in Sections 4.0 and 5.0 and will address only some of the fundamental challenges outlined therein. An enormous amount of modelling and experimental effort will be needed to develop an ideal MSM as envisaged here that will be generic enough to apply to different alloy systems.

Modellers will first need to decide whether their MSM will need to be a 3-scale model (e.g., [10]) or a 2-scale version (e.g., [75]). That decision will hinge on the degree of resolution sought at the various levels and will be dictated by project goals. As argued in Section 4.0, a realistic MSM for the development of corrosion-resistant alloys and inhibitors should be coupled to an MSM on alloy solidification. It appears that a parallel framework (Fig. 2 and [9]) is the most suitable option for this coupling as shown in Fig. 6 for a hypothetical case.

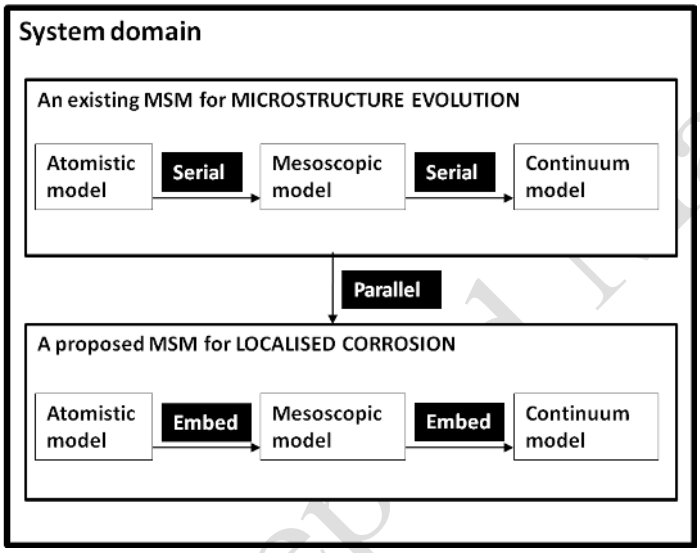

Figure 6: The different classes of integrating multiscale frameworks proposed for a hypothetical case where an existing MSM for microstructure evolution is coupled with a proposed MSM for localised corrosion.

As shown in Fig. 6, we favour an embedded framework (Fig. 2 and [9]) for an MSM on localised corrosion. This approach will reduce the overall computational burden by limiting the volumes computed at the lower scales. A rather detailed conceptual MSM on localised corrosion envisioned by the present authors is presented in Fig. 7.

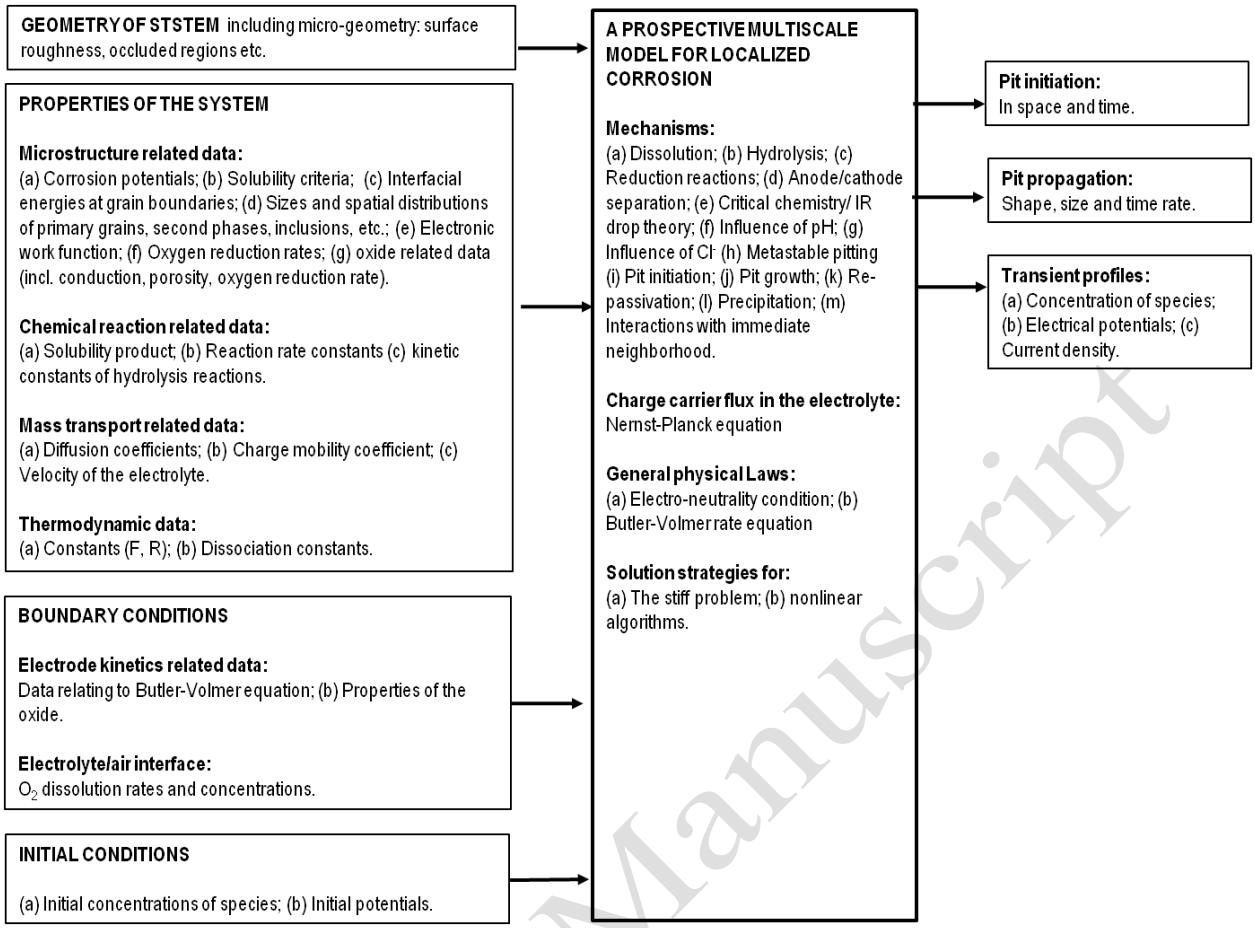

Figure 7: A general description of a prospective MSM on localised corrosion including potential inputs and outputs.

In developing a barebones MSM for corrosion, the following processes must be envisaged:

1. Metal oxidation
2. Metal ion dissolution, diffusion, speciation and hydrolysis
3. Oxygen reduction
4. OH- ion dissolution, diffusion and further solution reactions
5. Precipitation of corrosion products from the solution
6. Effect of initial oxide layer
7. Solution Chemistry (migration and diffusion of other ions like Cl- and inhibitors)

The favourable attack sites for corrosion on the metal surface are the defects and the grain boundaries. Hence, while developing an MSM for corrosion, it is imperative to model the surface atomistically using lattice techniques. However, unlike fracture, corrosion is basically a surface phenomenon that could potentially, in the long run, lead to a situation where the pits or crevices are large enough to cause material failure. Although apparently coupled, in the first version of the MSM we can delink the modelling of the electrochemical reactions from the modelling of material failure due to crack growth (which can be handled efficiently by many methods proposed in the literature [12] such as LMPM and the Quasi continuum method). Instead, corrosion modelling could concentrate on the interface and the large surface area over which pits initiate, grow, interact, stay metastable and/or die. However, the surface of most active metals is covered by an initial oxide layer, and localised corrosion occurs when this oxide layer is damaged. The PDM [26, 276], in principle, addresses defects and has a subtle connection with MD methods in the solid phase, although the PDM treats defects in a macrohomogenous fashion. While it is tempting to argue that the PDM or its variant [276] can

contribute to coupling algorithms, the connection between vacancy density and atomistic vacancies needs to be established through conservation principles. On the other hand, the interaction of an inhibitor with the metal surface is a vast subject that is currently gaining momentum [126]. While DFT methods have been employed primarily to understand how inhibitors interact with metal surfaces in solvated environments, the computational constraints dictate that this interaction, once well understood, must be only semi-empirically accounted for using MD methods that can later be coupled with one of the candidate continuum methods (FEM, CVFEM, SPH or LMPM) and mesoscale methods (CA and DPDE) described above.

6.1 Reactions

At an international workshop [13] attended by eminent electrochemists, it was concluded that progress in deterministic modelling will depend critically on progress made in the understanding of the reaction kinetics of crucial corrosion reactions, although specific reactions were not identified. The present authors discussed this in some detail in section 4.7.2. The workshop mentioned also identified (i) a chasm between fundamental studies that focus primarily on ideal surfaces; (ii) the challenges associated with real surfaces such as surface defects, surface films, adsorbed species and water molecules; and (iii) a lack of knowledge about the morphology and composition of porous films and the influence of alloying elements on film properties. Such knowledge is now beginning to appear in the literature thanks to state-of-the-art experimental techniques, e.g., in situ electrochemical scanning tunnelling microscopy [103], which sheds light on the initiation of nano-scale pits on nickel surfaces.

6.2 Mass transport

It may be convenient to use the dilute solution theory [277] for the initial versions of the MSM, although this is not recommended for real solutions. Activity coefficients that account for the non-ideal behaviour of charged species at non-dilute concentrations should be used where possible.

6.3 Micro Climate

As outlined in Fig. 1, the lower level and pitting models will need to be connected to models that can predict the "state" of the exposed surface where local attack occurs. By state, we refer to the presence or absence of moisture, the chemistry of aqueous phases, and the temperature of the metal surface. The models derived by Cole et al.[278-281] that link surface state to climate parameters and sources and distribution of pollutants can be used or adapted for this purpose.

7.0 Conclusions

This review has highlighted both the complexity of developing MSMs and the possibility that a first generation MSM for localised corrosion that spans from molecular to component scales may be developed in the not-so-distant future. This MSM will have great utility for design, as it will allow the effects of atomic scale changes on the component performance to be determined. Thus, the molecular design can be optimised. Furthermore, processes that lead to the most rapid deterioration can be focused upon at their characteristic scales for additional research or development.

Current design approaches are based on continuum models. We outlined how these models were based on assumptions of homogeneity and were consequently limited for applications to heterogeneous materials and processes that require a heterogeneous description. This was most evident in the cases of material heterogeneity, such as complex multi-phase microstructures, oxide films, paint films and corrosion products. Most present models assumed homogeneous properties for the material units. Where limited heterogeneity was permitted, it was introduced by linking two homogeneous units and ignoring the boundaries. An example is the application of the porous electrode theory to model corrosion processes where the solid-fluid boundary was accounted for by superposing continua. On the contrary, molecular or atomic modelling in MSM will allow heterogeneities to be studied directly without the overbearing assumption of sweeping homogeneity, but at the same making necessary allowances for information exchange at the "handshake" regions where the continuum and discrete models intersect. For example, percolative transport of fluid through the oxide pores and its subsequent interaction with the metal surface underneath is a strong candidate where percolation could be modelled using statistical considerations (i.e., partially disregarding the discreteness in the distribution), and the reaction of the fluid with the metal surface could be modelled by DFT or MD techniques. As in the case of material structure, atomistic and molecular modelling can examine specific interactions between atoms and molecules that can then be linked back into a continuum scheme.

There are, however, significant challenges to developing a multiscale model. These challenges include:

a) The overall formulation of the model so that processes and structures are modelled on appropriate scales;
b) The development of models at each scale that are computationally efficient and provide results of appropriate accuracy and resolution;
c) The linking of models on different scales in a computationally efficient manner, and
d) The validation of the model overall and at each level.

This paper described a structure in terms of overall formulation and presented a number of possible approaches to this problem. The main computational costs occur on the atomic or molecular scale. As outlined by Elliot [5], efficient methods are required to accelerate molecular modelling and effective partitioning, and linking molecular and higher-level scales may be part of the solution. The exact method to link different scales probably will depend on the particular material and processes involved, and thus a tool-box rather than a prescriptive approach may be best. As discussed in Section 4.3.2.4, a "nano-gap" still exists between molecular modelling and continuum modelling of inhibitor effects. Addressing this gap is essential because most of the observed electrochemical phenomena depend on the double-layer properties. We discussed some of these strategies for linking DFT and MD to expand the fine scale or developing phenomenological models of electrochemical processes supplemented by refined measurements to model finer scales. Lastly, the validation of the MSM will be critical at each scale and at the overall model level. We emphasise that more refined experimental techniques will be required for this purpose.

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